A PROJECT REPORT ON

IGCC – FUTURISTIC TECHNOLOGY FOR UPGRADING RESIDUE INTO FUELS AND CHEMICALS

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CERTIFICATE

This is to certify that the project report entitled **"IGCC – FUTURISTIC TECHNOLOGY FOR UPGRADING RESIDUE INTO FUELS AND CHEMICALS"** submitted to **University of Petroleum and Energy Studies, Dehradun** by **Mr. Himanshu Narang** in partial fulfillment for the award of degree of **Bachelor of Technology in Applied Petroleum Engineering (Academic Session 2003-2007)** is a bonafide work carried out by him under my supervision and guidance. This work has not been submitted anywhere else for any other degree or diploma.

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R.P. Badoni

May 01, 2007

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Distinguished Professor

TABLE OF CONTENTS

Topic	Page No.

EXECUTIVE SUMMARY

The refining industry is an ever evolving industry where in the advancements in technology are constantly altering the various processes used. These advancements are brought about by the change in the nature of the products that are desired and their properties and qualities.

In view of the further tightening of environmental specifications, modern refiners are faced with two major dilemmas. The first one involves improving the quality of existing fuels by increasing their ratings and decreasing the amount of impurities especially sulphur. This process requires increase in the amount of hydrogen that is produced in the refineries. Hydrogen production in the refineries also leads to aromatics production which are used as blending components for gasoline. With the decrease in the percentage of aromatics that can be added to gasoline, this further reduces the amount of hydrogen that can be produced in the refinery. So, more hydrogen is required from some other processes without compromising on the product slate of the refineries.

The other problem involves reducing their own emissions of toxic gases mainly sulphur and nitrogen oxides. Most of the refinery emissions come from burning of fuel oil and fuel gas in the heaters to produce steam for boilers to generate power and heating of various streams. Many emerging technologies are being envisaged to help the refiners meet their targets and achieve an optimum configuration.

One of the front runners for solving the above problems is **GASIFICATION** of the residue produced in a refinery consisting of heavy hydrocarbons which are highly impure and direct burning of which will be very ineffective as it will produce very less heat and also contribute a great deal to the release of toxic gases into the atmosphere.

Gasification offers many advantages. Apart from reduced emissions, this technology can be altered for many applications from producing power, hydrogen, chemicals to high quality fuels from Fischer-Tropsch synthesis of the produced syn gas. The excess hydrogen produced can be used for deep desulphurization of fuels and the high quality fuels produced from F-T synthesis can be used as blending components to better the overall quality of the aggregate fuel produced in the refinery.

Another advantage of this technology is its ability to accept any kind of feedstock to convert it into syn gas i.e. a mixture of Carbon Monoxide (CO) and Hydrogen (H_2). The ratio of the two gases produced depends on the type of feedstock and its relative percentages of carbon and hydrogen.

INTRODUCTION

Crude oils are complex mixtures containing many different hydrocarbon compounds that vary in appearance and composition from one oil field to another. Crude oils range in consistency from water to tar-like solids, and in color from clear to black. An "average" crude oil contains about 84% carbon, 14% hydrogen, 1%-3% sulphur, and less than 1% each of nitrogen, oxygen, metals, and salts. Crude oils are generally classified as paraffinic, naphthenic or aromatic based on the predominant proportion of similar hydrocarbon molecules. Mixed-base crudes have varying amounts of each type of hydrocarbon. Refinery crude base stocks usually consist of mixtures of two or more different crude oils.

Relatively simple crude oil assays are used to classify crude oils as paraffinic, naphthenic, aromatic, or mixed. One assay method (United States Bureau of Mines) is based on distillation, and another method (UOP "K" factor) is based on gravity and boiling points. More comprehensive crude assays determine the value of the crude (i.e., its yield and quality of useful products) and processing parameters. Crude oils are usually grouped according to yield structure.

Crude oils are also defined in terms of API (American Petroleum Institute) gravity. The higher the API gravity, the lighter is the crude. For example, light crude oils have high API gravities and low specific gravities. Crude oils with low carbon, high hydrogen, and high API gravity are usually rich in paraffins and tend to yield greater proportions of gasoline and light petroleum products; those with high carbon, low hydrogen, and low API gravities are usually rich in aromatics.

Crude oils that contain appreciable quantities of hydrogen sulfide or other reactive sulphur compounds are called "sour." Those with less sulphur are called "sweet." Some exceptions to this rule are West Texas crudes, which are always considered "sour" regardless of their H_2S content, and Arabian high-sulphur crudes, which are not considered "sour" because their sulphur compounds are not highly reactive.

Raw oil or unprocessed ("crude") oil is not very useful in the form it comes in out of the ground. Although "light, sweet" (low viscosity, low sulphur) oil has been used directly as a burner fuel for steam vessel propulsion, the lighter elements form explosive vapors in the fuel tanks and so it is quite dangerous, especially so in warships. For this and many other uses, the oil needs to be separated into parts and refined before use in fuels and lubricants, and before some of the byproducts could be used in petrochemical processes to form materials such as plastics, and foams. Petroleum fossil fuels are used in ship, automobile and aircraft engines. These different hydrocarbons have different boiling points which means they can be separated by distillation. Since the lighter liquid elements are in great demand for use in internal combustion engines, a modern refinery will convert heavy hydrocarbons and lighter gaseous elements into these higher value products using complex and energy intensive processes.

Oil can be used in so many various ways because it contains hydrocarbons of varying molecular masses, forms and lengths such as paraffins, aromatics, naphthenes (or cyclo-alkanes), alkenes, dienes, and alkynes. Hydrocarbons are molecules of varying length and complexity made of only hydrogen and carbon atoms. Their various structures give them their differing properties and thereby uses. The trick in the oil refinement process is separating and purifying these.

Once separated and purified of any contaminants and impurities, the fuel or lubricant can be sold without any further processing. Smaller molecules such as iso-butane and

propylene or butylenes can be recombined to meet specific octane requirements of fuels by processes such as alkylation or less commonly, dimerization. Octane grade of gasoline can also be improved by catalytic reforming, which strips hydrogen out of hydrocarbons to produce aromatics, which have much higher octane ratings. Intermediate products such as gas oils can even be reprocessed to break a heavy, long-chained oil into a lighter short-chained one, by various forms of cracking such as Fluid Catalytic Cracking, Thermal Cracking, and Hydrocracking. The final step in gasoline production is the blending of fuels with different octane ratings, vapor pressures, and other properties to meet product specifications.

Typical Characteristics of various crudes

Crude source (% vol.)	Paraffins (% vol.)	Aromatics (% vol.)	Naphthenes (% wt)	Sulphur (approx.)	API gravity (% vol.)
Nigerian-Light	37	9	54	0.2	36
Saudi-Light	63	19	18	2	34
Saudi-Heavy	60	15	25	2.1	28
Venezuela-Heavy	35	12	53	2.3	30
Venezuela-Light	52	14	34	1.5	24
USA -W. Texas Sour	46	22	32	1.9	32
North Sea-Brent	50	16	34	0.4	37

REFINING
PROCESS

An **oil refinery** is an industrial process plant where crude oil is processed and refined into more useful petroleum products, such as gasoline, diesel fuel, asphalt base, heating oil, kerosene and liquefied petroleum gas. Oil refineries are typically large sprawling industrial complexes with extensive piping running throughout, carrying streams of fluids between large chemical processing units.

Oil refineries are large scale plants, processing from about a hundred thousand to several hundred thousand barrels of crude oil per day. Because of the high capacity, many of the units are operated continuously (as opposed to processing in batches) at steady state or approximately steady state for long periods of time (months to years).

HISTORY OF REFINING

Petroleum refining consists in the transformation of a raw material, crude petroleum, into a number of useful products. The number and the type of products produced at any given time depend on the uses made of such products, that is on the demand for them, and on the technology available. At the very beginning of the industry the uses of oil were limited to heating and lighting. The oil industry began with the successful drilling of the first commercial well in 1859, and the opening of the first refinery two years later to process the crude into kerosene. The whole development of the petroleum refining industry can be described as the evolution of the methods to separate crude petroleum into its constituents and to transform chemically these constituents.

The main objective of petroleum refining is to separate the components used in different applications and to eliminate the dangerous ones. During the evolution of the industry different types of separation techniques have been used in order to provide the fractions that at each time were in greater demand.

In the early years of the industry there was an understandable tendency among refiners to select amongst the crudes available those with the lowest amounts of difficult materials. Subsequently, due both to the growing demand for this industry products and to improvements in refining technology, less clean crudes were employed.

The number of uses of petroleum derivatives has increased enormously throughout the 20th century. This has been the consequence of the development of a number of industries that use oil derivatives as inputs, such as the automobile, air transport, chemicals etc.

Petroleum refining technology evolved from simple distillation processes to a highly sophisticated and differentiated mixture of processes aimed both at separating fractions and at modifying chemically their constituents. This evolution can be represented by the following milestones.

- At first a refinery consisted of a simple batch, or discontinuous, distillation in which hydrocarbons of successively higher boiling points were vaporized, condensed, and segregated according to the boiling ranges of kerosene, gas oil, and fuel oil (1861, Oil Creek, Pennsylvania). Continuous distillation was soon adopted (1880-1890). The subsequent evolution of the technology was due to the combined effect of the changing demand for the products of petroleum refining and of changes in the feedstocks used. As the main uses of the products of refining shifted away from heating and lighting towards motoring and chemical applications, the light fractions

obtained by distillation became relatively more valuable. On the other hand, the expansion of demand could be satisfied by using as inputs heavier and dirtier crudes. Both sets of circumstances induced changes in petroleum refining technology.

- The discovery (1913) of thermal cracking (a time-temperature dependent decomposition of large molecules into smaller, more desirable molecules) made it possible for the refiner to meet the growing demand for gasoline with a better (higher octane) product.

- The addition of lead alkyls proved a relatively inexpensive way to upgrade gasoline by increasing their octane degree (1922).

- Then the catalytic era began. Catalytic polymerization provided a way to utilize the light olefins (principally propylene and butylenes) to produce a high octane gasoline material. Catalytic cracking was considerably superior to thermal cracking in the production of olefins, gasoline, and distillates from gas oil (1937). Hydrocracking is a catalytic cracking process conducted with a high partial pressure of hydrogen relative to hydrotreating processes. It can produce a higher conversion of refractory stocks, that is stocks resistant to cracking, to products of lower molecular weight than those obtained in catalytic cracking processes. Catalytic alkylation was developed as a way to combine iso-butane with light olefins to produce very high octane gasoline. Initially, this alkylate was mainly used in aviation. Catalytic reforming followed as a means of upgrading the octane of gasoline range materials principally by converting naphthenes to aromatics. Combined with solvent extraction, this provided a source of benzene, toluene, and of xylene. Catalytic isomerization permitted conversion of normal paraffins to their more desirable iso forms.

Petroleum refineries are designed and operated to run within a narrow range of crude oil feedstock, and/or to produce a relatively fixed mix of petroleum products, which should match a local market. However, since the 1970s refiners had to increase their flexibility in order to adapt to a more volatile environment. Several possible paths may be used by refiners to increase their flexibility within existing refineries. Examples of these paths are change in the severity of operating rules of some process units by varying the range of inputs used, thus achieving a slight change in output. However, this option is available only within a narrow range. Other possible paths are to buy some chemical intermediate products rather than making them, or to use more efficient catalysts. Alternatively refiners can invest in new processes. This alternative offers the greatest flexibility, but is limited by the constraint of strict complementarily of the new units with the rest of the existing plant and involves a higher risk than the previous ones. Thus, we can expect refiners to decide in favor of modifying existing processes or of adopting new ones depending on a) new technological opportunities, and b) new market factors.
New scientific and technological opportunities can either reduce refining costs for a constant petroleum products mix, or enable refineries to use a modified mix of petroleum products to supply the changing markets of the refinery. Incentives to reduce costs are

partly linked to the conditions of competition existing within a given market. The previous considerations imply that the adoption of a new refining process will take place only after other options to increase the flexibility of existing refining processes have been exhausted. Incentives may also be linked to a drastic change in the crude market, as it happened for example with the two oil price shocks in 1973 and 1979/1980. As a consequence of those shocks the relative price of 'sweet' and 'light' crudes, that contained either a low fraction of sulphur and a high proportion of more valuable petroleum fractions, increased with respect to the price of the sour and low API gravity ones. Adapting to this change refiners tend to buy increasingly the cheapest crudes i.e. the dirtiest and lowest API gravity ones, on the world market. This shift requires a higher conversion ratio, which can be obtained by cracking the residue of previous units, thus transforming it into usable products. Thus, whether modifications of existing plants or the adoption of completely new processes prevail is likely to depend on the extent of the extent of change in the external environment.

Indian Refiners can adopt this "buyer" strategy because most Indian refineries are "very complex" ones i.e. they include the highest conversion intensity and the most sophisticated hydrotreatment process units. Such refineries are able to process sour and heavy crude oil, despite the more severe specifications for petroleum products quality. The same interaction could be found within catalyst development: "In general, new products introduced by catalyst manufacturers are designed specifically to meet environmental and safety concerns or to improve performance and cost. Often, new catalysts do both" (OGJ, Oct 9, 2000, p.66). These developments illustrate the intimate relationship between demand-pull and supply-push factors.

Petroleum refining has evolved continuously in response to changing consumer demand for better and different products. The original requirement was to produce kerosene as a cheaper and better source of light than whale oil. This was done by simple atmospheric distillation. Its by-products included tar and naphtha. It was soon discovered that distilling petroleum under vacuum could produce high-quality lubricating oils. However, for the next 30 years kerosene was the only product that the consumers wanted. But, the invention of the electric light decreased the demand for kerosene. The development of the internal combustion engine led to the production of gasoline and diesel fuels. The evolution of the airplane created an initial need for high-octane aviation gasoline and then for jet fuel, a sophisticated form of the original product, kerosene. Present-day refineries produce a variety of products including many required as feedstock for the petrochemical industry.

Year	Process	Purpose	By-Products, etc.
1862	Atmospheric distillation	Produce kerosene	Naphtha, tar, etc.
1870	Vacuum distillation	Lubricants originally, then cracking feedstocks (1930's)	Asphalt, residual, Coker feedstocks
1913	Thermal cracking	Increase gasoline yield	Residual, bunker fuel

1916	Sweetening	Reduce sulphur & odor	Sulphur
1930	Thermal reforming	Improve octane number	Residual
1932	Hydrogenation	Remove sulphur	Sulphur
1932	Coking	Produce gasoline basestock	Coke
1933	Solvent extraction	Improve lubricant viscosity index	Aromatics
1935	Solvent dewaxing	Improve pour point	Waxes
1935	Cat. polymerization	Improve gasoline yield and octane number	Petrochemical, feedstocks
1937	Catalytic cracking	Higher octane gasoline	Petrochemical, feedstocks
1939	Visbreaking	Reduce viscosity	Increased distillate, tar
1940	Alkylation	Increase gasoline octane & yield	High-octane aviation gasoline
1940	Isomerization	Produce alkylation feedstock	Naphtha
1942	Fluid catalytic cracking	Increase gasoline yield & octane	Petrochemical feedstocks
1950	Deasphalting	Increase cracking feedstock	Asphalt
1952	Catalytic reforming	Convert low-quality naphtha	Aromatics
1954	Hydrodesulphurization	Remove sulphur	Sulphur
1956	Inhibitor sweetening	Remove mercaptan	Disulphides
1957	Catalytic isomerization	Convert to molecules with high octane number	Alkylation feedstocks
1960	Hydrocracking	Improve quality and reduce sulphur	Alkylation feedstocks
1974	Catalytic dewaxing	Improve pour point	Wax
1975	Residual hydrocracking	Increase gasoline yield from residual	Heavy residuals

PETROLEUM REFINING OPERATIONS:

Petroleum refining begins with the distillation, or fractionation, of crude oils into separate hydrocarbon groups. The resultant products are directly related to the characteristics of the crude processed. Most distillation products are further converted into more usable products by changing the size and structure of the hydrocarbon molecules through cracking, reforming, and other conversion processes as discussed in this chapter. These converted products are then subjected to various treatment and separation processes such as extraction, hydrotreating, and sweetening to remove undesirable constituents and improve product quality. Integrated refineries incorporate fractionation, conversion, treatment, and blending operations and may also include petrochemical processing.

Petroleum refining processes and operations can be separated into five basic areas:
- **Fractionation** (distillation) is the separation of crude oil in atmospheric and vacuum distillation towers into groups of hydrocarbon compounds of differing boiling-point ranges called "fractions" or "cuts."
- **Conversion** processes change the size and/or structure of hydrocarbon molecules. These processes include:
   - ❖ Decomposition (dividing) by thermal and catalytic cracking;
   - ❖ Unification (combining) through alkylation and polymerization; and
   - ❖ Alteration (rearranging) with isomerization and catalytic reforming.
- **Treatment** processes are intended to prepare hydrocarbon streams for additional processing and to prepare finished products. Treatment may include the removal or separation of aromatics and naphthenes as well as impurities and undesirable contaminants. Treatment may involve chemical or physical separation such as dissolving, absorption, or precipitation using a variety and combination of processes including desalting, drying, hydrodesulphurizing, solvent refining, sweetening, solvent extraction, and solvent dewaxing.
- **Formulating and Blending** is the process of mixing and combining hydrocarbon fractions, additives, and other components to produce finished products with specific performance properties.
- **Other Refining Operations** include: light-ends recovery; sour-water stripping; solid waste and wastewater treatment; process-water treatment and cooling; storage and handling; product movement; hydrogen production; acid and tail-gas treatment; and sulphur recovery.

Auxiliary operations and facilities include: steam and power generation; process and fire water systems; flares and relief systems; furnaces and heaters; pumps and valves; supply of steam, air, nitrogen, and other plant gases; alarms and sensors; noise and pollution controls; sampling, testing, and inspecting; and laboratory, control room, maintenance and administrative facilities.

DESCRIPTION OF VARIOUS PETROLEUM REFINING PROCESSES

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 i.e. chemical and electrostatic separation use hot water as the extraction agent. In chemical desalting, water and chemical surfactant (de-emulsifiers) 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 involves 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.

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 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 operations are 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 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.

❖ **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.

❖ **Other Distillation Towers (Columns):** Within refineries there are numerous other, smaller distillation towers called columns, designed to separate specific and unique products. 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.

SOLVENT EXTRACTION AND DEWAXING

Solvent treating is a widely used method of refining lubricating oils as well as a host of other refinery stocks. Since distillation (fractionation) separates petroleum products into groups only by their boiling-point ranges, impurities may remain. These include organic compounds containing sulphur, nitrogen, and oxygen; inorganic salts and dissolved metals; and soluble salts that were present in the crude feedstock. In addition, kerosene and distillates may have trace amounts of aromatics and naphthenes, and lubricating oil base-stocks may contain wax. Solvent refining processes including solvent extraction and solvent dewaxing usually remove these undesirables at intermediate refining stages or just before sending the product to storage.

❖ **Solvent Extraction:** The purpose of solvent extraction is to prevent corrosion, protect catalyst in subsequent processes, and improve finished products by removing unsaturated, aromatic hydrocarbons from lubricant and grease stocks. The solvent extraction process separates aromatics, naphthenes, and impurities from the product stream by dissolving or precipitation. The feedstock is first dried and then treated using a continuous countercurrent solvent treatment operation. In one type of process, the feedstock is washed with a liquid in which the substances to be removed are more soluble than in the desired resultant product. In another process, selected solvents are added to cause impurities to precipitate out of the product. In the adsorption process, highly porous solid materials collect liquid molecules on their surfaces. The solvent is separated from the product stream by heating, evaporation, or fractionation, and residual trace amounts are subsequently removed from the raffinate by steam stripping or vacuum flashing. Electric precipitation may be used for separation of inorganic compounds. The solvent is then regenerated to be used again in the process.

The most widely used extraction solvents are phenol, furfural, and cresylic acid. Other solvents less frequently used are liquid sulphur dioxide, nitrobenzene, and 2,2'-dichloroethyl ether. The selection of specific processes and chemical agents depends on the nature of the feedstock being treated, the contaminants present, and the finished product requirements.

❖ **Solvent Dewaxing:** Solvent dewaxing is used to remove wax from either distillate or residual basestocks at any stage in the refining process. There are several processes in use for solvent dewaxing, but all have the same general steps, which are: (1) mixing the feedstock with a solvent, (2) precipitating the wax from the mixture by chilling, and (3) recovering the solvent from the wax and dewaxed oil for recycling by distillation and steam stripping. Usually two solvents are used: toluene, which dissolves the oil and maintains fluidity at low temperatures, and methyl ethyl ketone (MEK), which dissolves little wax at low temperatures and acts as a wax precipitating agent. Other solvents that are sometimes used include benzene, methyl iso-butyl ketone, propane, petroleum naphtha, ethylene dichloride, methylene chloride, and sulphur dioxide. In addition, there is a catalytic process used as an alternate to solvent dewaxing.

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.

- ❖ **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 is 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 upon the reaction mechanism, time, temperature, and the crude feedstock.

- ❖ **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.

❖ **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 where the larger coke particles are removed as product. The remaining coke is dropped into the pre-heater 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.

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 extrudites.

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
  ➢ 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 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.

❖ **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.

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 a high polycyclic aromatic content and/or high concentrations of the two principal catalyst poisons i.e. sulphur 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 sulphur and nitrogen compounds present in the feedstock to hydrogen sulfide and ammonia.

Hydrocracking produces relatively large amounts of iso-butane 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.

In the first stage, preheated feedstock is mixed with recycled hydrogen and sent to the first-stage reactor, where catalysts convert sulphur 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 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.

CATALYTIC REFORMING

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

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 hydrotreatment 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.

CATALYTIC HYDROTREATING

Catalytic hydrotreating is a hydrogenation process used to remove about 90% of contaminants such as nitrogen, sulphur, 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 sulphur 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 sulphur removal is called hydrodesulphurization. In a typical catalytic hydrodesulphurization unit, the feedstock is de-aerated 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 sulphur and nitrogen compounds in the feedstock are converted into H_2S and NH_3. 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 H_2S is sent to a gas treating unit where H_2S 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 H_2S and other undesirable components. In cases where steam is used for stripping, the product is sent to a vacuum drier for removal of water. Hydrodesulphurized 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 naphthenes, 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 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 sulphur and nitrogen removal, to impart specific properties not achieved at mild conditions. Hydrotreating also can be employed to improve the quality of pyrolysis gasoline (pygas), a by-product from the manufacture of ethylene. Traditionally, the outlet for pygas 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 pygas, which is high in diolefin content, can be satisfactorily improved by hydrotreating, whereby conversion of di-olefins into mono-olefins provides an acceptable product for motor gas blending.

ISOMERIZATION

Isomerization converts n-butane, n-pentane and n-hexane into their respective iso-paraffins 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 iso-butane, 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 iso-paraffins.

There are two distinct isomerization processes, butane (C_4) and pentane/hexane (C_5/C_6). 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 (de-iso-butanizer) to separate n-butane from the iso-butane 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 C_5/C_6 isomerization process, dried and desulphurized 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 iso-paraffins. 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.

POLYMERIZATION

Polymerization in the petroleum industry is the process of converting light olefin gases including ethylene, propylene, and butylene into hydrocarbons of higher molecular weight and higher octane number that can be used as gasoline blending stocks. Polymerization combines two or more identical olefin molecules to form a single molecule with the same elements in the same proportions as the original molecules. Polymerization may be accomplished thermally or in the presence of a catalyst at lower temperatures.

The olefin feedstock is pretreated to remove sulphur and other undesirable compounds. In the catalytic process the feedstock is either passed over a solid phosphoric acid catalyst or comes in contact with liquid phosphoric acid, where an exothermic polymeric reaction occurs. This reaction requires cooling water and the injection of cold feedstock into the reactor to control temperatures between 300° and 450° F at pressures from 200 psi to 1,200 psi. The reaction products leaving the reactor are sent to stabilization and/or fractionator systems to separate saturated and unreacted gases from the polymer gasoline product.

ALKYLATION

Alkylation combines low-molecular-weight olefins (primarily a mixture of propylene and butylene) with iso-butene in the presence of a catalyst, either sulphuric acid or hydrofluoric acid. The product is called alkylate and is composed of a mixture of high-octane, branched-chain paraffinic hydrocarbons. Alkylate is a premium blending stock because it has exceptional antiknock properties and is clean burning. The octane number of the alkylate depends mainly upon the kind of olefins used and upon operating conditions.

❖ **Sulphuric Acid Alkylation Process:** In cascade type sulphuric acid (H_2SO_4) alkylation units, the feedstock (propylene, butylene, amylene, and fresh iso-butane) enters the reactor and contacts the concentrated sulphuric acid catalyst (in concentrations of 85% to 95% for good operation and to minimize corrosion). The reactor is divided into zones, with olefins fed through distributors to each zone, and the sulphuric acid and iso-butanes flowing over baffles from zone to zone. The reactor effluent is separated into hydrocarbon and acid phases in a settler, and the acid is returned to the reactor. The hydrocarbon phase is hot-water washed with caustic for pH control before being successively depropanized, de-iso-butanized, and debutanized. The alkylate obtained from the de-iso-butanizer can then go directly to motor-fuel blending or be rerun to produce aviation-grade blending stock. The iso-butane is recycled to the feed.

❖ **Hydrofluoric Acid Alkylation Process:** Phillips and UOP are the two common types of hydrofluoric acid alkylation processes in use. In the Phillips process, olefin and iso-butane feedstock are dried and fed to a combination reactor/settler system. Upon leaving the reaction zone, the reactor effluent flows to a settler (separating vessel) where the acid separates from the hydrocarbons. The acid layer at the bottom of the separating vessel is recycled. The top layer of hydrocarbons (hydrocarbon phase), consisting of propane, normal butane, alkylate, and excess (recycle) iso-butane, is charged to the main fractionator, the bottom product of which is motor alkylate. The main fractionator overhead, consisting mainly of propane, iso-butane, and HF, goes to a depropanizer. Propane with trace amount of HF goes to an HF stripper for HF removal and is then catalytically defluorinated, treated, and sent to storage. Iso-butane is withdrawn from the main fractionator and recycled to the reactor/settler, and alkylate from the bottom of the main fractionator is sent to product blending.

The UOP process uses two reactors with separate settlers. Half of the dried feedstock is charged to the first reactor, along with recycle and makeup iso-butane.

The reactor effluent then goes to its settler, where the acid is recycled and the hydrocarbon charged to the second reactor. The other half of the feedstock also goes to the second reactor, with the settler acid being recycled and the hydrocarbons charged to the main fractionator. Subsequent processing is similar to the Phillips process. Overhead from the main fractionator goes to a depropanizer. Iso-butane is recycled to the reaction zone and alkylate is sent to product blending.

SWEETENING AND TREATING PROCESSES

Treating is a means by which contaminants such as organic compounds containing sulphur, 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 sulphur 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 sulphur 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:** Sulphuric acid is the most commonly used acid treating process. Sulphuric acid treating results in partial or complete removal of unsaturated hydrocarbons, sulphur, 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 sodium (or potassium) hydroxide is used to improve odor and color by removing organic acids (naphthenic acids, phenols) and sulphur compounds (mercaptans, H_2S) by a caustic wash. By combining caustic soda solution with various solubility promoters (e.g., methyl alcohol and cresols), up to 99% of all mercaptans 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.

- ❖ **Sulphur Recovery:** Sulphur recovery converts hydrogen sulfide in sour gases and hydrocarbon streams to elemental sulphur. The most widely used recovery system is the Claus process, which uses both thermal and catalytic-conversion reactions. A typical process produces elemental sulphur 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 sulphur. Sulphur vapor from burning and 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.

UNSATURATED GAS PLANTS

Unsaturated (unsat) gas plants recover light hydrocarbons (C_3 and C_4 olefins) from wet gas streams from the FCC, TCC, and delayed coker overhead accumulators or fractionation receivers. In a typical unsat gas plant, the gases are compressed and treated with amine to remove hydrogen sulfide either before or after they are sent to a fractionating absorber where they are mixed into a concurrent flow of debutanized gasoline. The light fractions are separated by heat in a reboiler, the off-gas is sent to a sponge absorber, and the bottoms are sent to a debutanizer. A portion of the debutanized hydrocarbon is recycled, with the balance sent to the splitter for separation. The overhead gases go to a depropanizer for use as alkylation unit feedstock.

AMINE PLANTS

Amine plants remove acid contaminants from sour gas and hydrocarbon streams. In amine plants, gas and liquid hydrocarbon streams containing carbon dioxide and/or hydrogen sulfide are charged to a gas absorption tower or liquid contactor where the acid contaminants are absorbed by counterflowing amine solutions (i.e., MEA, DEA, MDEA). The stripped gas or liquid is removed overhead, and the amine is sent to a regenerator. In the regenerator, the acidic components are stripped by heat and reboiling action and disposed of, and the amine is recycled.

SATURATE GAS PLANTS

Saturate (sat) gas plants separate refinery gas components including butanes for alkylation, pentanes for gasoline blending, LPG's for fuel, and ethane for petrochemicals. Because sat gas processes depend on the feedstock and product demand, each refinery uses different systems, usually absorption-fractionation or straight fractionation. In absorption-fractionation, gases and liquids from various refinery units are fed to an absorber-deethanizer where C_2 and lighter fractions are separated from heavier fractions by lean oil absorption and removed for use as fuel gas or petrochemical feed. The heavier

fractions are stripped and sent to a debutanizer, and the lean oil is recycled back to the absorber-deethanizer. C_3/C_4 is separated from pentanes in the debutanizer, scrubbed to remove hydrogen sulfide, and fed to a splitter where propane and butane are separated. In fractionation sat gas plants, the absorption stage is eliminated.

ASPHALT PRODUCTION

Asphalt is a portion of the residual fraction that remains after primary distillation operations. It is further processed to impart characteristics required by its final use. In vacuum distillation, generally used to produce road-tar asphalt, the residual is heated to about 750° F and charged to a column where vacuum is applied to prevent cracking.

Asphalt for roofing materials is produced by air blowing. Residual is heated in a pipe still almost to its flash point and charged to a blowing tower where hot air is injected for a predetermined time. The dehydrogenization of the asphalt forms hydrogen sulfide, and the oxidation creates sulphur dioxide. Steam, used to blanket the top of the tower to entrain the various contaminants, is then passed through a scrubber to condense the hydrocarbons.

A third process used to produce asphalt is solvent deasphalting. In this extraction process, which uses propane (or hexane) as a solvent, heavy oil fractions are separated to produce heavy lubricating oil, catalytic cracking feedstock, and asphalt. Feedstock and liquid propane are pumped to an extraction tower at precisely controlled mixtures, temperatures (150°-250° F), and pressures of 350-600 psi. Separation occurs in a rotating disc contactor, based on differences in solubility. The products are then evaporated and steam stripped to recover the propane, which is recycled. Deasphalting also removes some sulphur and nitrogen compounds, metals, carbon residues, and paraffins from the feedstock.

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, desulphurized 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 naphthas in the gasoline boiling range may be employed, including fuel containing up to 35% aromatics. Following pretreatment to remove sulphur compounds, the feedstock is

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

BLENDING

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

LUBRICANT, WAX, AND GREASE MANUFACTURING PROCESSES

Lubricating oils and waxes are refined from the residual fractions of atmospheric and vacuum distillation. The primary objective of the various lubricating oil refinery processes is to remove asphalts, sulfonated aromatics, and paraffinic and iso-paraffinic waxes from residual fractions. Reduced crude from the vacuum unit is deasphalted and combined with straight-run lubricating oil feedstock, preheated, and solvent-extracted (usually with phenol or furfural) to produce raffinate.

❖ **Wax Manufacturing Process:** Raffinate from the extraction unit contains a considerable amount of wax that must be removed by solvent extraction and crystallization. The raffinate is mixed with a solvent (propane) and pre-cooled in heat exchangers. The crystallization temperature is attained by the evaporation of propane in the chiller and filter feed tanks. The wax is continuously removed by filters and cold solvent-washed to recover retained oil. The solvent is recovered from the oil by flashing and steam stripping. The wax is then heated with hot solvent, chilled, filtered, and given a final wash to remove all oil.

❖ **Lubricating Oil Process:** The dewaxed raffinate is blended with other distillate fractions and further treated for viscosity index, color, stability, carbon residue, sulphur, additive response, and oxidation stability in extremely selective extraction processes using solvents (furfural, phenol, etc.). In a typical phenol unit, the raffinate is mixed with phenol in the treating section at temperatures below 400° F. Phenol is then separated from the treated oil and recycled. The treated lube-oil base stocks are then mixed and/or compounded with additives to meet the required physical and chemical characteristics of motor oils, industrial lubricants, and metal working oils.

❖ **Grease Compounding:** Grease is made by blending metallic soaps (salts of long-chained fatty acids) and additives into a lubricating oil medium at temperatures of 400°F-600°F. Grease may be either batch-produced or continuously compounded. The characteristics of the grease depend to a great extent on the metallic element (calcium, sodium, aluminum, lithium, etc.) in the soap and the additives used.

GENESIS OF
THE PROJECT

The increasing demand of clean fuel products going along with the tendency of growing heavier crude oil availability and petroleum coke will force many refiners to further reduce the "bottom of the barrel" by changing the basic configuration of the refineries.

Numerous legislations in various parts of the world like Euro-III norms, US Clean Fuel Act as part of the new definition of automotive fuel quality around the world are causing drastic limitations for sulphur and aromatics. Especially these two parameters will change the internal hydrogen balance of the refineries because of their counter-current effect. The deep desulphurization of various fuel streams requires more hydrogen and the reduction of aromatics will lead to less hydrogen surplus from catalytic reforming due to low severity operations.

In such a situation, the catalytic reforming as the major source of hydrogen in refineries will not be sufficient anymore to satisfy the growing demand for hydrogen. Consequently, two options for hydrogen production are becoming more important. Steam reforming of light hydrocarbons i.e. natural gas or LPG, is used to produce bulk of hydrogen today or partial oxidation of residues or petroleum coke.

The disadvantage of the relatively higher investment for a gasification unit compared to steam reforming will be compensated for several reasons; one of those is the search for the best techno-commercial way to dispose of refinery residues.

In this situation, gasification offers a very versatile process for the conversion of even the heaviest "bottom of the barrel" refinery residues into clean synthesis gas, which can be used to produce hydrogen, fuel gas or steam for any refinery purposes as well as gases for the chemical industries.

Besides the globally increasing demand for hydrogen, the refineries are looking for the best techno-commercial way to consume their final residues- heavy liquid feedstocks, fuel oil or petroleum coke.

Additionally, the refineries are searching for solutions of their emission problems by replacing old furnaces used for the production of power, steam and heat. Gasification is able to serve the refineries with these products, which underlines its excellent integration flexibility.

The special situation of India has to be considered-natural gas reserves are limited and a significant part of this is dedicated to the fertilizer industry. Therefore, a number of Indian refineries have already published their intention to proceed or consider gasification projects for Integrated Gasification Combined Cycle (IGCC), for hydrogen production or in combination for hydrogen and power.

Indian companies have excellent expertise with oil and coal gasification dated back the 1960's. Oil gasification offers a technology, which has been proven under Indian conditions to provide a reliable source of synthesis gas in industrial service.

From a refiner's perspective, residual fuel is a "leftover." Refineries are run with a focus on the higher valued products, such as gasoline and distillate. Residual fuel oil in 1997 represented only about 5.4 percent of crude oil input to refiners, down from 7.1 percent in 1990, and from 12.0 percent at its share peak in 1977. Residual fuel is what is left after the higher valued products are removed from crude oil. The shrinking market for residual fuel, its low value, and an increasingly heavy crude oil slate have caused refiners to install upgrading equipment that converts residual material to higher valued products. One such conversion process leaves refiners with petroleum coke. As more residual fuel

is upgraded by using cokers, more petroleum coke is produced, some of which is used as fuel.

A large part of the diminishing market for residual fuel derives from the fact that the environmental qualities of residual fuel have been deteriorating as a result of the changing slate of crude oils being processed by refiners. Refiners have been using more high-sulphur crude oil and more crude oil with high heavy metal content. Most of the sulphur, metals, and inert material found in the crude oil are not removed as the oil is processed, but are concentrated in the residual fuel oil. Coking has been a standard process used to convert residual fuel with high sulphur and heavy metals content; however, coking further concentrates the sulphur and metals into the petroleum coke.

Metals content can be an even greater problem than sulphur content. Burning either residual fuel or coke containing high sulphur in a boiler can be handled with standard emissions control devices, but heavy metals content can result in hazardous airborne pollution and high-metal-content ash, which can become a disposal problem. In the future, high-sulphur, high- metals residual fuel and coke may even become "wastes" to be disposed of rather than fuels to be sold.
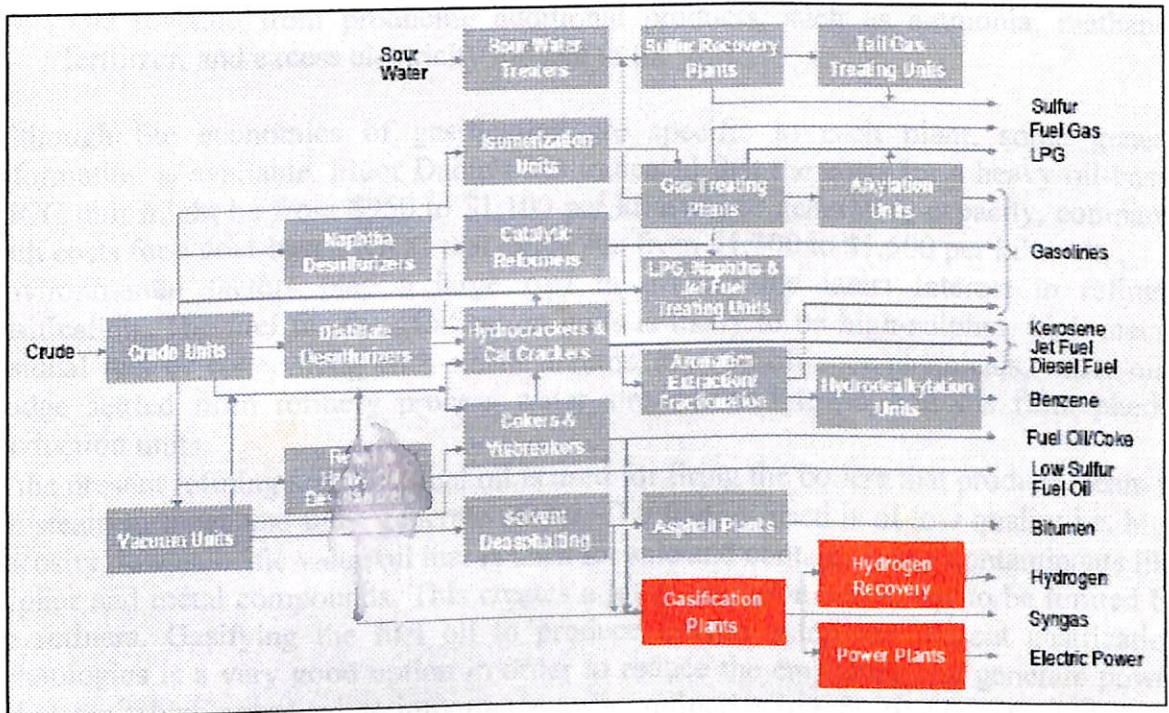
Generally, emissions form an IGCC unit using petroleum coke or residual fuel approach the low emissions profile of a natural-gas-fired combined-cycle unit. Solid waste from an IGCC is much less than from a boiler with flue gas desulphurization or from a circulating fluidized-bed boiler. Although IGCC produces more carbon dioxide (CO_2) than a natural-gas-fired combined cycle, IGCC has much lower CO_2 emissions than other solid fuel plants.

Gasification is a globally emerging technology in commercial markets for the conversion of a variety of feedstocks, including coal, heavy residue oil, biomass, solid waste, and others, to a variety of products, including electricity, steam, sulphur, transportation fuels,

and other chemicals. One of the most developed and versatile gasification technologies is based upon entrained-flow reactors, which typically employ high temperatures and therefore can gasify a broad range of materials.

Refiners probably are one of the best markets for gasification technology because of their ability to use the various products that can be produced and their need to dispose of materials that can be used as feedstock in gasification units. The refinery gasification application has been referred to as a "trigeneration system" that produces steam, power, and synthesis gas, which in turn, can be used to produce hydrogen and/or chemicals, such as ammonia.

Gasification economics are driven by the following factors:
- The capital costs of the facility, including the need for an air separation plant to produce oxygen
- The trend toward heavier, and, in some cases, higher metal content, crude oils that result in high-sulphur, high-metals residual fuel or coke, which are facing more environmental restrictions
- The need to dispose of a variety of wastes
- The cost savings realized from the ability to produce some needed products in the refinery, such as hydrogen, industrial gas, steam, and electricity
- The revenue from producing additional products, such as ammonia, methanol, fertilizer, and excess electricity for sale to the grid.

Although the economics of gasification are specific to each plant, some general information is available. Fluor Daniels has indicated that the costs for a heavy-oil-based IGCC unit might be from $950 to $1,100 per kilowatt of generating capacity, compared with costs for a coal-based IGCC that might run from $1,300 to $1,500 per kilowatt.

Environmental factors play a large part in driving the latest interest in refinery gasification. The fuel for the gasification units is likely to be high-sulphur, high-metals residual fuel or coke, along with waste streams, such as off-spec chemicals, waste oils, sludge settled from refinery process water streams, and tower bottoms from phenol production units.

In the present refining scenario, fuel oil is used for firing the boilers that produce steam to run steam turbines and thus, generate power. The fuel oil used is of low quality i.e. high viscosity, low calorific value oil that is unfit for sale and contains many contaminants like sulphur and metal compounds. This creates a lot of pollution which has to be limited by the refiners. Gasifying the fuel oil to produce syngas using the present gasification technologies is a very good option in order to reduce the emissions and generate power and steam which are of prime importance to the refineries irrespective of where they are situated. Gasification in addition to power and steam also produces syngas i.e. a mixture of hydrogen (H_2) and carbon monoxide (CO). Since, heavy residue is used the ratio of the two compounds is approximately 1:1.

This syngas can be used to either produce high quality blending stocks via the Fischer-Tropsch synthesis process or the hydrogen can be used for various hydrotreating purposes and the carbon monoxide can be converted to carbon dioxide (CO_2) in a shift reactor generating even more power and the can CO_2 be captured and sequestered and stored in

underground storage to reduce greenhouse emissions and thus contribute to limit the global warming effect of CO_2 gas.

Synthesis gas requires the indicated compositional adjustment and treatment before use in the following major applications:

- The dried syngas can be used without further adjustment for methanol synthesis since there is a net conversion of both CO and CO_2 to methanol.
- Ammonia synthesis gas, requiring maximum hydrogen production and removal of oxygen-bearing compounds.
- Oxo synthesis gas, requiring composition adjustment and CO_2 removal to give a 1:1 H_2:CO synthesis gas.
- Industrial gases, as a source of high purity CO, CO_2 or H_2,
- Reducing gas, a mixture of CO and H_2 requiring CO_2 removal before being used to reduce oxides in ores to base metals.
- Fuels either as a substitute fuel gas from a liquid or solid feedstock or as an intermediate for Fischer-Tropsch or zeolite-based alternative liquid fuel technologies. GTL not only adds value, but capable of producing products that could be sold or blended into refinery stock as superior products with less pollutants for which there is growing demand.

Gasification is among the cleanest and most efficient technologies for the production of power, chemicals and industrial gases from hydrocarbon feedstocks, such as coal, heavy oil, and petroleum coke. Gasification converts hydrocarbon feedstocks into clean synthesis gas, or syngas, composed primarily of hydrogen (H_2) and carbon monoxide (CO). In a gasification plant, the feedstock is mixed with oxygen (O_2) and they are injected into a gasifier. Inside the gasifier, the feedstock and the O_2 are subjected to a high-temperature and a high-pressure. As a result, the feedstock and the O_2 break down into syn gas.

The integration of the IGCC into refineries leads to additional synergies for both plants – less emissions and lower investment cost by optimum integration of steam, power and fuel gas produced by the IGCC. The following atmospheric emissions recorded for an IGCC with the SGP process emphasize its environmental advantages:

|	
NO$_x$	25 mg/Nm³ (dry – 15 % O2)
SO$_2$	0 mg/Nm³ (dry – 15 % O2)
CO	10 mg/Nm³ (dry – 15 % O2)
Particulates	1 mg/Nm³ (dry – 15 % O2).

Despite the poor quality feedstocks, the emissions are still extremely low. The sulphur recovery efficiency, defined as a ratio between the liquid sulphur recovered and the sulphur in the feedstock is > 99.5 %.
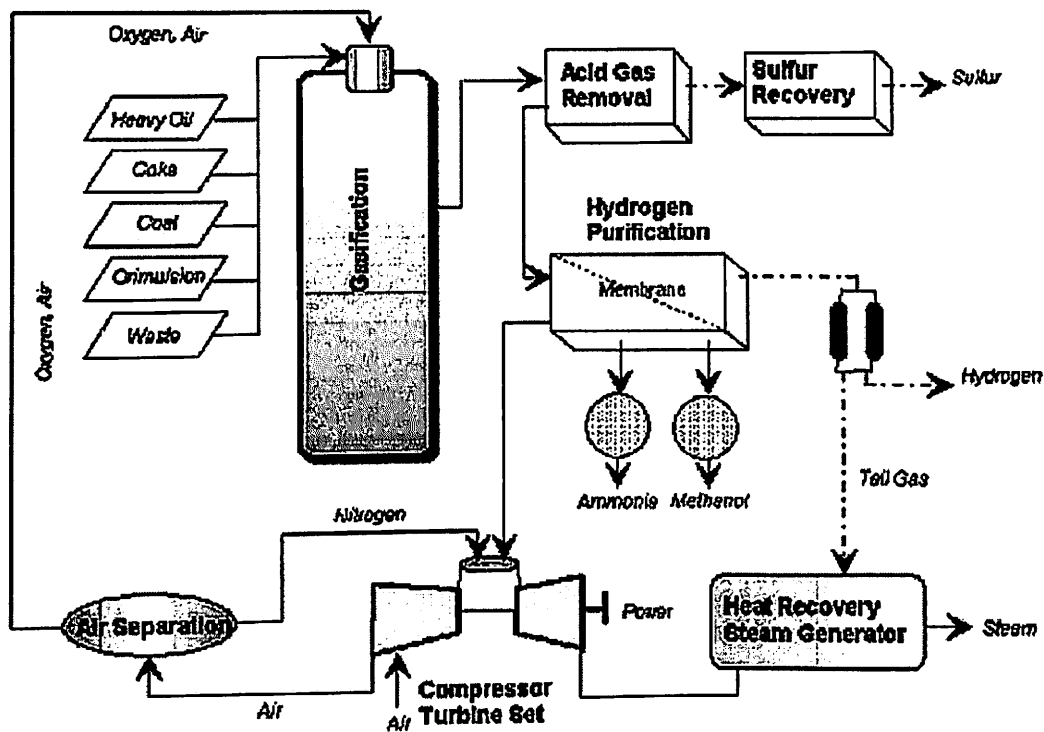
In addition to H_2 and CO, the syngas contains other gases in small quantities, such as ammonia, methane and hydrogen sulfide (H_2S). As much as 99% or more of the H_2S present in the syngas can be recovered and converted to elemental sulphur form and used in the fertilizer or chemical industry. Ash and any metals are removed in a slag-like state, and the syngas is cleansed of particulates. The clean syngas is then used for generating electricity and producing industrial chemicals and gases.

Gasification allows refineries to self-generate power and produce additional products. Thus, gasification offers greater efficiencies, energy savings, and a cleaner environment. For example, a gasification plant at a refinery in El Dorado, Kansas converts petroleum coke and refinery wastes into electricity and steam, making the refinery entirely self-sufficient for its energy needs and significantly reducing waste and coke handling costs. For these reasons, gasification has increasingly become popular among refiners worldwide. Currently, there are several hundred gasification plants in operation worldwide.

GASIFICATION PROCESS
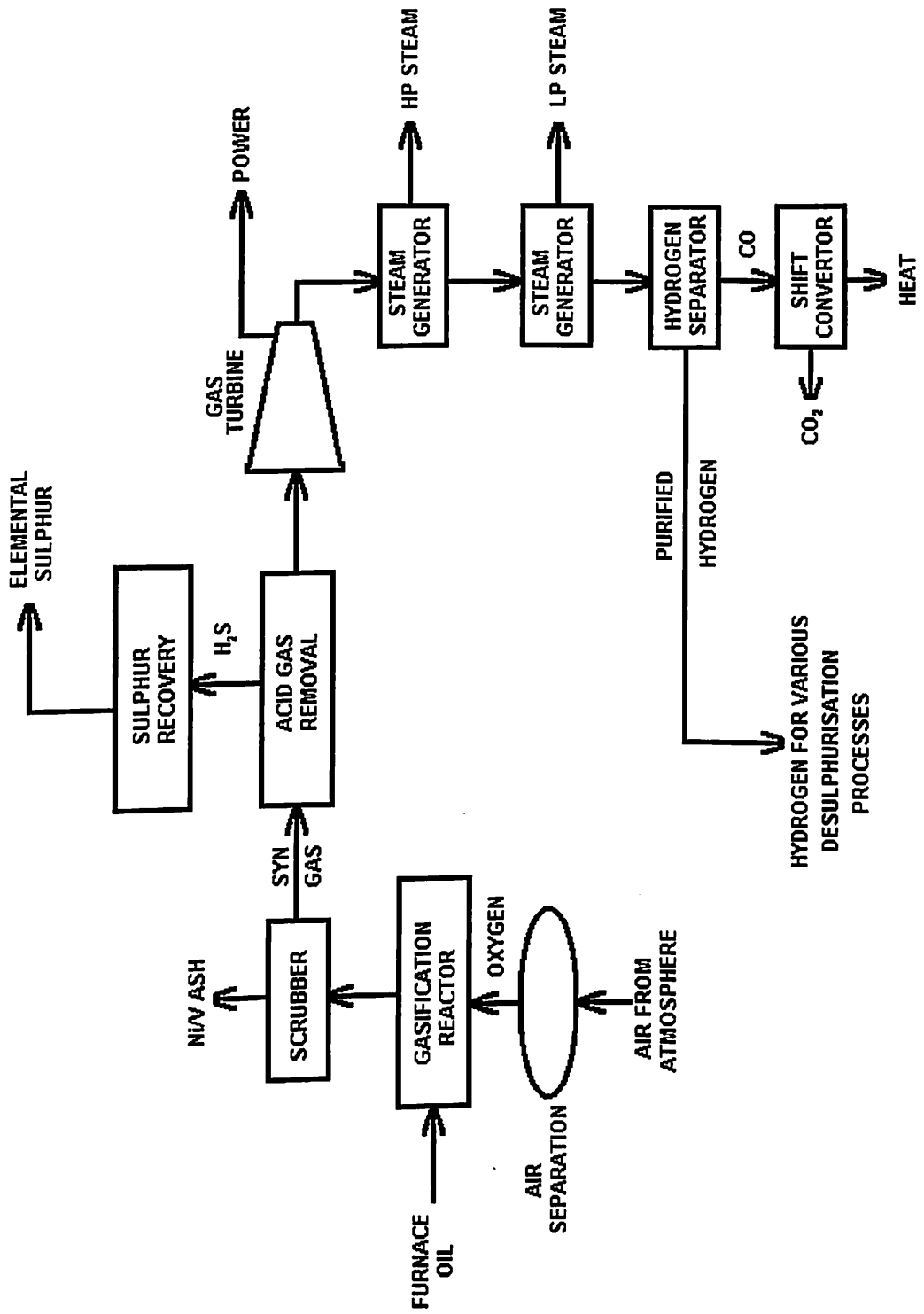
Gasification is the only technology to convert even the heaviest "bottom of the barrel" into a wide range of chemical gases as well as power. In addition to the mentioned gas composition i.e. CO and H_2, the other impurities, namely H_2S, NH_3, COS, HCN and ash have to be removed from the produced raw gas. Further, a small amount of unconverted carbon is present, ranging from 0.5 to 1.0 %wt on liquid feedstocks or 50 – 200 ppm wt for gaseous feedstocks.

Hydrocarbon fuels, such as natural gas, refinery gas, vacuum residue, vacuum-flashed cracked residue, asphalt, liquid waste etc. can all be used as feedstock for the gasification process.
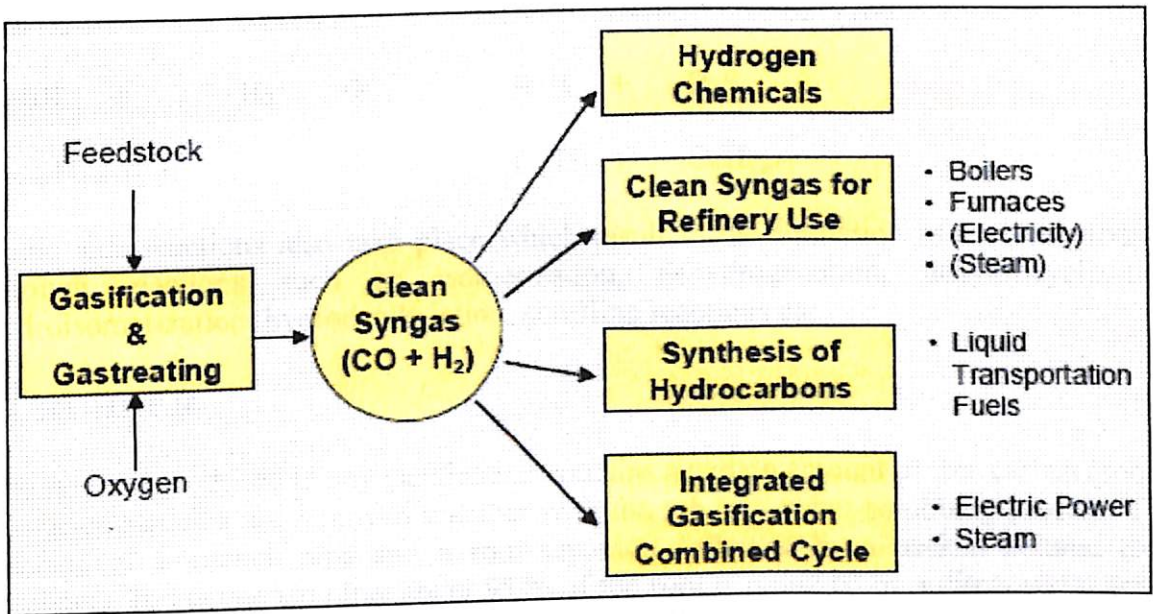
GASIFICATION REACTOR

The process of gasification as the name suggests involves conversion of the feedstock into synthesis gas i.e. a combination of CO and H_2. Although, some unconverted hydrocarbons, H_2S and CO_2 may also be present. H_2S and CO_2 are extremely harmful to the process equipments since they are corrosive to steel and also, H_2S is toxic and poses a health hazard to the personnel involved in operations in the unit. They are subsequently removed from the process by various methods but the equipments that are contacted with them should be suitably selected so as not to get affected by their presence in the process stream.

Furnace oil from within the refinery complex itself is the feedstock for this unit. The gasification process can convert any type of hydrocarbon feedstock right from methane to liquid hydrocarbons to coal which is a solid hydrocarbon into syn gas. The ratio of CO and H_2 generated depends on the quality and the type of feedstock used. It can be as high as 1:2 in case of natural gas rich in methane and can be more than 1 in case of extremely heavy fuel oil with a very high carbon number. Oxygen is supplied to the gasification unit from the air separation unit.

The reaction of hydrocarbons also known as non-catalytic partial oxidation since no catalyst is involved in the process takes place at a very high temperature which again depends on the type of feedstock varying from 800°C to 1300°C. Because of such high temperatures, effective utilization of the heat involved becomes extremely important and also plays a major role in the design of the equipments as well as the entire process flow sheet.

The hydrocarbon molecules are first broken down into smaller hydrocarbons by cracking process and they are subsequently converted into syn gas when further cracking cannot take place or the energy required for cracking becomes much larger than that required for gasification. This is particularly the case for smaller molecular weight hydrocarbons mainly methane which cannot be cracked further.

The main reactions that take place in the gasification unit are:

$$C_nH_{2n+2} + (n/2)O_2 \rightarrow nCO + (n+1)H_2$$

$$R\text{-}SH + H_2 \rightarrow R\text{-}H + H_2S$$

$$C_{m+n}H_{2m+2n+2} \rightarrow C_mH_{2m} + C_nH_{2n+2}$$
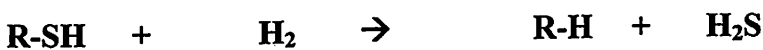
Some side reactions also take place which result in the formation of various products through reactions such as isomerization, dehydrogenation, dehydrocyclization, hydroisomerization, hydrodealkylation, shuffling reactions etc.

SCRUBBER

The raw gas produced in any gasification contains a certain amount of free carbon (soot). The soot particles are removed together with the ash in a water scrubbing process. This consists of a quench pipe and a soot separator followed by a packed column (soot scrubber). In the quench pipe, about 95 % of the soot is removed by a direct water spray. The remaining soot is removed in counter current flow in packed beds. After leaving the scrubber, the gas has a residual soot content of less than 1 mg/Nm³. The temperature of the gas depends on the final application of the synthesis gas. For hydrogen production, it is about 40°C. The gasification process not applying a recycling of soot leads to a heavy metal build-up in the system since all the metal accumulates with the soot. These metal compounds are extremely abrasive as well as corrosive to the process equipment and may lead to premature failure of the same. Therefore, the removal of these metals becomes essential to safeguard the equipments. Also, a recycle of the soot would lead to an increase in the overall carbon content of the feedstock which will adversely affect the efficiency of the gasifier to convert it into syn gas. Also, the deposition of soot on the process equipments may take place altering their operating performance. This is not just the case for the gasifier but all the process units downstream of the gasifier. The scrubbing water containing soot and heavy metals is routed to a filter press. The main part of the water is recycled as recycle water to the top of the scrubber; excess water is sent to the Sour Water Stripper. This water is free of heavy metals and can be treated in a biotreater. The carbon on the filter-cake is burnt off in a multiple hearth furnace and the

ash collected (rich in Vanadium and Nickel) is sold to metals reclaiming companies. This ash on further purification can also be sold to cement companies depending upon the composition. The installation of Soot Ash Removal Unit (SARU) has a better operating efficiency compared to the Naphtha Soot Recycling Unit (NSRU). Additionally, the normally occurring heavy metal enrichment in the gasification reactors based on NSRU is avoided by use of the SARU concept.

ACID GAS REMOVAL

Acid gas as the name suggests are those gases which are acidic in nature and thus lead to corrosion of the equipment which leads to lessening of the stress bearing capacity and ultimately premature failure of the same. Acid gases mainly concerned with the entire process are mainly H_2S and CO_2. Of the two, H_2S predominates since the relative acidity and amount of H_2S produced in the process is much more significant as compared to the latter. Because of the fact that most of the sulphur compounds are accumulated in the heavier streams on account of it forming high molecular weight compounds, the amount of sulphur in the feedstock becomes a major problem during the design stage of the process units and the choice of the materials for them. Acid gases like H_2S can not be vented directly into the atmosphere because of the stringent environmental norms as they are highly toxic and thus have to be treated or converted into a less hazardous form. H_2S is highly inflammable and its burning produces SO_2 which is again extremely toxic and there are environmental limits on its emission into the atmosphere also. Thus, as soon as H_2S is formed in the gasifier reactor because of the availability of the H_2 produced within the gasifier process, it is desired to remove it as soon as possible. The H_2S removed from syn gas can be used to produce elemental sulphur which is a major specialty element used to manufacture various compounds like sulphuric acid as well as being a prominent fertilizer feedstock requirement. This enhances the revenue of the refinery and adds to the commercial viability of the project. The process involves separating of the H_2S from the syn gas by adsorption on a suitable adsorbent like molecular sieves. The H_2S thus separated, is incinerated at around 1350°C to form elemental sulphur which is in liquid form. This sulphur is then allowed to cool and deposits as a yellow powdery substance at normal temperature.

POWER GENERATION

One of the most important uses of fuel oil in the modern refining scenario is that it fires the burners of the boilers that are used to generate steam and then run the steam turbines of the refinery's captive power plants thus, generating electricity for the refinery as well as, if possible, for commercial purposes to be sold to outside customers. After the syn gas has been cleaned of almost all the impurities by the preceding processes, it is sent to the gas turbine in order to rotate the shaft and generate power for the entire plant. This adds to the process viability since finding an alternate use for fuel oil will render the refinery unable to meet its power demands and seek alternate fuel to fire the burners which are more expensive than the existing means of generation. That is why any process requiring fuel oil as its feedstock has to be able to generate power for at least the use of the refinery

ort generate an alternate fuel which would be economical to burn. The latter case is not possible since the processing of fuel oil will add to the cost and the render the alternate fuel un-economical. That is the reason why the first case has to be adopted. The amount of electricity generated will depend on the quantity of syn gas produced and the inlet and outlet temperature and pressure of the gas. The main reason why this technology is better than the existing technology is that fuel oil which is rich in sulphur compounds leads to polluting of the environment when it is burnt to produce steam. In the case of gasification, the emissions are significantly reduced as compared to conventional technology and are even better than solid fuel fired power plants in terms of overall emissions. It is a well known fact that most of the emissions of harmful and toxic gases in a refinery come from burning of furl oil directly. So, in view of environmental norms being further tightened, the most efficient way to reduce these emissions will involve the revamping and re-engineering of the power generation system of the refineries. Gasification not only does that but also offers higher efficiencies of the order of 60-70% as compared to a thermal power plant where it can reach a high of at maximum of 45%. This will mean more power and less wastage of the available resources.

STEAM GENERATION

Another important resource of any refinery is the steam that is generated in various units in a refinery. Steam helps in a big way in increasing the overall efficiency of the refinery by taking heat wherever the component is to be cooled and transferring it to a component that is to be heated up depending on process requirements. Steam is used in heat exchangers, strippers, turbines etc. Steam used in the refinery is classified on the basis of its pressure as HP (High Pressure), MP (Medium Pressure) and LP (Low Pressure). The above classification is based on the heat content of the steam which in turn is dependent on pressure. The syn gas that comes out of the gas turbine has lost some of its energy to the turbine. It still has a very high temperature which can be used to generate steam to be used in the refinery elsewhere. Steam generators are nothing but heat exchangers which provide a surface for the exchange of heat between water and syn gas and transfer of heat from syn gas to water. Thus, the temperature of syn gas decreases while that of water increases to such a level that it vaporizes and forms steam. The generation of steam is done in various steps and in each step the pressure of steam generated decreases. The other effect of this process is that the temperature of syn gas comes down to a manageable level from whereon it can be used for other processes. Steam is a major utility for any refinery and its generation in the process makes this process commercially more attractive.

HYDROGEN PRODUCTION

The most important utilization of the entire gasification process apart from power generation is that it also produces hydrogen as a product which is of extreme importance in any refinery. As of now, in a conventional refinery, only CCR (Continuous Catalytic Reformer) unit produces hydrogen which is used by various processes for improving the quality of the fuel especially diesel by getting rid of impurities like sulphur and decreasing the carbon content of the fuel. The decreased carbon content will lead to less

soot forming tendency of the fuel concerned. In view of environmental norms being further tightened based on the quality of the fuel that come into the market especially regarding the sulphur content, more hydrogen is required for achieving the same. This excess hydrogen required has to be met by some other source and that is where this technology plays an even greater role. Hydrogen can be extracted from the combination of syn gas by various processes, the most prominent being PSA (Pressure Swing Adsorption) process or cryogenic processes. In PSA process, adsorption of hydrogen takes place on a suitable adsorbent at increased pressure and release of hydrogen at a lower pressure. The change in pressure from high to low leading to adsorption and then desorption gives it the name of pressure swing. This process produces very high purity hydrogen, of the order of 99.9% purity, but the yield of hydrogen is low to the tune of only around 90%. It contains CO to as low as 50 ppm. In cryogenic processes, as the name suggests, the feed is cooled in successive fashion to cryogenic conditions wherein the liquefaction of various gases takes place and hydrogen having a very low boiling point, around -155C is left in gaseous sate. This process is characterized by very high yield of around 97-98% but at the same time the purity of the hydrogen thus obtained is very less at around 90-92%. That is the reason why PSA is preferred over cryogenic processes owing to the high purity levels that are essential when hydrogen is being used for other processes. The effluents of this process are either flared or added to the fuel gas that is used in burners for heat generation or steam generation.
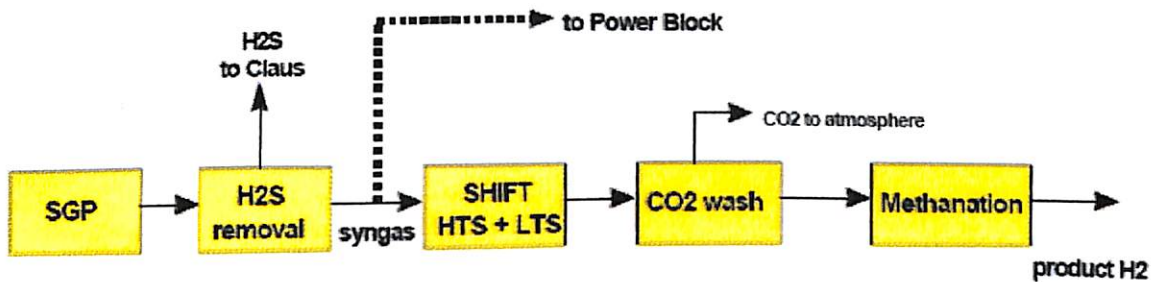
SHIFT CONVERTOR

The raw gas leaving the gasification unit contains CO which has to be converted to CO_2 by means of a catalyst (CO-Shift). The exothermic reaction leads to a considerable increase of temperature. Two different alternatives can be chosen regarding syngas use in gas turbines – "sour" or "sweet" shift. The hydrogen production for "sweet" shift is where the H_2S removal is executed upstream of the catalytic shift reaction. For the treating of the raw gas i.e. "sour" gas containing H_2S, the Rectisol process can be chosen. This is a single train unit that integrates sulphur removal with the CO_2 removal downstream the CO-shift. COS and HCN is removed from the syngas by the Rectisol process. If other treating processes are used, a separate COS/HCN hydrolysis (catalytic step) has to be installed. The water (steam)-to-dry gas ratio can be adjusted between 1.8-2.4. In case that all syngas is used for hydrogen production, H_2S removal as well as CO_2 removal is carried out simultaneously in one step after the "sour" CO-shift. Simultaneously to the CO conversion, COS is hydrolyzed to H_2S and CO_2 by a side

reaction with water. Similarly, HCN is hydrolyzed to NH_3 and CO. The water (vapor)-to-dry gas ratio can be adjusted between $1.3 - 1.8$. The H_2S is converted into elemental sulphur in a Sulphur recovery Unit. The main reaction involves the conversion of CO to CO_2. The reaction is highly exothermic i.e. a lot of heat is involved in the process which can be further utilized for generating steam and/or to be used within the process itself to increase its total heat utilization and make the process more efficient. The CO_2 thus, generated can be vented directly into the atmosphere since the amount of CO2 emitted is much less than conventional solid fuel powered thermal power plants. Another effective way of getting rid of CO_2 is to sequester it into the ground because CO_2 being a greenhouse gas leads to global warming. Since, CO_2 is available in a pure form, it can be sequestered but the cost of sequestering is high and depends on the location of the refinery itself. This cost of sequestering adds to the cost of the entire process but it almost reduces the overall emissions of the refinery to nil if such a system is used. That would be a great boon for the environment in recent view of the growing concerns for the impact of greenhouse gas emissions from the burning of fossil fuels which have led to wide-spread protests against installations contributing to their emissions which also includes refineries.

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