PROCESSING OF PRIMARY AND SECONDARY FUELS: PERSPECTIVE ON PETROLEUM REFINING

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Keywords: refining processes, primary fuels, secondary fuels, distillation, crude oil, gas oil, kerosene, petroleum refinery, naphtha, LPG, separation processes, conversion processes, paraffins, naphthenes, aromatics, asphalt, waxes, lubricating oils, heating oils, unit operations, hydrocarbons, catalysts, octane number.

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Summary

A petroleum refinery is a highly organized processing plant, which consists of many chemical and physical processes designed to convert crude petroleum into products with the qualities required and in volumes demanded by the market.

Refining processes involve two major categories: production of primary fuels by separation processes and secondary fuels by conversion processes. In the area of conversion, there are literally hundreds of processes in use, many of them patented. Even in a given refinery running a single crude, daily changes to accommodate changing markets and changing parameters of the conversion processes take place. The object of this article is to set forth the most important processes, illustrate their general principles, and discuss the applications to which they may be put. No refinery on any day will operate exactly as described in this article, but all refineries operate using the similar basic processes. Perspective on natural gas processing is also presented in this article.

1. Introduction

Chemical energy is a very important part of overall energy supply for industries, transportation, commerce and residential applications. Chemical energy entails energy derived by thermal or electrochemical means from fossil fuels such as coal, oil and gas as well as biomass. Chemical production has been fundamental to our modern civilization and often involves complex chemical plants processing and converting fuels from their crude forms to refined forms. A typical example of chemical energy plants is oil refinery. As advised by the UNESCO/EOLSS Joint Committee, this theme focuses only on the processing of primary and secondary fuels with respects to oil and gas.

Petroleum refining involves the separation of crude petroleum into fractions and subsequently treating of these fractions to make them into petroleum products. Petroleum is a complex mixture of hydrocarbons plus small amounts of water and organic compounds of sulfur, oxygen and nitrogen, as well as compounds with metallic constituents, particularly vanadium, nickel and sodium. Crude oils vary in composition because of different proportions of the various molecular types and molecular weights of hydrocarbons. One crude oil may contain mostly paraffins, another mostly naphthenes; one may contain a large quantity of lower hydrocarbons, another may consist mainly of higher hydrocarbons and highly viscous components. Crude oils are usually characterized to one of three types depending on the relative amounts of waxes (higher molecular weight paraffins that are solid at room temperature) and asphalts present. The wax content correlates with the extent to which the crude is paraffinic. The presence of asphalts indicates an aromatic crude.

Petroleum is processed in order to obtain fuels, lubricants and petrochemical raw materials. Refinery processes are either simple, such as those used to separate crude oil into fractions, also called primary fuels, or more complicated when chemical reactions take place and the structure of the molecules is changed, the so called secondary fuels. The most important physical separation process is distillation -atmospheric and vacuum, based on differences in boiling points of the components of a mixture. Crude oil is primarily a complex mixture of hydrocarbons, some of which have the same or nearly the same boiling point. Consequently, except for the lowest-boiling hydrocarbons, it is

not possible to separate crude oil into pure compounds by distillation. Crude oil is, therefore, separated into mixtures having a rather narrow boiling point range. This distillation is carried out at atmospheric pressure and produces several cuts and a residue, or column bottom, boiling at temperatures higher than 300 ºC. Fractionation of the column bottom at atmospheric pressure is not possible because it is cracked before distilling. For this reason, it is fractionated by vacuum distillation. In order of their boiling ranges, the main cuts obtained in atmospheric distillation are liquefied petroleum gas (LPG), straight-run light and heavy naphtha, kerosene, gas oil and fuel oil. In vacuum distillation of the atmospheric residue, the main products are gas oil, fractions of lubricant oils and asphalt. The amount of gasoline precursor obtained by distillation is, in general, less than that required by the market, consequently, it is frequently necessary to transform heavier cuts into gasoline. This transformation is achieved by various cracking processes such as thermal cracking, catalytic cracking and hydrocracking. The percentage of heavier cuts available to be cracked depends on the type of petroleum and on the required distribution of the other products.
Most of the products from a refinery are processed to improve their quality with hydroprocessing and reforming as principal processes. Hydroprocessing removes undesirable components, mainly sulfur and nitrogen compounds, and processes such as catalytic cracking and , catalytic reforming improve the quality of gasoline by increasing its octane number. The petroleum industry also provides hydrocarbons that are the raw materials for the petrochemical industry.

Most petroleum products, including kerosene, fuels oils, lubricant oils and waxes are fractions of petroleum that have been treated to remove undesirable components. Other products, like gasoline, aromatic solvents, and isomers, are even totally or partly synthetic in that they have compositions that are impossible to achieve by direct separation from crude oils. They result from complex chemical processes that change the molecular nature of the selected compounds of the crude oil; in other words, they are the products of refining or they are refined products. They are obtained by the called processing of secondary fuels.

Modern refinery operations are very complex, and to an individual not familiar with the industry it seems to be an impossible task to reduce the complexity to a coordinated group of understandable processes. In a typical refinery operation the main goal is the conversion of as much of the crude oil into more valuable fuels as can be economically practical.

The quality of the crude oil that will be processed in the future is expected to worsen, with the sulfur and nitrogen contents, as well as densities, increasing. Greater densities will mean heavier crude oil, and the refineries will be challenged to process the entire crude oil spectrum. This means that extensive refinery additions and modifications will be required, and the shift in market requirement and strategies among gasolines and reformulated fuels for transportation, will challenge catalyst suppliers and refinery engineers to develop sustainable and innovative solutions to these challenging problems.

The other important factor, the environmental impact of processing crude oil derivatives, will require that a major shift take place in product distribution (i.e.

alternative and less conventional fuels). This will have a major effect on refinery processing operations and will place a burden on refinery construction in addition to be able to cope with increased capacity for high sulfur and heavier crude oils.

A refinery is defined as essentially a group of manufacturing plants that vary in number in accordance with the variety of products produced; refinery processes must be selected and products manufactured to give a balanced operation in line with refinery profitability. For this reason the refinery must be flexible and able to change operations as needed. On the other hand, this could mean more processes to accommodate the ever changing demands of the market.

Furthermore, a refinery complex must also include all necessary non-processing facilities, adequate tank capacity for storing of crude oil, intermediate and finished products, all power systems, and maintenance shops. It must be capable of operating continuously round the clock 24 hours a day, seven day per week.
The production of liquid product streams by distillation or by cracking processes is only the first of a series of steps that leads to the production of marketable liquid products. Several other unit processes are involved in the production of a final product. Such processes may be generally called secondary processes since they are not used directly on the crude petroleum but are used on primary streams that have been produced from the crude oil.

2. Types of Refineries

Early refineries separated petroleum components into wanted fractions by some type of distillation. Some chemical or heat treatment often followed to improve the quality of the crude product obtained. Around 1912, the demand for gasoline began to exceed the supply, and it was found that the application of heat and pressure to heavier, unwanted fractions converted the large molecules into smaller ones in the boiling range of gasoline. Refineries were originally batch units with cylindrical shell stills operated as topping units. Pumping oil continually through heaters knows as pipes or tube stills and separating the constituents into continuous fractionating columns that separate many fractions between gas and asphalt, is now universally practiced. Primary separation is followed by various conversion processes designed to optimize yields of the more profitable and wanted products. Generally this means maximum yield of gasoline. Technologically, it would be quite possible to convert the crude entirely to gasoline, but the cost would be quite prohibitive. Depending on the processes used, refineries can be classified as simple, complex or fully integrated.

A simple refinery will include crude oil distillation, catalytic reforming and treating. Its range of products is relatively limited: LPG, motor fuels, kerosene, gas oil, diesel fuel and fuel oil.

A more complex refinery will make a greater variety of products and require the following additional processes: vacuum distillation, catalytic cracking with gas recovery, polymerization, alkylation, asphalt oxidation. Cracked gases will feed polymerization and alkylation units to produce high-octane gasoline (motor and aviation) and may also be feedstock for petrochemical processing. Residue from the vacuum still will go to asphalt manufacture.

The fully integrated refinery makes a full range of products. A number of complex units will have been added to those already mentioned just to produce a line of finished lubricating oils, greases and waxes. These will include high vacuum fractionation, solvent extraction, deasphalting, dewaxing and treating.

Depending on the type of crude oil used, the refinery may have to include one or more hydrogen processes. If sour crude oil is used, and if sulfur can be recovered in profitable volumes, a unit for this purpose will be installed. If a coke market exists, some type of coking unit will be made a part of the refinery

Process are chosen, arranged and interrelated according to the market the refinery serves and the products its manufactures. A refinery must have flexibility; that is, its management must be able to alter operations as needed to maintain a balanced output. For example, a refinery cannot produce a given volume of light oil (gasoline and the like) without simultaneously producing a certain quantity of higher boiling materials, say heavy fuel oil. If the gasoline moves to market faster than the fuel oil, the later will accumulate in the storage tanks and eventually force the plant to shut down. A flexible refinery will help solve this problem. It would include a cracking unit to change the excess heavy fuel into more gasoline along with coke as the residual product, or it might include a vacuum still to separate the heavy fuel oil into lube oil stocks and asphalt.

3. Types of Crude Oil to be Processed

A significant controlling factor in the processes to be used is the type of crude oil to be run. Crude petroleum is primarily a liquid of widely varying physical and chemical properties. Common colors are green, brown and black and occasionally almost white or straw color. Specific gravity ranges from 0.73 to 1.02; however most crudes are between 0.80 and 0.95. Viscosity varies too. Principal elements in crude petroleum are carbon and hydrogen, usually in a carbon/hydrogen ratio between 6 and 8. The hydrocarbons are mainly liquids and gases, with some solids in dispersion or solution. Among the many other materials usually present are small amounts of sulfur, nitrogen and oxygen in the form of hydrocarbon derivatives, traces of such metals as nickel, vanadium and iron; and water (emulsified in the oil and sometimes as high as 30 percent). The water is generally in the form of saturated solutions of calcium and magnesium sulfates and sodium and magnesium chlorides.

The hydrocarbons are of three major types: paraffins, naphthenes and aromatics. The very large range in their proportions and the ratio in which specific series of hydrocarbons appear determine the physical operations to be used in separating these components, such as by distillation. The presence and extent of some of other materials such as sulfur and oxygen determine the chemical conversion operations to be used.

Apparently, the simpler molecular structures are more abundant than the highly branched ones in the lower boiling ranges. Therefore the simpler paraffins, naphthenes and aromatics predominate, and the isomers occur only in small percentages. At higher boiling ranges, the content of polynuclear aromatics and polycycloparaffins increases while that of normal paraffins, branched chain paraffins and monocycloparaffins drops.

The refiner uses paraffins first for producing high-octane motor fuels and second for conversion to chemical intermediates. Very stable at atmospheric conditions, paraffins react mainly at elevated temperatures and pressure.

Crudes are commonly classified according to the residue from their distillation, this depending on their relative contents of the three basic hydrocarbons: paraffins, naphthenes and aromatics. About 85 percent of all crude oils fall into the following three classifications:

- **Asphalt-Based:** containing very little paraffin wax and a residue which is primarily asphaltic (predominantly condensed aromatics). Sulfur, oxygen and nitrogen contents are often relatively high. Light and intermediate fractions have high percentages of naphthenes. These crude oils are particularly suitable for making high quality gasoline, machine lubricating oils and asphalt.
- **Paraffin-Based:** containing little or no asphaltic materials, are good sources of paraffin wax, quality motor lube oils, and high grade kerosene. They usually have lower non-hydrocarbon content that do the asphalt base crude.
- **Mixed-Based:** containing considerable amounts of both wax and asphalt. Virtually all products can be obtained, although at lower yields than from the other two classes.

Knowledge of the characteristics of individual crude oils is essential to the achievement of maximum efficiency in refining. Application of such knowledge and the great flexibility of modern processing methods can prevent or minimize variations in the characteristics of finished products that can result from differences in crude oil feedstocks.

4. Refinery Processes

Refining starts with crude oil distillation. A simplified schematic of the most important distillate fractions and their subsequent processing in a typical petroleum refinery can be shown in Figure 1. The crude oil is heated in a furnace and charged to an atmospheric distillation tower, where it is separated into butanes and lighter wet gas, unstabilized light naphtha, heavy naphtha, kerosene, atmospheric gas oil, and topped crude. It should be noted that the designation of these fractions is somewhat arbitrary, and the cuts may vary from one refinery to another, depending upon application. Moreover, the composition of crude oils varies greatly, for example, a light crude from Kuwait may contain as much as 30 wt % in the boiling range of 0 - 200 °C, whereas a heavy Venezuelan crude may have only 5 - 10 wt % in this boiling range.

The lightest ends of the distillation column are the dissolved gases (methane to butanes) which boil at less than 70 °C. They are primarily used in light heating applications and sold as bottled gas for home heating, campers and barbecues, and usually do not require much upgrading. Commercially they are pressurized and sold as liquefied gases or LPG. They have the highest hydrogen/hydrocarbon ratios of all the crude oil products, greater than about 2.5. The linear butanes are often isomerized to branched-isomers to be used for alkylating linear butanes and pentanes to make higher-octane products for the gasoline pool.

The reduced crude bottom from the vacuum tower is then thermally cracked in a delayed coker to produce wet gas, coker gasoline, coker gas oil, and coke. Without a coker, this heavy resid would be sold for heavy fuel oil or asphalt. Historically, these heavy bottoms have sold for about 70 percent of the price of crude oil.

The atmospheric and vacuum crude unit gas oils and coker gas oil are used as feedstocks for the catalytic cracking or hydrocracking units. These units crack the heavy molecules into lower molecular weight compounds boiling in the gasoline and distillate fuel ranges. The products from the hydrocracker are saturated. The unsaturated catalytic cracker products are saturated and improved in quality by hydrotreating or reforming.

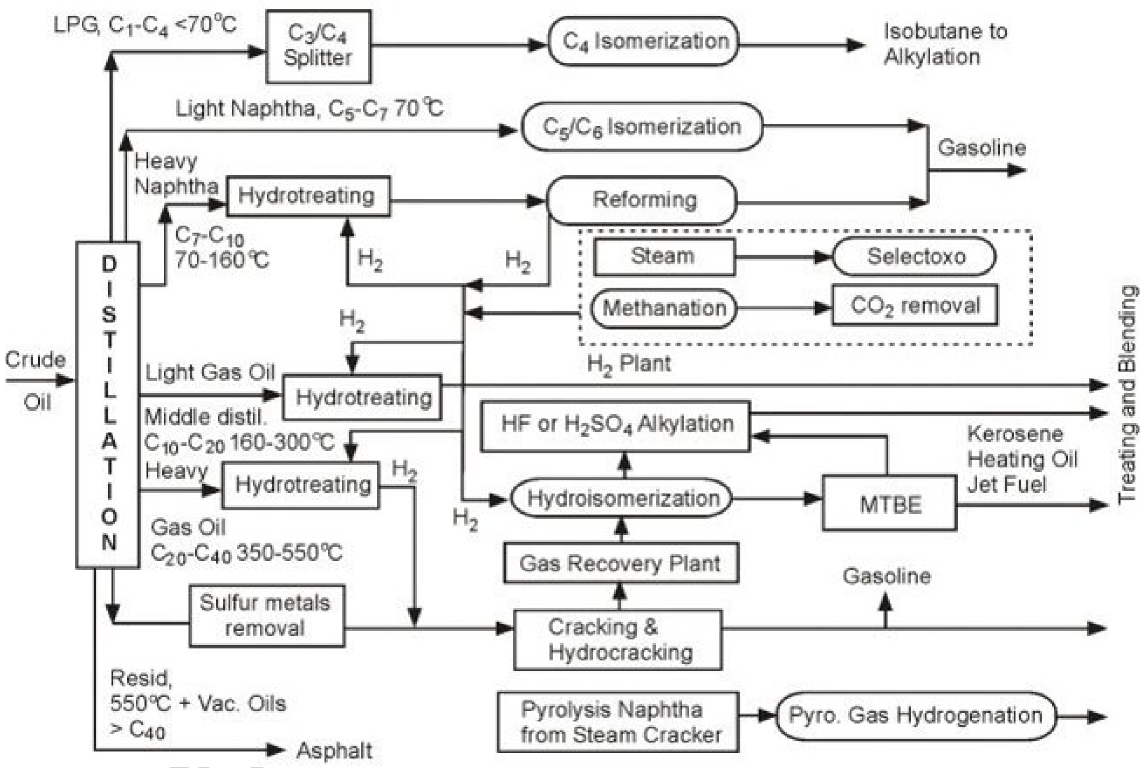

Figure 1. Schematic flow chart of a modern refinery

The light naphtha streams from the crude tower, coker and cracking units are sent to an isomerization unit to convert straight chain paraffins into isomers that have higher octane numbers. The heavy naphtha streams from the crude tower, coker and cracking units are fed to the catalytic reformer to improve their octane numbers. The products from the catalytic reformer are blended into regular and premium gasolines for sale. The heavy naphtha fraction is composed primarily of saturated hydrocarbons, monocyclic aromatics and derivatives of cyclohexane. Depending on the source of the crude, organic sulfur, nitrogen and metal compounds may be present in significant quantities. These contaminants can negatively affect downstream processing. In this case this stream is hydrotreated with addition of hydrogen to the feed to remove the largest part of sulfur, nitrogen and metals.The straight run gasoline and light virgin naphtha cuts find application mainly as gasoline, while the heavy naphtha possesses less than satisfactory burning characteristics for use in the spark ignited internal combustion engine and hence is converted to jet fuel or kerosene. The quality of the gasoline fuels is evaluated on the basis of octane number. During the compressive portion of an internal combustion engine cycle, the gaseous air fuel mixture may spontaneously combust before full compression and ignition are realized. This results in a substantial inefficiency in power generation and is observed as a knocking in the engine. High quality gasoline reaches combustion only when the piston is at maximum compression, leading to maximum power. The octane number is an empirically determined number associated with a molecule's ability to resist combustion until maximum compression and ignition and is the number that appears on gasoline tanks in service stations.

The next lower cut is called light gas oil with carbon numbers of C_{10} to C_{20} and a boiling point range of 160 -300 °C. The light end of this fraction may be blended into the gasoline pool and/or used for fuel oil. A special cut, which boils between 200 and 260 °C is kerosene, which is used as common heating oil and jet fuel. Some of the heavier ends of this fraction are used for diesel fuel.

The next most important fraction of the crude is called heavy gas oil, which distills between 350 and 500 °C at atmospheric pressure. It is represented by molecular species with carbon numbers of C_{20} to C_{40}, usually as multi-ringed aromatics with a hydrogen/carbon ratio of less than one. This cut after catalytic cracking is a source of gasoline and commercial heating oils, and jet fuels; it contains a relatively high percentage of sulfur, nitrogen compounds and organometallic compounds, all three of which function as poisons to downstream processing catalysts, equipment, or to the environment. Accordingly, the more heavily contaminated gas oils must undergo mild hydrotreating to reduce these contaminants to acceptable levels before feeding to a catalytic cracking unit.A heavier lowest cut, 550 °C vacuum residue is derived from the necessity of heating to 550 °C, while vacuum distilling this portion of the crude oil. It also tends to concentrate the impurities such as sulfur, nitrogen and heavy metal-containing organic compounds. The hydrogen/hydrocarbon ratio is significantly less than 1. Depending on the origin of the crude, the sulfur content can be between 3% and 5%. For crude with moderate metal and sulfur contents, fluid catalytic cracking (FCC) is used to break the larger molecular weight range (C_5 to C_{10}). Successful cracking results in greater yields of gasoline and heating oils from each barrel of oil and thus improves the overall economics of the refinery end products.For feeds with metal contents above the tolerable limits for the FCC process, there are two options:

- Hydrotreating and hydrocracking decrease the molecular weights, increase the hydrogen content and remove metals, sulfur, nitrogen and oxygen-containing compounds.
- Thermal coking removes heavy metals while rejecting carbon to improve its value.

The final, heaviest cut, asphalt, is not distilled; its primary function is in surfacing highways, and it has little other value.

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Biographical Sketches

Associate Professor Jorge Beltramini is a member of the Nanomaterials Centre (NanoMac), Department of Chemical Engineering at University of Queensland, Australia, where his present research interest is focus on the development of nanoporous materials such as mesoporous molecular sieves and clays and their application in catalysis in the energy and environmental areas. He had more than 20 years of teaching, research and consultancy experience in the main areas of Solid State Catalysis, Surface Characterization, Material Science and Reactor Design and Modelling. He held academic and industrial appointments in Argentina, Australia and Saudi Arabia. He worked in the design, development, testing, selection and commercialization of different petroleum refining and petrochemical catalysts. He is a recognized authority in the field of catalysis sciences as testified by the more than 110 scientific and technical papers delivered at international forums and published in international refereed journals. He is the co-author of the recently published book 'Naphtha Reforming: Science and Technology'.

Professor Max Lu is Chair of Chemical Engineering in Nanotechnology, and Director of the Nanomaterials Centre (NanoMac) at the University of Queensland. He has co-authored over 200 scientific papers published in international journals and conferences. He has been invited keynote and plenary speaker to several international conferences. He received the Young Scientist Award (International Union of Materials research Societies) in 1997 and University of Queensland Foundation Research Excellence Award in 1999, The Orica Award of Excellence in Chemical Engineering, 2001, and the Le Fevre Prize by the Australian Academy of Science in 2002. Dr Lu is also an editorial board member of four international journals including Carbon, Journal of Porous Materials and Journal of Nanoscience and Nanotechnology. Dr Lu, as visiting professor, has associated with University of Illinois-Urbana-Champaign, Princeton University, PennState University, University of Antwerp (Belgium), Nanyang Technological University (Singapore), Princeton University and Hong Kong University of Science and Technology. He is Fellow of IChemE, member of RACI and AIChE. Dr Lu is co-inventor of four patents on nanostructured materials, which are currently being commercialised by a University start-up company, of which he is a Director.