

OIL REFINING INDUSTRY: GENERAL ASPECTS

Structures and schemes

1.1.1 The aims of refining

The series of treatments to which crude oil is subjected in order to obtain the desired range of products is generically known as crude oil refining; as a consequence, refineries are the industrial plants where these treatments are carried out. Originally, the term refining referred more specifically to an appropriate procedure for purifying a raw material (or unprocessed product), to render it more suitable for use. In the past, only a single product was obtained from petroleum by distillation, and sometimes by treatment with chemicals: lamp oil (kerosene). These treatments, which required only modest technology, constituted refining. Later, the term refining came to be used to refer to all the increasingly complex technological activities carried out to obtain a series of intermediate outputs and commercial products from crude mineral oils. For most practical purposes, pure compounds are not required, but rather blends with specific marketable properties. In other words, the properties of these products are determined more by their suitability for practical use than by their chemical composition. This gives the refining industry a certain degree of flexibility, not available to those producing pure compounds with a specific formula, such as the petrochemical industry.

The products of refining can be grouped into a number of main classes: *a*) industrial and domestic fuels (gas oils, fuel oils, Liquefied Petroleum Gas or LPG); *b*) motor fuels (gasolines, diesel, kerosene, LPG); *c*) feedstocks for the chemical and petrochemical industry (virgin naphtha, LPG, olefins); *d*) other products (lubricating oils, bitumens, paraffins, solvents, sulphur).

The tendency to integrate refining with the petrochemical industry from the beginning has led to

some processes, typical of the latter, being incorporated into refineries, with the result of an additional production of hydrogen, MTBE (methyl-tert-butyl ether) and olefins.

1.1.2 Historical development of the refining industry

The first refineries and their products

Traditionally, the birth of the modern petroleum industry is dated to 1859, with reference to colonel Edwin Laurentine Drake's discovery of the Titusville reservoir in Pennsylvania. However, its beginnings can be brought forward to 1855, when Benjamin Silliman jr., a professor of chemistry at Yale University, after having analysed a sample of crude oil, wrote a farsighted report which concludes: "Your companies have in their possession a raw material from which, by a simple and not expensive process, they may manufacture very valuable products. It is worthy of note that my experiments prove that nearly the whole of the raw product may be manufactured without waste, and this solely by a well directed process which is in practice one of the most simple of all chemical processes (in other words distillation)". Silliman also demonstrated experimentally that one fraction of petroleum was particularly suitable for use in Franklin lamps in place of whale oil, whose price had become extremely high. The report gave rise to a series of initiatives and research projects, crowned with success thanks in part to the determination of colonel Drake, who began to use the percussion drilling technique in the search for petroleum.

This event would not have had the decisive historical importance that it did, were it not for the contribution made by the high quality of Pennsylvania crude: paraffinic, light, almost free from sulphur, rich

in the kerosene fraction and capable of supplying good lubricants.

After Drake's discovery, extraction and refining activities developed very rapidly in the United States. Towards the end of 1870 there was already a flourishing petroleum industry, with about 150 refineries. The largest of these, employed 200 staff to treat about 12,000 t/y of crude oil, mainly to produce lamp oil. The main process carried out by the early refineries was distillation, first run in batch in cheese-box stills, and later in a semi-continuous way using batteries of horizontal shell stills (Giavarini, 1989). The stills were connected to one another in a battery, with the residue passing from one to another, allowing the heaviest fractions to be separated out gradually. In the most sophisticated models, the crude oil was preheated, recovering heat from the hot products exiting the system.

Lamp oil was first treated with sulphuric acid and then with caustic soda to remove the acid itself; it was subsequently washed with water. Often it was then redistilled with live steam and treated with bleaching earths to render it white and odourless like whale oil, and of higher quality than coal oil or shale oil which were foul smelling and smoky. The various types of lamp oil were named for their colour and odour (Prime White, Standard White, Straw Colour, etc).

The distillation residue also began to be sold as a lubricant, without treatment or after treatment with sulphuric acid (bright stock). The lubricants obtained from Pennsylvania crude had fairly good properties, and became established despite the primitive refining technique.

Towards the end of the Nineteenth century, Herman Frash, known for having revolutionized the sulphur market with his innovative extraction process, had an idea which allowed the range of treatable crudes to be broadened considerably; such range was previously restricted to those with an extremely low sulphur content. By using copper oxide he managed to 'sweeten' the fraction used for lamp oil, obtaining a product which did not give off unpleasant odours when burned. The same period also saw the first attempts of the combustion of the 'long' residues of distillation, in fixed industrial plants or to propel ships; however, these fuels became widespread only very slowly.

At the end of the Nineteenth century, two revolutionary inventions by Thomas Edison and Gottlieb Daimler and Carl Benz begin to make their influence felt in the petroleum world, too, marking the beginning of a new era. In the United States, Edison had developed a new lighting system: the electric light bulb. In Germany, Daimler and Benz had successfully

applied their internal combustion engine to a variety of vehicles.

At the turn of the Twentieth century, the demand for lamp oil thus fell drastically, and the demand for gasoline skyrocketed. Exploration was intensified and new wells were drilled; simultaneously, however, a system was sought to obtain more gasoline from crude oil. The concept was clear: the molecules of the heavier components had to be cracked to produce the light constituents of gasoline.

English researchers had noted that heat and pressure influenced cracking reactions. The first patents appeared, but their practical implementation ran into difficulties: if the residue from distillation is overheated, the main product is coke. At this point, another chemist gifted with imagination and great perseverance entered the scene: the American William M. Burton, who in 1911 perfected the cracking process. This was not easy: more than two years of tests, complicated by the need to work at high temperature and high pressure, when riveting was still the most reliable way of joining metal sheets.

Due to funding problems, Burton saw his reactors (9 metres tall) installed only in 1913, and immediately demonstrated that the amount of gasoline obtainable from a barrel of crude could be doubled at the expense of heavy distillates. This represented a significant turning point for the oil industry. It immediately became clear that technological innovations in this sector were extremely profitable, leading to the development of more organized and systematic research. It is worth remembering that the first Burton-Clarke units used coal on a moving grid in the process furnace.

The first decade of the Twentieth century did not bring any great novelties, with the exception of the use of the first coil heaters (pipestill), which encouraged the spread of continuous distillation. These heaters represented a significant technological advance, since they allowed the crude oil to be heated in a controlled way. The construction technique derived from that used for steam boilers. However, the pipestill became widespread only many years later.

The foundations of the modern refining industry

The second decade of the Twentieth century was crucial for the definitive take-off of the modern refining industry, especially in Europe. The growing spread of the automobile led to the increasingly widespread installation of gasoline pumps. A growing number of applications were also found for diesel engines; however, these were for the time being limited to fixed plants and ships' engines. The First World War demonstrated the usefulness of motorized transport, and also saw the first use of aeroplanes for

war; even in preceding years it was easy to forecast an increase in the need for fuels, aggravated by the fact that many new reservoirs (for example, Mexico 1907, Iran 1908) did not have the same quality and yields of the first Pennsylvania crudes.

One disadvantage of the Burton process was the heavy deposition of coke, which made it necessary to stop and clean the unit after a few hours of operation; the process therefore required further improvement. Another famous oil industry pioneer devoted himself to this task: the American Carbon Petroleum Dubbs, a rare example of perfect correspondence between someone's name and their profession. Alongside his father James, Dubbs was a member of a formidable group of scientists who set up the first genuine process company in the petroleum sector (now UOPs, Universal Oil Products). Dubbs' father had developed, and applied in 1912, a simple process to separate petroleum from the emulsified water which it frequently contains: it was sufficient to heat it in coils and then send it for separation. Dubbs applied this idea to cracking: he heated the feedstock in small-diameter pipestills and then sent it to an unheated chamber where cracking continued. The coke was deposited in this chamber, which could be by-passed and cleaned (**Fig. 1**). The process was now really continuous; in addition, non-converted products could be recycled. The plant was ready in 1919 and immediately became a success, so much so that the oil companies most interested in it chose to buy Dubbs' company directly, rather than pay the considerable royalties.

The idea of preheating the crude oil in coil furnaces was eventually applied to distillation; the first fractionation column of modern design, however, only came into operation in 1928. The Dubbs' innovations probably marked the beginning of the modern refining industry.

Dubbs' introduction of cracking was followed by a decade (1920-30) of continuous development: distillation technologies were perfected; vacuum distillation appeared to increase the yield of distillates

and produce bitumen; the thermal reforming process was introduced, which, fed with gasoline fractions, improved their octane number and thus their quality. Other thermal processes, such as visbreaking and coking, can be considered derivatives of Dubbs' basic scheme. In those same years, again in the United States, the production of lead tetraethyl began, used as an antiknock additive for gasolines (Giavarini, 1990).

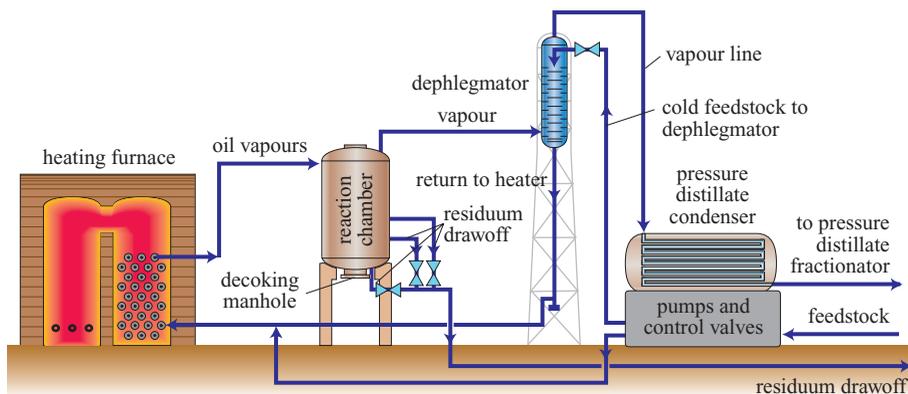
Europe was not without developments in petroleum technologies: suffice it to think of Bormann distillation plants, the Bergius hydrogenation process, the refining processes for mineral oils, and so forth. Without counting the numerous European scientists working in many American process and refining companies. However, from an industrial and strategic point of view, Europe still lagged behind in the second decade of the Twentieth century. During the First World War, the major Empires could depend upon a good refining infrastructure and sufficient oil resources; Great Britain could count on supplies from the East and Russia, though lacking in organization and technology, had vast resources. France and Italy were the least well-prepared, and therefore had to be supplied by the United States during the war.

The advent of catalytic processes

It is well-known that catalysts are substances able to selectively accelerate chemical reactions, and thus to propel specific chemical processes in the desired direction.

The first conversion processes used in the oil industry (of thermal type as seen above) were inefficient from the point of view of specific yields, and produced significant quantities of by-products. Thermal cracking in particular had demonstrated all its limitations by the early 1930s; these limitations become evident halfway through the decade, when the warning signs of war began to appear. Squadrons of fighter planes, with their increasingly efficient engines, required large quantities of high octane gasoline; it was already clear that whoever had the

Fig. 1. Diagram of the first Dubbs thermal cracker (Aalund, 1977).



most efficient air force would have an advantage in any potential war. The Germans, rich in coal resources, chose to follow the (catalytic) route of producing fuels from this.

In the refining industry the time was ripe for the birth of the 'king of processes': catalytic cracking. Few events in the history of industry have had such a profound impact as the introduction of this process, immediately followed by the transformation of numerous other petroleum processes into catalytic processes. The advent of catalytic cracking, linked to the name of Eugène Houdry, marked the end of the phase of the great inventors; after this, developments (though numerous and significant) were increasingly less the result of individual initiatives.

Houdry, an engineer of French origin, worked on a catalytic process allowing more and higher quality gasoline to be produced. For three years he tested all potential catalysts, and discovered that materials based on alumina-silicate, such as certain fired clays, worked well. However, a layer of coke resulting from the pyrolysis of the hydrocarbons formed on the catalyst; Houdry resolved this problem by burning the coke and recycling the catalyst. Unable to put his idea into practice on an industrial scale in Europe, Houdry departed for the United States where, with the help of funding from an oil company, he set up the Houdry Process Corporation. In 1937, the first fully commercial unit came on stream. When war broke out in 1939, the United States already had 12 catalytic cracking plants.

The catalytic alkylation process was also developed simultaneously in Great Britain and the United States during the late 1930s; by blending together light hydrocarbons, not otherwise used in gasolines, alkylation made it possible to produce aviation gasoline of exceptionally high quality.

The first catalytic cracking processes were cyclic, with the catalyst placed in fixed bed reactors, and caused numerous problems. The Houdry Corporation itself developed the first moving bed process. Almost simultaneously, in 1942-43, the fluid bed process appeared, representing another formidable technological innovation.

The purposes of cracking are mainly quantitative: its main aim, as seen above, is to increase gasoline yields. Reforming, by contrast, serves to increase the octane number of gasoline or to produce aromatics. The precursor of catalytic reforming was hydroforming, which used a molybdenum based catalyst; during the Second World War this supplied the United States with the toluene needed to produce trinitrotoluene.

The first modern catalytic reforming process for gasolines, using a platinum-based catalyst, dates to

1949, and led to the immediate abandonment of thermal reforming.

As a valuable by-product the catalytic process produces large quantities of hydrogen: this allowed for the development of catalytic desulphurization processes based on the use of hydrogen (hydrodesulphurization), making it possible to commercialize products more in keeping with increasing environmental concerns.

On the eve of the Second World War, worldwide refining capacity had reached 354 million tonnes per year, two thirds of this in the USA. By the year 2000, this capacity had multiplied tenfold, spread over more than 700 refineries.

The environment and energy saving in the most recent developments in the refining industry

During the second half of the Twentieth century, the refining industry was affected by two significant phases of transformation; while these did not radically alter its structure, they did contribute significantly to the evolution of processes and technologies. The first of these phases mainly affected the decade 1970-80, following the first so-called oil crisis (1973), marking the end of a long period of 'easy petroleum' (in other words at modest prices).

The response of industry was to rationalize all processes (especially distillation) involving significant energy consumption, in order to drastically reduce waste through more rigorous energy recovery (optimization of the heat exchange between effluent streams and incoming crude). Rationalization also involved an improved exploitation of the capacity of individual refineries, and the closure of those which were less efficient in terms of technology and energy use.

The second phase of transformation, characterizing the final two decades of the Twentieth century and the first of this millennium, has been characterized mainly by interventions dictated by environmental factors (Giavarini, 1993). These can be summarized as follows: *a*) reduction of residue, in other words of the 'bottom of the barrel' and therefore of black products (fuel oils), with a consequent increase in distillate products, especially gas oil and diesel; *b*) increasingly drastic reduction of sulphur in fuels on the one hand, and the need to desulphurize a larger number of products on the other, as a consequence of the increase in middle distillates; *c*) removal of lead from gasolines; *d*) reduction of aromatic compounds, especially benzene, in fuels.

In some countries, the main objective was achieved partially in the medium term by revitalizing old visbreaking processes, suitably adapted to meet these new requirements. However, the most rational

solution, though not the cheapest, involved installing catalytic conversion processes using hydrogen (hydrocracking), served by purpose-built plants for the production of hydrogen. In some countries, residue gasification processes were introduced, with the simultaneous production of electrical energy.

The resulting need to treat more distillates, and to carry out a more stringent desulphurization (down to 10 ppm or less) of some products led to a significant increase in severe desulphurization units. This increased desulphurization capacity augmented the need for hydrogen, required in larger quantities than those supplied (as a valuable by-product) by catalytic reforming units. The larger quantities of hydrogen sulphide produced by desulphurization also led to an increase in the number of plants to turn this gas into sulphur.

Mild hydrocracking units were also developed by improving the hydrodesulphurization process.

The removal of lead from gasolines led to significant technical modifications of the catalytic reforming process, which now operated at extremely low pressures and with more active catalysts. In practically all refineries, the isomerization process for fractions C_5 - C_6 was introduced, in its high conversion efficiency version.

Catalytic cracking processes also evolved qualitatively to produce gasolines with a higher octane number. The benzene content was controlled with separation and hydrogenating conversion processes. The need to use MTBE in some cycles led a number of refineries to construct plants to produce this.

In recent decades, the refining industry has benefited from the significant development of quantitative methodologies (models of reactions, kinetics, reaction engineering, automation and control, etc), which have allowed the control of processes and the quality of products to be considerably improved. Thanks to its characteristic flexibility and rapid adaptation, the refining industry has always been able to respond to the numerous quality requirements and variations in demand.

1.1.3 Refining schemes

A refinery is a complex plant consisting of various components (see Section 1.1.4). The most important and characteristic part consists of the plants, or process units, used to refine crude oil. The various processes can be subdivided into the following typologies: *a*) separation units, which obtain the various (intermediate) fractions from crude petroleum, usually sent for further treatments; this separation is obtained mainly with distillation processes, and other

processes of physical type; *b*) conversion (cracking) units to turn heavy fractions into lighter fractions, in order to increase the yield of specific products (such as gasoline); *c*) units to improve the quality of some fractions (or 'cuts') by acting on the chemical composition of their constituents; *d*) units for the removal of unwanted components (such as sulphur); *e*) units to produce lubricating oils (present only in a limited number of refineries).

Units for the blending of the various cuts, and additivition units, which contribute to making the finished commercial products, are not generally considered process units in the strict sense.

Separation units

The most important and widespread physical separation units are those for distillation. All refineries have at least one atmospheric distillation (primary distillation or topping) unit, which separates the crude oil into various fractions with different boiling ranges. Simple in concept, since this is an elementary physical separation, the process is complex from an engineering point of view, since it includes a series of heat recovery units and also incorporates the desalting of the crude oil. This is the only unit which treats all the feedstock crude, and is therefore also extremely large.

Generally speaking, atmospheric distillation is followed by vacuum distillation in order to recover additional distillates from the topping residue (obtained at about 350-380°C) without increasing the temperatures; at higher temperatures, the molecules of the heavier hydrocarbons would crack uncontrollably.

Separation units also include deasphalting processes which extract non-asphaltic hydrocarbons from the vacuum distillation residues using solvents (light paraffins); the non-soluble residue is a solid or semi-solid product, rich in asphaltenes, metals, salts and sediments.

Other separation processes (treatment with amines or other solvents) are used to extract hydrogen sulphide (H_2S) from refinery gases; this is then sent to the sulphur production plant. Various separation processes using solvents are also used to obtain lubricating oils.

Conversion units

Not all refineries are equipped with conversion units; traditionally, in fact, refineries have been subdivided into simple cycle refineries and conversion refineries, referring especially to catalytic cracking units.

Conversion may be of exclusively thermal type, and involve distillation residues (visbreaking and coking units), or distillates (thermal cracking). The

classical conversion processes, however, mainly involve catalytic crackers, traditionally used to treat the heavier distillate fractions obtained from vacuum operation (and in part also the residues), and hydrocracking units. Originally developed to treat heavy paraffinic distillates, hydrocracking units can today be fed with residues (hydroconversion); these residues can also be used as fuel oils or, if suitable, as bitumens. Lower demand for fuel oil has led to the development of special deep conversion processes, based on the cracking of residues in the presence of hydrogen to produce distillates with a modest sulphur content.

In more recent times, the drastic conversion of residues into gas has also been obtained with the introduction of gasification (partial oxidation) processes, based on technology previously applied to solid fuels. In the presence of steam and oxygen, heavy hydrocarbons are turned into hydrogen and carbon oxide which, suitably purified, can also be used as a fuel for the production of electrical energy, exportable outside the refinery.

Units to improve the quality of distillates

The first and best known unit of this type is the catalytic reformer, developed to improve the octane number of the heavier fractions of gasoline (heavy virgin naphtha) by increasing aromatic hydrocarbons and those of isoparaffinic type.

The isomerization unit, on the other hand, is fed with the paraffinic fractions of light virgin naphtha (especially C_5 and C_6), to turn these into isoparaffins. In some cases, it may also be used for C_4 fractions, especially to prepare the feedstock for alkylation plants.

The alkylation plant, by contrast, is used to treat the olefinic fractions C_3 and C_4 from crackers, turning them into branched C_7 e C_8 components with a high octane number by reaction with isobutane.

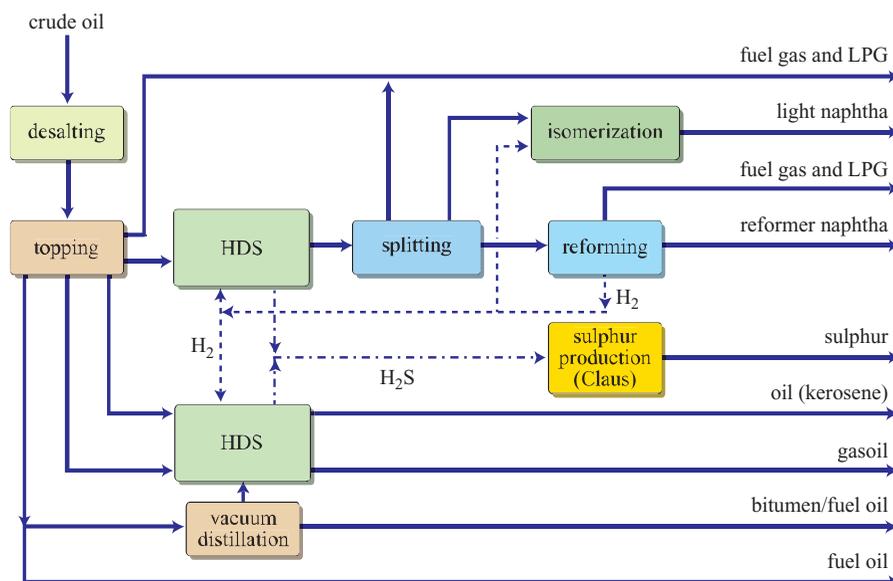
This category also includes polymerization (or more accurately dimerization or oligomerization) units, which recombine specific gaseous fractions of lower value in the form of liquid hydrocarbons, and etherification units for the production of high octane components (for example MTBE or ETBE, methyl-tert-butyl ether or ethyl-tert-butyl ether).

Units for the removal of unwanted components

Generally speaking, all components of crude oil which are not hydrocarbons in the strict sense (in other words formed of C and H) cause problems both of environmental type and relating to the quality of products. These components include salts, sulphur and nitrogen compounds and metals. The salts dissolved in the water emulsified with the petroleum are removed by a desalting unit inserted within the topping column. Sulphur, present in molecules with a varying degree of complexity, is removed using purpose-built hydrodesulphurization units (HDS), which also act on molecules containing nitrogen, oxygen and heavy metals.

The hydrotreating units (HDS) are the most widespread in refineries: the sulphur is turned into hydrogen sulphide, which is in turn turned into elementary sulphur in special units (Claus-type units). Specific light fractions, rather than being treated with hydrogen, may be subjected to other processes to convert mercaptans into less corrosive and foul-smelling compounds (Merox-type units); if the compounds thus formed are not removed, the processes are described as 'sweetening'.

Fig. 2. Diagram of a simple cycle (hydroskimming) refinery.



Plants for lubricants

Lubricants are among the most sophisticated products of refining, and have a high added value. However, considering that demand for these is lower than for other petroleum products, they are produced only in a limited number of refineries; some side cuts and the residue from vacuum distillation are used to produce the base stocks for lubricants. These fractions are then treated in a series of purpose-built

units to improve their viscosity index, behaviour at low and high temperatures, colour, stability etc. Blending and additivation represent the final stages of this process.

Very frequently the base stocks for these oils are sold to specialized companies outside the refinery, which make the finished product. Lubricating oils prepared using synthetic base stocks are increasingly common (see Chapters 1.2 , 8.1 and 8.2).

Fig. 3. Thermal conversion cycle with visbreaking and thermal cracking.

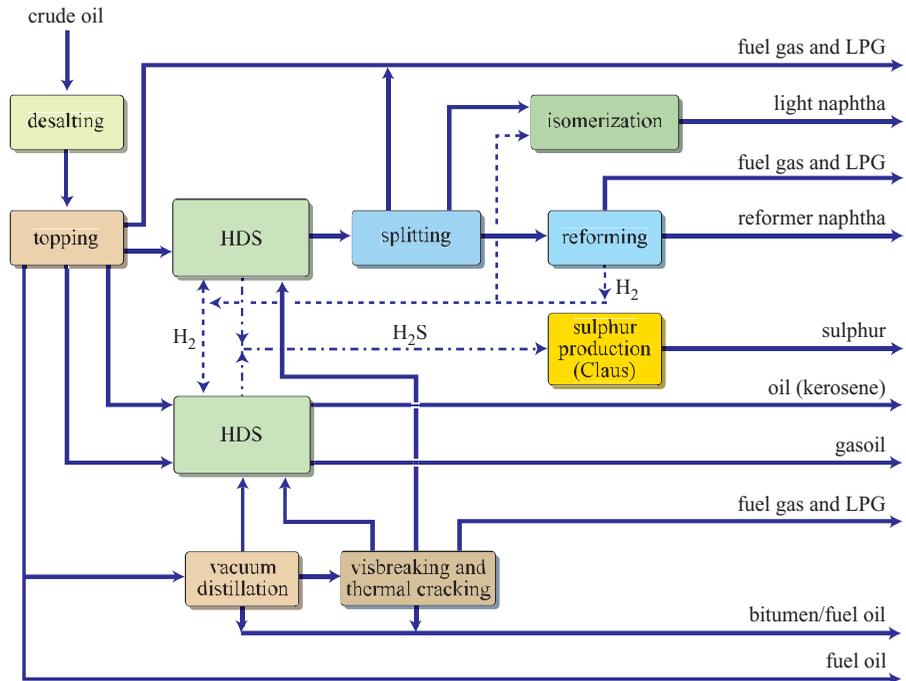


Fig. 4. Thermal conversion cycle with coking.

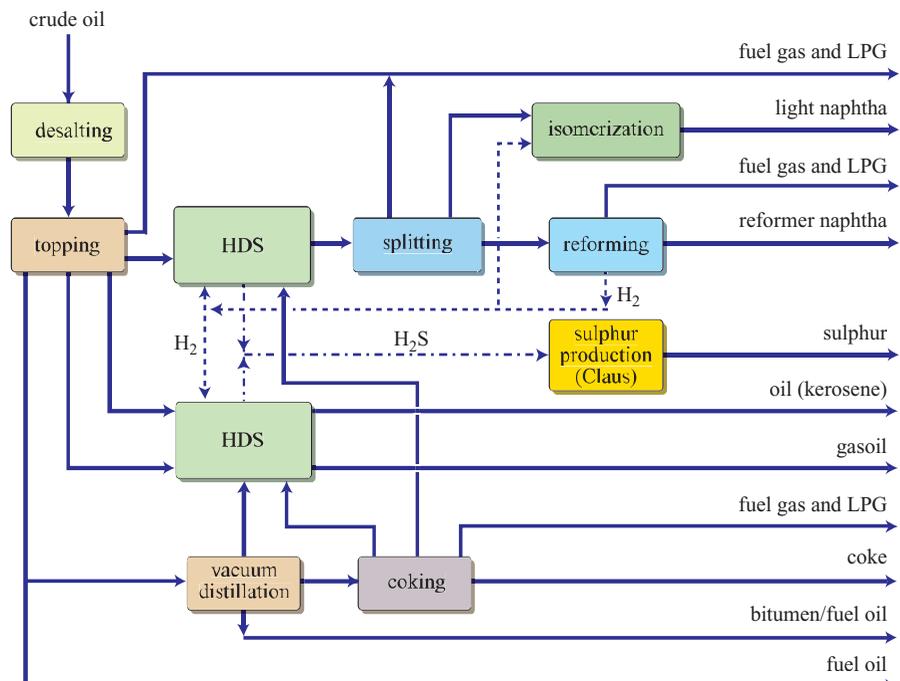


Fig. 5. Catalytic conversion cycle with FCC and alkylation.

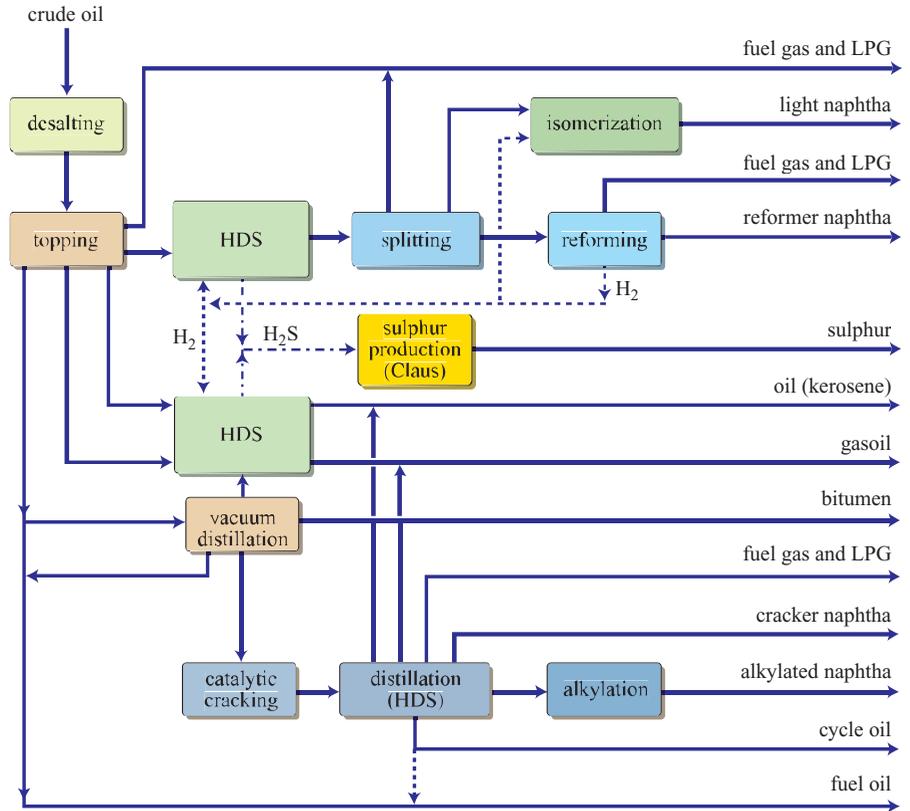
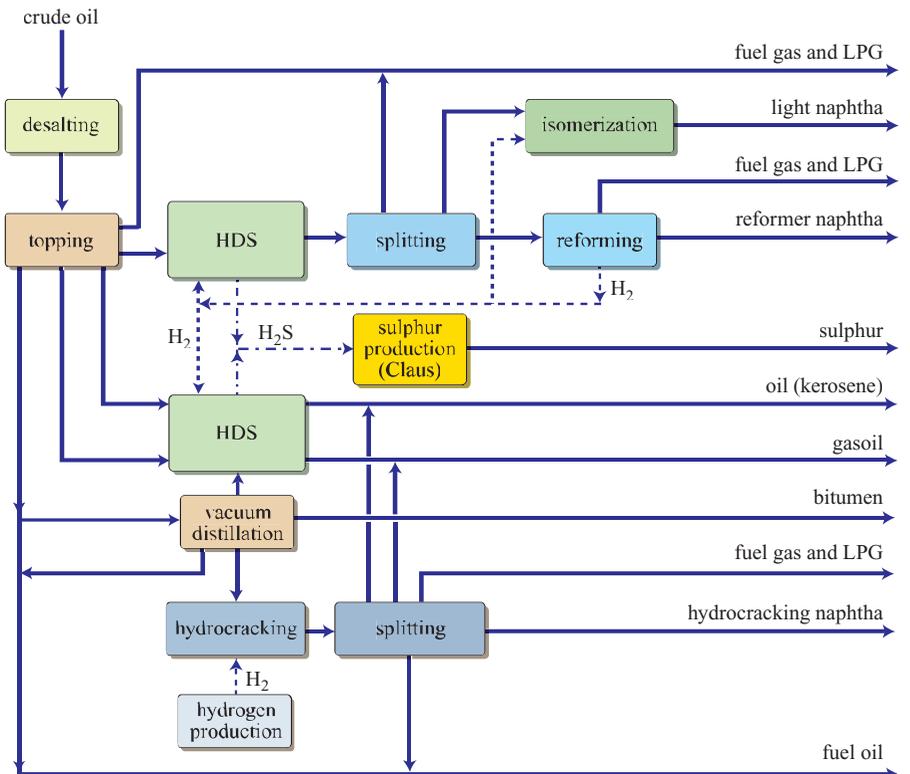


Fig. 6. Catalytic conversion cycle with hydrocracking.



Refining cycles

With the exception of unusual cases of refineries devoted, for example, to the exclusive production of bitumens and fuel oils or lubricants, refining schemes may be of simple type (hydroskimming) or more complex type; the latter typology comprises both conversion (thermal and/or catalytic) refineries and the more complex deep conversion refineries.

Bearing in mind that two identical refining schemes are unlikely to exist, we can attempt to make a subdivision into the following typical cycles: *a*) simple cycle (hydroskimming); *b*) thermal conversion cycle: scheme with visbreaking (and thermal cracking) and scheme with coking; *c*) catalytic conversion cycle: scheme with cracking (FCC, Fluid Catalytic Cracking) and scheme with hydrocracking (HDC); *d*) deep conversion cycle: scheme including the hydroconversion of residues and scheme with deasphalting and gasification; *e*) production of lubricants. For the sake of brevity and clarity, the schemes described below have been simplified.

Many refineries fall into more than one category; for example, they may have both visbreaking or coking, and catalytic conversion plants (FCC, HDC).

Simple cycle refineries (Fig. 2) are traditionally equipped with crude oil distillation plants, desulphurization units for distillates, and with units, above all for reforming, to increase the octane number of gasolines. The hydrogen for hydrodesulphurization is supplied by the reforming units. More recently, due to the reduction or elimination of antiknock additives, reforming units have been accompanied by units for the isomerization of the C₅-C₆ cut. During the second half of the Twentieth century, units for the transformation into sulphur of the H₂S produced by hydrodesulphurization units and separated in purpose-built units also became widespread. Once fairly common in Europe and elsewhere, this cycle is now rarely used in industrialized countries.

In addition to the units in the hydroskimming scheme, the *thermal conversion cycle* also includes visbreaking units (plus thermal cracking) or cokers (Figs. 3 and 4); these represented the first generation of conversion processes (see Chapters 5.1, 5.2 and 5.3). Visbreaking (VB) and coking have always been relatively important, given their ability to treat the residues of distillation (atmospheric and now also vacuum distillation) in a relatively simple and economical way. Coking in particular may also represent the basic process in a deep conversion refinery if a use is found for the coke produced (combustion, sale or gasification). Yields, especially in the case of visbreaking, are not high; the same is true of the quality of the products. However, there is an increase in middle distillates (in the case of VB) or

light products in general (in the case of coking), and this improves the refinery's operational flexibility. However, this cycle is unable, at least in its simplest form, to meet the quality and environmental requirements of a modern industrialized country.

Catalytic conversion refineries are equipped, in addition to the other units, with more traditional conversion plants (see Chapters 6.1 and 6.2), especially those for catalytic cracking and/or hydrocracking (Figs. 5 and 6). From the beginning, catalytic cracking, or FCC, has been more popular in the American refining system than in the European system. Often, the catalytic cracker is followed by an alkylation plant which uses the gaseous by-products of FCC. Hydrocracking, which necessarily requires the presence of purpose-built plants for the production of hydrogen (*steam reforming*), became widespread later, and represents the basis of many modern refining cycles.

Deep conversion refineries have upgrading units suitable for the conversion of residues, to make these more environmentally friendly and to maximize the production of distillates and light products. Traditionally, upgrading processes are classified into carbon rejecting and hydrogenation typologies. Alongside coking and visbreaking, the former category includes deasphalting processes using solvents. The second category includes the various versions of hydroconversion processes. A separate category comprises gasification processes of IGCC type (Integrated Gasification Combined Cycle, see Chapter 7.3). The catalytic cracking process (FCC) itself can be partially fed with residues (see Chapter 6.1). The choice of process depends on the properties of the residue to be treated: above all viscosity and its content in contaminants, such as asphaltenes and metals (see Chapter 7.2).

Among the various possible configurations, Figs. 7 and 8 show two possible deep conversion cycles. Gasification may also be included after coking (see again Fig. 4) to use the coke produced, or visbreaking (see again Fig. 3) to gasify the residue (tar).

The *production of lubricants* requires the presence of special units, usually in addition to those present in the preceding cycles. The feedstocks used are distillates selected to optimize quality and yields, and minimize by-products.

As stated earlier, the traditional bases for lubricants are the products of vacuum distillation, which are first subjected to an extraction process using solvents to separate out aromatics and paraffinic waxes. Residue may also be used, with a prior removal of asphaltic components.

Treatments with solvents may be replaced by hydrorefining processes (such as HDC, see Chapter 8.2), perfectly integrated and already present in

some of the refining schemes considered. This allows for the production of base stocks for lubricants with good yields and excellent quality, starting from crudes traditionally unsuited to this purpose.

Fig. 9 shows an integrated scheme for the production of oils, both with solvent extraction and with HDC.

Refinery's conversion ratio and complexity index

The *conversion ratio* is generally defined as the ratio of the sum of the capacities of individual conversion units to the capacity of the atmospheric distillation plant. The conversion units are compared to catalytic cracking using coefficients (FCC equivalent) which 'weigh' the capacity of individual units to convert heavy products into lighter and more valuable fractions. So for example:

- FCC 1.00
- VB 0.33
- coking 1.70
- hydroconversion 1.20
- deep conversion 2.10

$$\text{conversion ratio} = \frac{\text{FCC capacity} + 0.33 \text{ VB capacity} + 1.70 \text{ coking capacity} + \dots}{\text{distillation capacity}}$$

The *complexity index*, or *factor*, of a refinery serves to give an idea of its structure and 'value', since it takes into account the cost of each plant relative to its unit production capacity; this is then related to the cost of the distillation unit per tonne of capacity.

Thus, if a given plant required an investment five times higher than that of the topping plant per unit of feedstock, but its capacity is 1/6 that of the topping unit, the partial complexity index for that plant can be calculated by multiplying the coefficient 5 by its capacity relative to the topping unit, and therefore:

$$\text{complexity index} = 5 \cdot 1/6 = 0.84$$

As an example, the complexity indexes for reforming and catalytic cracking are 3.4 and 7.2 respectively. The overall complexity index for the whole refinery is the sum of all the partial complexity indexes.

To give an idea of orders of magnitude, a simple cycle refinery may have a complexity index of 3-5; a conversion refinery using classic processes will have an index of 7-9; a complex refinery will generally have an index of over 10.

Treating crude oil requires the consumption of energy in the form of various types of fuel (refinery gases, methane, fuel oil, coke); in other words, the

Fig. 7. Deep conversion cycle using hydroconversion processes.

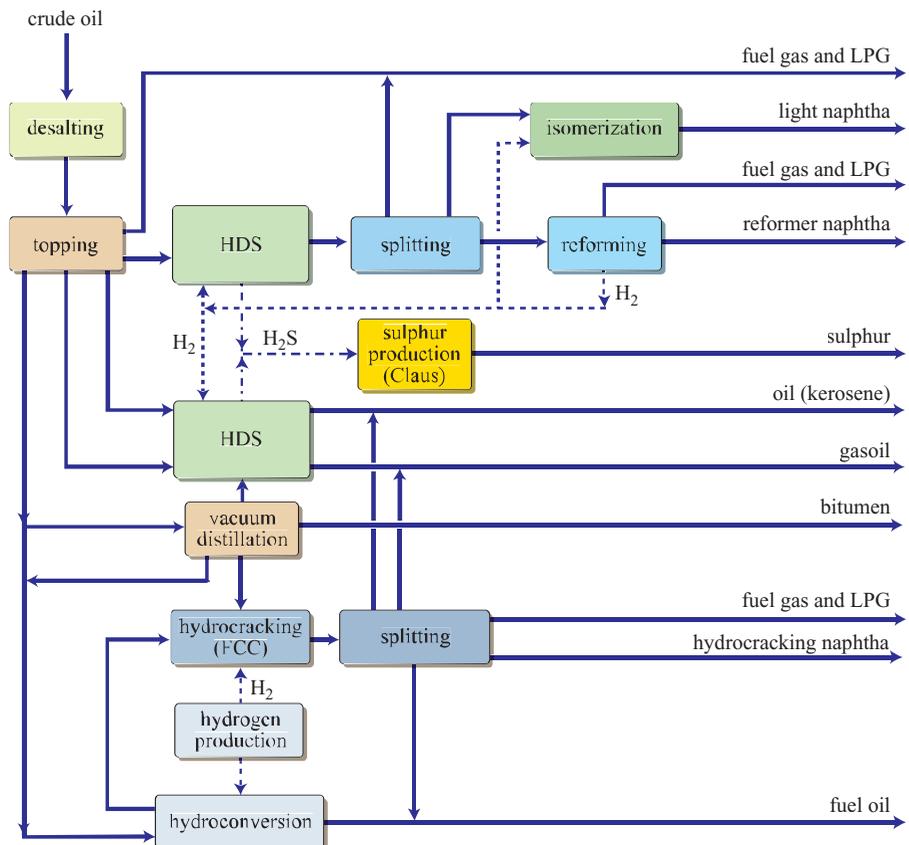


Fig. 8. Deep conversion cycle with deasphalting (precipitation of asphaltenes with solvent) and gasification (IGCC).

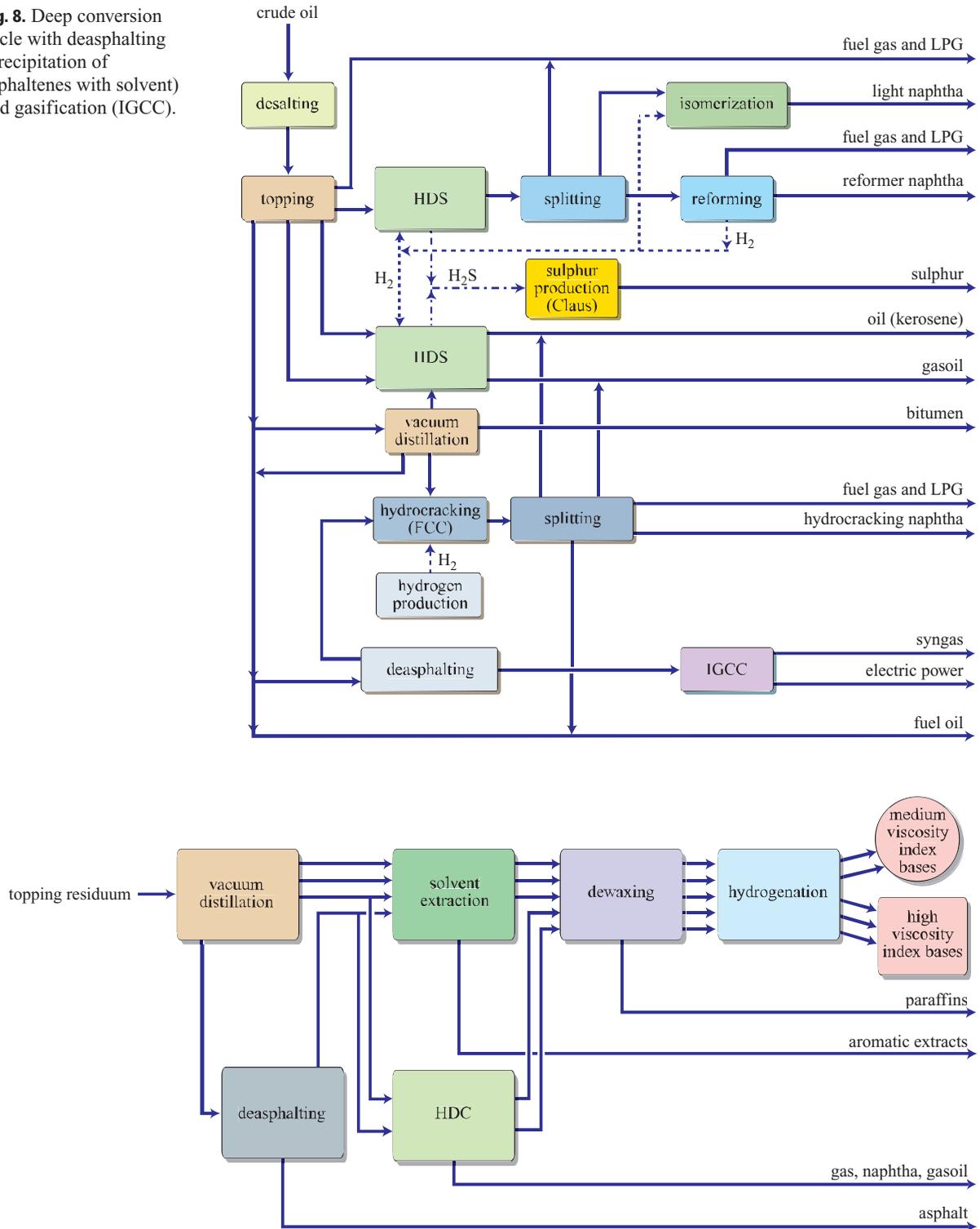


Fig. 9. Integrated cycle for the production of lubricating oils in a refinery equipped with hydrocracking units (HDC).

refinery consumes a certain amount of the incoming crude. A smaller percentage is consumed due to losses of various types (vaporization, accidental losses, discharge from relief valves, etc.). Obviously, the more

complex a refinery is, the greater both consumption and losses.

The diagram in **Fig. 10**, showing a conversion cycle equipped with FCC, alkylation and hydrocracking

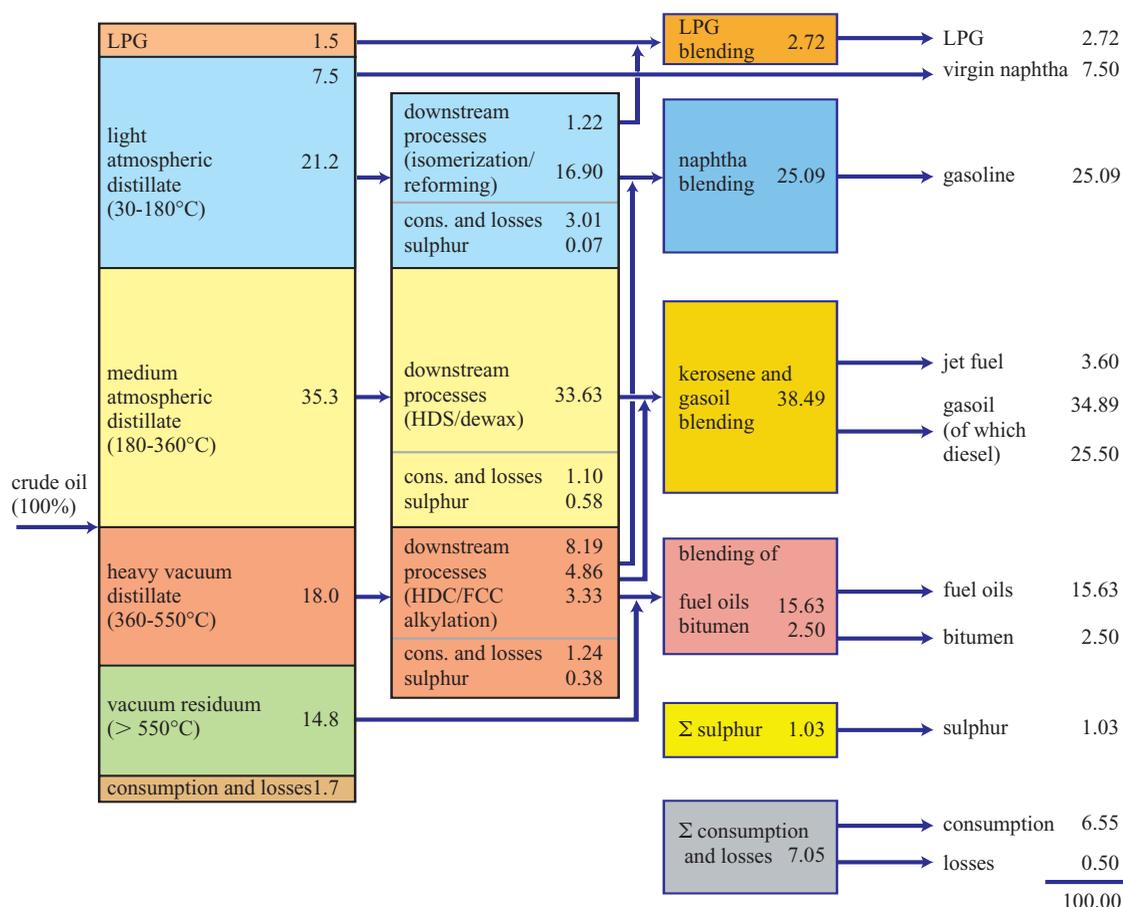


Fig. 10. Typical yields of a conversion refinery (% of crude oil mass).

units, in addition to reforming and isomerization units, gives a quantitative indication of typical yields and consumption for the various treatments (Iadanza, 2004).

1.1.4 The structure and complexity of refineries

Refineries, in other words the plants where crude oil is treated to obtain the desired range of products, are complex entities consisting of: *a*) a sequence of process units linked together according to different schemes, as seen above; *b*) utilities to generate and distribute electrical energy, steam, purified water, compressed air, nitrogen, fuels for internal use, etc.; *c*) storage tanks for crude oil, intermediate and finished products; *d*) systems to transport crude oil, intermediate and finished products.

At the beginning of the year 2000, there were around 730 refineries worldwide, with a treatment capacity of about 4 billion tonnes of crude oil. Refineries are classified on the basis of their

capacity, expressed in t/y or in barrels of crude oil treated per working day (to calculate the latter from the former divide by 50), and on the basis of the treatment scheme adopted. No two refineries work in a completely identical way; the differences are determined by market conditions for the product and the properties of the raw material. A considerable amount of space is taken up by the tanks used to store crude oil (working storage), intermediate products and the various finished products; the area needed is thus much larger than that of a chemical plant, in part also due to safety requirements (safety distances).

In the years before the Second World War, the ground plan of refineries differed considerably from that of today. Starting from the second half of the 20th century, plants characterized by greater practicality were built, based on the following concepts: *a*) creation of one or more areas for storage tanks separate from the plants; *b*) unitary design of the treatment cycle and its predictable developments; *c*) grouping of plants in a single zone, but covering various areas, with a single control room;



Fig. 11. Typical ground plan of a refinery of the second half of the Twentieth century.

d) concentration of the production of steam and electrical energy in a single plant; e) centralization of maintenance programming; f) concentration of effluent treatment systems in specific sites; g) identification of areas for expansion and development, for both plants and storage tanks.

Fig. 11 (Rumbold, 1971) shows the ground plan of a typical refinery of the second half of the Twentieth century, which is in some ways still relevant to today. The refinery is divided into a number of areas ('islands'), each of which hosts one or more plants; the islands are separated by safety zones which form a network of roads, essential for the plants to work safely. Storage tanks are grouped in separate areas. If the refinery is on the coast, it takes advantage of the availability of mooring facilities for reception and delivery.

Some fundamental design criteria derive from regulations and legal requirements, or from unification procedures. The type, shape and modular dimensions of storage tanks are thus standardized; the process

units are outside, with the exception of some specific machinery and appliances and the remote control instruments, grouped in a single building (control room). Heat exchangers, usually of the tubular type with floating heads, are generally of standardized length; also standardized are the diameters, thickness and flanging of pipelines. All electrical appliances are of explosion-proof type. The gaseous discharges from relief valves are sent to the flare.

The inspiring principles listed above remain fundamentally valid; to these have been added design and management criteria dictated by a greater sensitivity towards safety and the environment. So, for example, the old control rooms equipped with windows and initially located in the middle of the plants zone, have been replaced by bunkers in reinforced concrete, resistant to explosions and fires, and which 'see' the plants only through control instruments and television cameras. The complexities of safety and environmental protection are discussed



Fig. 12. Overview of a modern refinery (Eni, Sannazzaro de' Burgondi refinery).

in Chapters 9.1, 9.2. **Fig. 12** shows an overview of a modern refinery.

The evolution of processes is dictated by social and, especially today, environmental needs. As a consequence, the current structure of the cycles, and thus of the plants, takes into account the need to convert residues to obtain a greater production of distillates (especially higher quality diesel) and/or hydrogen. Partial oxidation (gasification), though requiring substantial investments, has become increasingly important. As a result, deasphalting processes have been revitalized, and thermal processes (such as cracking, visbreaking and coking), which supply the feedstock for IGCC plants have been maintained or even expanded. Desulphurization plants have been improved in terms of both quality and quantity.

The integration of refining and the petrochemical industry has followed two main principles: according to the first, the refinery must be adjacent to the petrochemical plant, but separate from it; according to the second (less frequent), the refining plants must be located inside the petrochemical complex, with shared utilities and integrated management.

Modern refineries have adopted some processes previously typical of the petrochemical industry;

principal among these is the production of hydrogen (steam reforming). The production of MTBE, too, introduced in some refineries during the last decades of the past century, is typical of the petrochemical industry, as was the gasification process (IGCC). This type of integration continues, turning the refinery into an increasingly chemical and sophisticated plant.

Some possible scenarios for the immediate future may have a significant impact on how the structure of refineries evolves from the second decade of this millennium onwards. These include the evolution of petroleum prices, aspects linked to the reduction of CO₂, the evolution of motor fuels (from gasolines to gas oil and hydrogen), the development of biotechnologies and so forth. Adding to these the developments which will affect the industry as a whole (process intensification, automation, energy saving, reduction of emissions, etc.), the changes forecast for the first 20 years of the Twenty-first century will probably be more significant than those of the past 60 years, and will affect all existing refineries. The most widely accepted and authoritative forecasts confirm that petroleum will continue to play a dominant role during the first three decades of the Twenty-first century.

For various reasons, the increase in the consumption of petroleum products in western Europe, Japan and the United States is less marked than in other countries which are rapidly developing

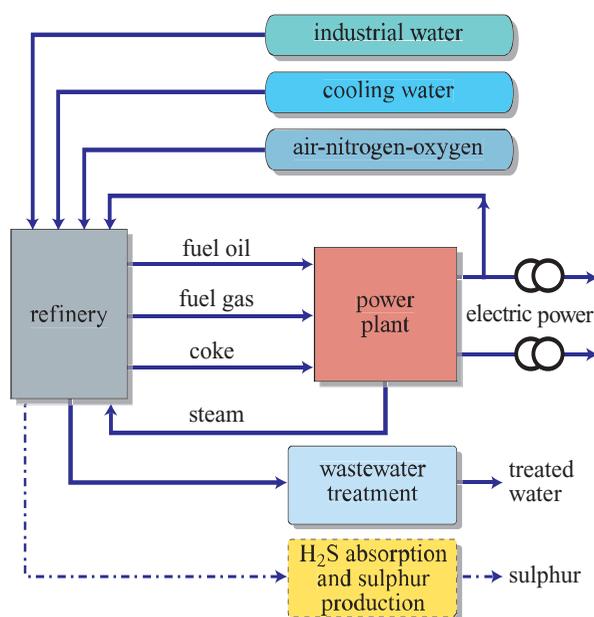


Fig. 13. General diagram of the main utilities in a refinery.

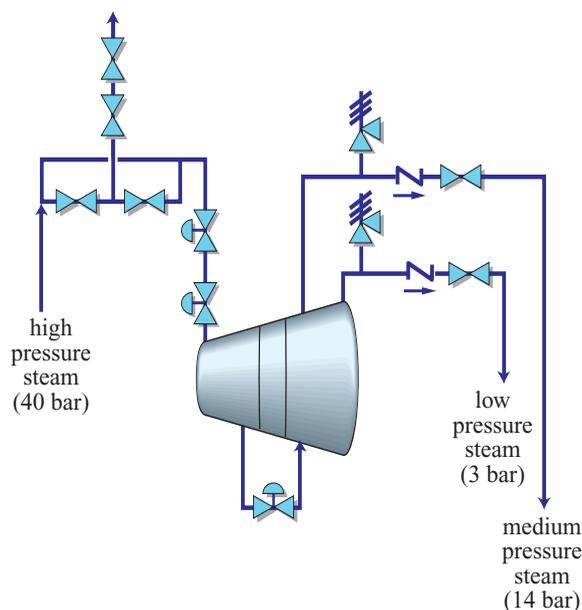


Fig. 15. Simplified diagram of a back pressure turbine with approximate values for steam extraction pressures.

(more complex in the case of seawater), which render them suitable to be fed into the boilers. The content of dissolved salts, silica, oxygen and metallic ions must be reduced to quantities even below one ppm, depending on operating conditions. In the case of fresh water from wells or rivers, clarification, filtering (sand, active carbons) and demineralization treatments using cationic and anionic resins are required. For seawater a desalination plant is needed.

The system traditionally used to produce power consists of a direct-fired boiler, a back pressure turbine (sometimes with intermediate bleed valves), a reducer and an alternator. The fuel burned inside the boiler produces heat energy which turns the process water into steam. The latter, strongly superheated, acts on the blades of a steam turbine; the mechanical energy thus produced is transferred to the alternator which turns it into medium voltage electrical energy. The voltage level is raised by the step-up transformers which connect the power station to the high voltage network. After its energy content has been transferred to the turbine, the steam is discharged by it into the low pressure (LP) network in the case of back pressure turbines, or condensed and sent back into the boiler in the form of liquid (condensing turbine).

Refineries usually have two networks for utility steam; one at medium pressure (MP, about 10-15 bar) for process units and other utilities, and one at low pressure (LP, about 2-5 bar) for heating; normally the system is bled below the turbines' high pressure vessel

(HP, about 40-80 bar) (avoiding the condensation of the steam exiting at LP) to feed the refinery's MP network (**Fig. 15**).

For safety reasons, in many refineries some particularly important equipment (for example the recycle compressor for reforming, the air compressor for catalytic cracking) is operated by steam turbines (MP) in addition to electrical engines like the other machines.

In a conventional thermoelectric power station only part (about 38-40%) of the heat energy released by combustion in the boiler is converted into electrical energy. The remaining portion is lost in the various energy conversions (from chemical to thermal, from thermal to mechanical, from mechanical to electrical) and as the residual heat of the fumes and steam sent for condensation.

Another system used to generate electrical energy and steam is based on the use of gas turbines, and consists of the sequence: gas turbine, reducer, alternator and recovery boiler fed with the waste gases (fumes) from the turbine. In this case, steam is available only at the pressure of the recovery boiler. The two systems may be combined, as shown in Fig. 14.

The direct-fired boiler uses classic refinery fuels (fuel oil, refinery gas, coke where available). The gas turbine burns the gas produced by refinery treatments or methane gas imported from outside; the waste gases from the turbine are then used to produce steam in the recovery boiler before they are discharged into the atmosphere. The turbine is normally equipped with post-combustion burners, which increase its power and improve the efficiency of the cogeneration cycle.

Gas emissions are controlled by regulating the intake of the various available fuels (for example passing from fuel oil to refinery gas or to methane in the event of an environmental emergency), and maximizing the load on the boiler with highest performance.

The problem of producing electrical energy internally has found various solutions, which depend in part on the reliability offered by the existing electricity network in the area where the refinery operates.

Also, if a refinery decides to withdraw direct production of electrical energy, it may be good practice to produce the minimal amount of electricity. In fact, steam at medium and low pressure should be in any case available for the process units and the difference in cost between the production of steam at HP (40-60 bar) for turbines (with intermediate bleeds at MP for processes), and the direct production of steam at MP is amply compensated for by the benefits obtained. By contrast, if internal production is chosen it may still be necessary to maintain a small contract to

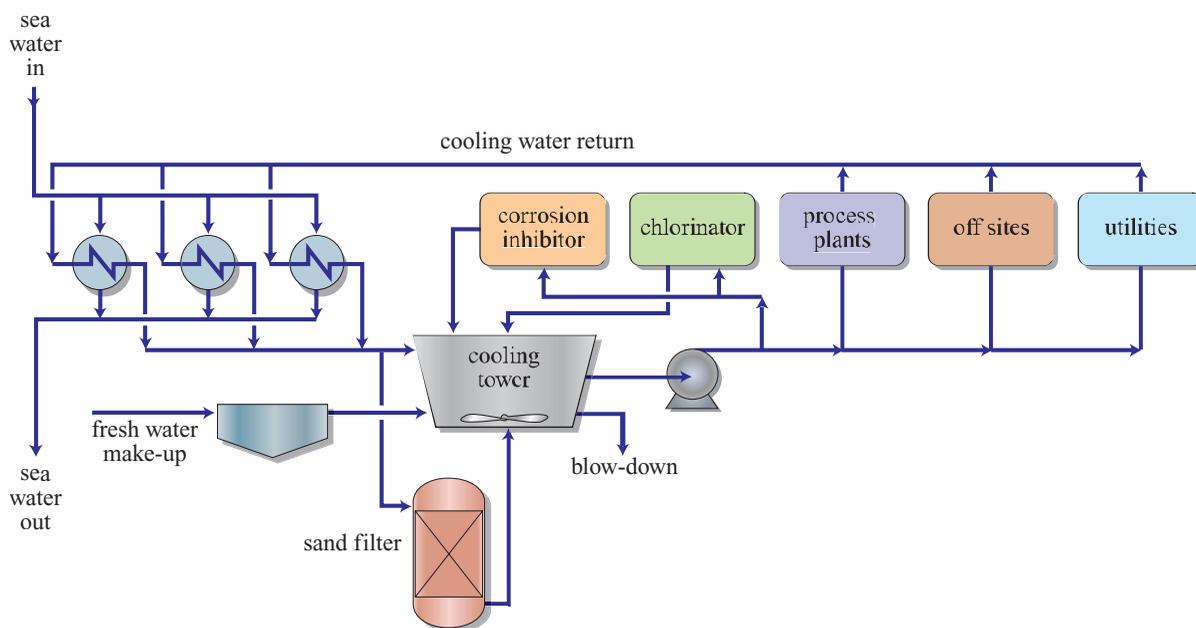


Fig. 16. Mixed cooling water circuit equipped with a fresh water/seawater thermal exchange (seawater is used in an open circuit). The main users for the closed fresh water circuit are the coolers of the process units.

purchase electricity from the external network, potentially necessary in the event of power station emergencies. The opposite situation occurs in refineries equipped with large cogeneration stations (for example IGCC, see Chapter 7.3), which, instead of purchasing, sell part of the energy produced to the external network.

Cooling water circuits

Refinery processes require the use of heat, which must then be removed through heat exchange and cooling with air and/or water. About 50% of the water requirements of a refinery are needed for cooling; the exact amounts depend on the complexity of the refinery itself.

The water used for cooling and for other thermal purposes increases in temperature; in order to be used in a closed circuit it must therefore be cooled with air in cooling towers and recirculated with the replacement of the amounts lost (due to partial evaporation in the towers and purges). The water replaced is pretreated to clarify it. Corrosion inhibitors, biocides and other additives are added to the water. The addition of a sand filtration helps to keep the water in circulation relatively clean.

The water must not leave scale, nor corrode the metal walls of the exchangers. Since equilibrium conditions depend on temperature, this problem is not easy to solve unless the water used is completely demineralized and suitably inhibited against corrosion.

In some cases, the cooling system may be completely open: in other words the water is drawn from an intake basin (river, lake, sea), and after having served its purpose is discharged back into it. This is, for example, the case with seawater, which may be used directly to cool process fluids. However, this water, which contains considerable amounts of salts and is a good conductor, presents severe corrosion problems.

An intermediate system uses a mixed circuit (or semi-closed circuit), shown in **Fig. 16**, where the water is first cooled after use with seawater; cooling is then completed in the cooling towers. This makes it possible to reduce the load on the cooling towers and evaporation losses.

Fire water

Fire water is used to make fire-fighting foams, and as a preventive coolant to avoid an ongoing fire from spreading. The system generally consists of: *a*) a basin (natural or artificial) containing a sufficient quantity of water; *b*) a group of pumps suited to keeping the fire-fighting network under pressure, with modest or no delivery; *c*) a group of pumps with sufficient head and high flow rate, suitable for supplying the water required when a fire occurs; *d*) an underground distribution network; *e*) fire hydrants with nozzles to which the hoses are attached.

Connected to the fire water network, and forming an integral part of it, are the sprinkler systems used to cool the vertical walls of storage

tanks, with the aim of protecting these from excessively high temperatures in the event of a fire nearby. The fire-fighting network must also be able to function in complete autonomy from any external or centralized energy source. Part of the pump group is therefore powered by diesel engines with a local fuel reserve.

Compressed air and nitrogen

There are generally two compressed air systems in refineries, each fed by its own compressors: that used to feed instruments and operate release valves (instrument air), and that used for various utilities, including the feed to mobile tools (utility air). The instrument air requires special care since it must not contain dust, oxides, oil or humidity. The compressors are of the non-lubricated type, and the air is filtered and dried after compression and cooling. Compression and delivery of the instrument air occurs at a pressure of 4-8 bar, the same as that of utilities air, for obvious reasons of interchangeability and emergencies. Near the points of use are decompression (reduction) stations, which bring the air to the normalized working pressure.

Utilities air is the traditional working fluid for mobile tools in areas where the use of electrical energy is not permitted for safety reasons.

If it is not used for other purposes in processes, nitrogen serves mainly to decontaminate catalytic units; this is not done with steam to avoid damaging the catalysts. Nitrogen is also used to pressurize liquids which may react with the oxygen in air; it is supplied from outside in cylinders, and the most commonly used storage system is traditionally that at high pressure and ambient temperature. Also common are the transportation and storage of liquid nitrogen at low temperature. In some cases, where nitrogen is produced by the liquefaction of air, it may be used as an inert gas for decontamination, and in place of air in instruments.

Treatment of liquid effluents

The waters from various parts of the refinery are sent to the waste water treatment plant (see also Chapter 9.2). The sewers (suitably designed to collect oily residues), also collect waters originating from: *a*) the reflux accumulators of columns; *b*) the crude desalter; *c*) condensate from various equipment; *d*) purges of the cooling circuit; *e*) purges of boilers; *f*) the fire-fighting circuit (in winter, to prevent freezing); *g*) meteoric waters from the refinery; *h*) waste waters from sludge treatment; *i*) various uses (washing, flushing, etc.).

The basic difference between the refinery's sewer system and that of towns lies in the insertion, in the

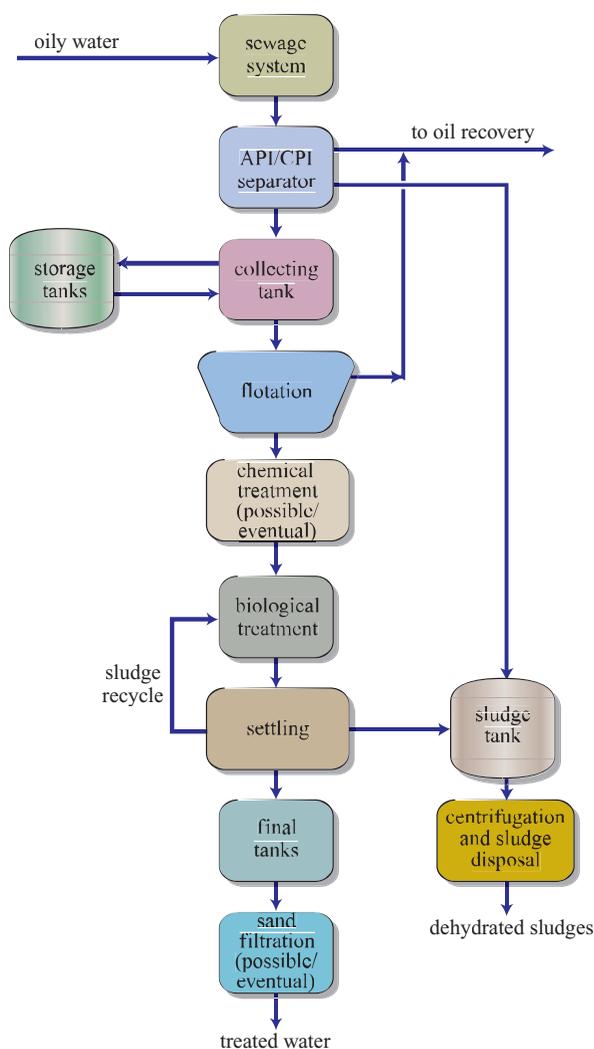


Fig. 17. Modular layout of a typical treatment system for refinery waste waters.

former, of water seal drains to prevent potential fires from spreading along the sewer.

Fig. 17 shows the typical modular layout of the system used to treat refinery waste waters, equipped with treatments of physical type (API, American Petroleum Institute; CPI, Corrugated Plate Interceptor; TPI, Corrugated Plate Interceptor or others, plus flotation) and chemical type, in addition to biological treatments.

The oily waters flow through a settling basin (API separator) or basins of smaller size equipped with systems to encourage sedimentation (CPI, TPI); due to the difference in density, the oil separates out at the surface and is recovered. The water is further clarified by flotation with air and is then sent for biological treatment (for example, active sludges); in some cases, where large open areas are available,

lagooning may also be used. Chemical treatment (pH regulation, addition of FeCl_2 , etc.) may be necessary to condition the water before it is sent to the biological plant.

The plant is designed for peak flow rates; however, these may not take account of unusually heavy rain. Large basins and/or accumulation tanks are therefore needed to stagger the intake to the treatment plant in these cases.

The diagram in Fig. 17 does not include the unit known as a *sour water stripper*, which is normally independent. This unit consists of a stripping column, heated with steam, which receives the streams rich in H_2S and NH_3 produced by distillation, hydrocracking, hydrodesulphurization, gas treatment, amine regeneration, sulphur and coking units. The vapours released at the top of the stripping columns are sent to the sulphur plant.

Distribution of fuels

On average, 4-8% of the crude oil is used to run the refinery. The most frequently used fuels are fuel oil and refinery fuel gas; auxiliary fuels may be natural gas, acquired from outside, and coke if the refinery has a coking unit.

Refinery fuel gas consists of all the light components (H_2 , CH_4 , C_2H_6 , H_2S , etc) separated in the overhead accumulators of the various columns; these components are partly contained within crude oil, but derive mainly from secondary pyrolysis and cracking processes.

Fuel oil is the residue from various treatments; refineries tend to use the more viscous oil with a lower commercial value, given its high content in asphaltenes and heteroatoms (sulphur).

Normally the burners in refinery furnaces are designed to burn both gas and oil. Natural gas is used if there is a lack of the aforementioned fuels, or more frequently due to environmental problems.

The feed circuit for the oil includes one or more purpose-built tanks, pumps, and the various control systems. The gas circuit may also include a store of LPG, which intervenes if there are variations in the flow rates and/or the calorific value of the refinery gas. As such, for example, it is not always possible to replace refinery gas directly and fully with methane (whose calorific value and density are fairly different) without influencing the performance of the furnaces. **Fig. 18** shows a diagram of the distribution of fuel gas in a refinery with a LPG storage facility.

Flare and blow-down system

The appliances belonging to the various units, designed to resist given pressures, are protected against potential overpressures by release valves. The discharges from these valves are sent to the flare, generally consisting of a vertical tube of sufficient height, equipped at its base with a water seal (to prevent air re-entering) and at the top by a pilot

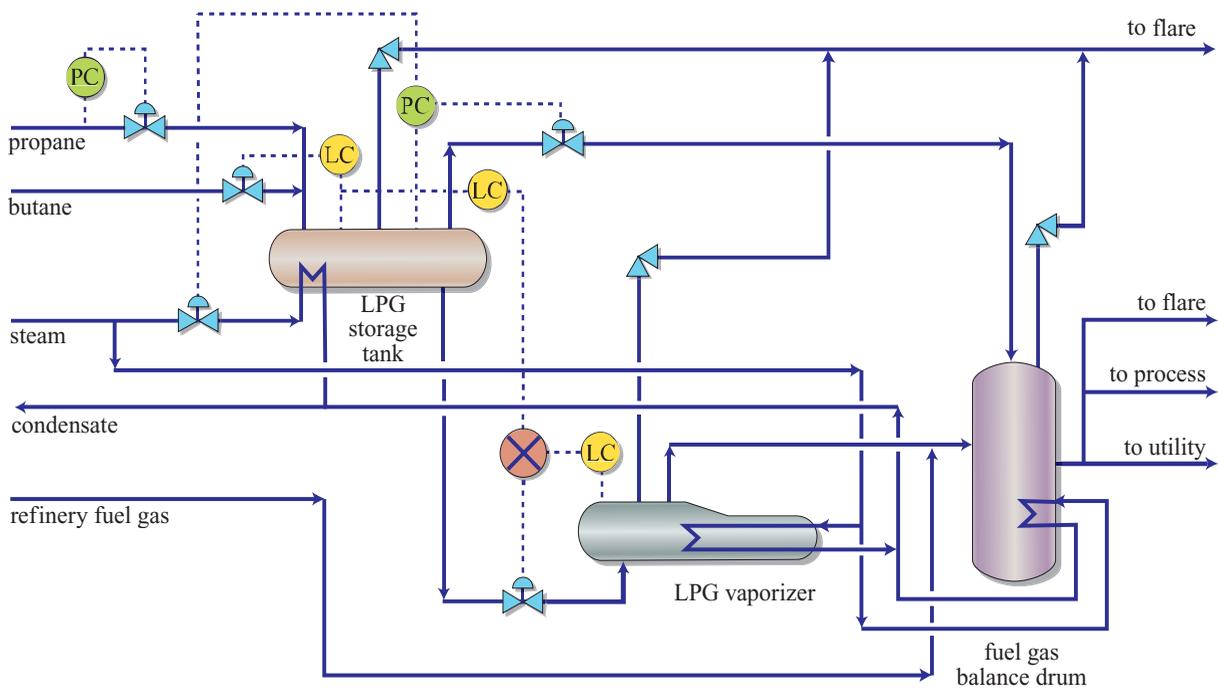


Fig. 18. System to distribute refinery fuel gas.

burner that is always on, and triggers the combustion of the discharged hydrocarbons.

Sending in a controlled amount of steam helps to reduce the amount of smoke, and improves the dispersion of combustion products; however, steam increases the noise levels of the flare.

The flare thus represents a practical and safe system for controlling the irregular intake of hydrocarbon vapours, both in emergencies, and when discharges occur from the numerous relief valves.

By burning the vapours emitted accidentally, direct discharges into the atmosphere are avoided which would otherwise cause safety and environmental problems. A careful management of processes, however, must avoid an excess of hydrocarbons being sent to the flare, to limit problems of thermal irradiation, luminance, smoke and noise.

In the intake manifold to the flare there is a separation drum for liquids to collect any (accidental) liquid condensation, so as to avoid this reaching the water seal.

So-called smokeless flares work on the principle of increasing the turbulence of fuel gases and air, with the potential help of steam, in order to improve blending and keep the formation of soot to a minimum.

Ground flares are only a few metres high and are very large in diameter; the absence of smoke is obtained without using steam in order to decrease noise levels. A further reduction in noise levels is obtained by subdividing the flame into numerous small burners and by using acoustic absorption systems. The cost of these appliances is higher than those for traditional flares; this is also true of operating costs. In all cases, the flare is located at a distance from the process units for safety reasons.

Fig. 19 shows a typical blow-down system with both a ground flare and traditional flare; the latter comes into operation if there are overloads in the ground flare.

1.1.6 Off sites

The expression *off sites* is normally used to describe all those structures used for the reception, storage and delivery of refinery products. Considering the size of the tank farm, the off sites represent, logistically as well, an extremely important part of the refinery, and ensure: *a)* the reception and storage of raw materials; *b)* the necessary feedstock for process units; *c)* the reception of products from the units; *d)* the preparation, storage and delivery of finished products.

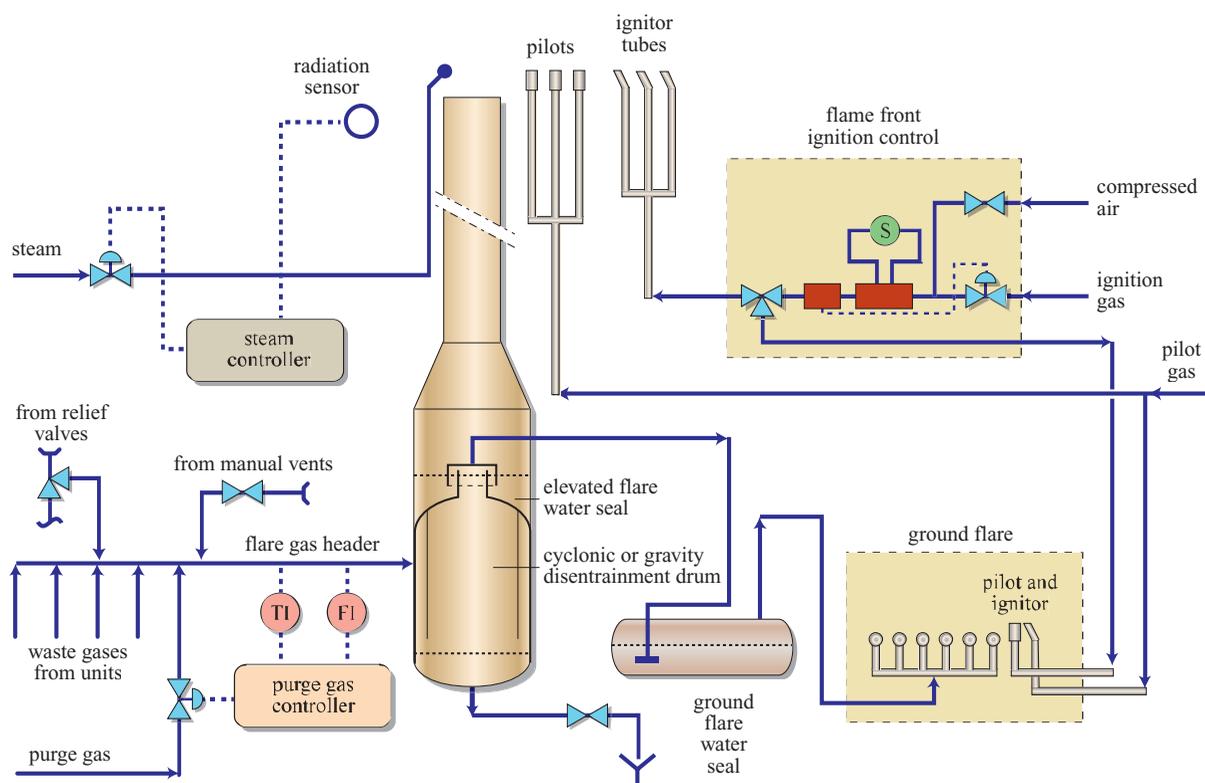


Fig. 19. Blow-down system equipped with elevated flare and ground flare (Parkash, 2003).

The products from treatment plants are almost always intermediate products, and become commercial products only after blending and any addition required. These are received in component tanks, and are then transferred to delivery tanks, in which the products are blended according to specific formulations.

Tanks

From an engineering point of view, tanks can be classified into various types which will be briefly listed below.

Tanks for products with low vapour pressure. These are used for residual fuel oils or distillates (up to gas oil) and for bitumens. They are cylindrical vertical tanks, in welded steel plate, with a fixed conical roof. They are grouped inside collective containment basins. They usually have heating coils on the bottom and, for the most viscous products (for example bitumens), are completely insulated on all exposed surfaces. Those with bare surfaces have water sprinkler devices for emergency cooling.

Tanks for products with medium vapour pressure. These are used for crude oil and light distillates. They are cylindrical tanks with floating roofs which prevent the formation of pockets of gas and air above the liquid. The bottom, roof and cylindrical shell are made of rolled and welded steel plates. The floating roof has for some time been the most effective, practical and economical system to contain evaporation losses. The tanks used for crude oil can be heated if necessary using steam coils placed on the bottom. Each tank is located inside a containment basin surrounded by earth banks or walls in reinforced concrete. The volume of the basin must be identical to that of the tank: the area of the basin is therefore much larger than that of the tank, and determines the characteristic appearance of tank farms (see again Fig. 11). Crude oil tanks may be extremely large (up to 160.000 m³).

Tanks for products with high vapour pressure. These tanks are used to contain, in the liquid form, products which would be gaseous under normal pressure conditions; in practice these are the hydrocarbons of propane and butane type which make up LPGs. Traditionally, the tanks are spherical for butane and LPG, and cylindrical for propane, capable of resisting to a pressure of a few bar. Today there is a tendency always to use the cylindrical shape, small in size and with a hemispherical bottom. For safety reasons, the current tendency is to cover these tanks with a layer of earth ('buried' tanks).

Preparation of finished products

As already noted, the process units produce various fractions which must be suitably blended in order to

obtain the properties required of finished commercial products. Very often, additives of various types are also added to improve quality and differentiate between the various products (colorants, denaturants). In the case of lubricants, addition is of fundamental importance.

Blending systems may be of discontinuous or continuous in-line type. In the discontinuous (batch) system, the components of a product are added and blended in a tank. Larger modern refineries use the continuous in-line blending system, which simultaneously blends measured quantities of all components and additives in the pipeline; the accuracy is such that the product formed conforms to specifications at all times, and can be drawn off the line directly.

Transportation of products

Crude oil and the finished products are transported using oil pipelines, tankers, rail tank wagons and tanker lorries.

Coastal refineries are equipped with marine structures (bridges, artificial islands) for loading and reception. Oil pipelines are effective and economical transportation systems which carry 'black' products (crude oil, fuel oil, bitumen) and 'white' products (gas-oils, gasolines, etc) in different pipelines.

Overland transportation may also make use of tanker lorries and/or rail tank wagons which run into the refineries on special rail links. Where marine transportation is used, the connection between moorings and the tankers is ensured by hydropneumatic arms or flexible nozzles. Large oil tankers may moor in open waters at purpose-built buoys or floating artificial islands resting on the seabed.

1.1.7 Operating procedures

The type of operations and the nature of the materials treated classify oil refineries as high risk industries (for aspects relating to safety see Chapter 9.1). Operating procedures are closely linked to the issues of safety and product quality; they play an essential role in running the plants in a refinery. The term *procedures* is used to refer to an ordered series of activities aimed at achieving a specific objective. The increasing complexity of chemical, petroleum and petrochemical plants requires operators to perform numerous delicate interventions during the various phases of a plant's life; these tasks must be performed according to clearly defined sequences and methodologies. In the case of petrochemical plants and refineries, the sequence and nature of these activities

are the result of best practice experience and engineering know-how. This allows for an optimization of the operations forming the object of the procedure, to ensure safety, the quality of operations and the economic viability of the company's management. Safety is certainly the most significant outcome of the application of operating procedures.

In refineries, written procedures are drawn up and applied, this provides precise instructions for the safe execution of the activities required by the process. These procedures must cover all principal operating situations (initial start-up; normal run; temporary shut-down; emergency shut-down, with the indication of the type of emergency; emergency operations; normal shut-down; start-up following maintenance and after emergency shut-down), and take account of both operating limitations (consequences of a deviation from normal operation; interventions required to correct or avoid deviation) and of safety and environmental hygiene (properties and hazards of the chemical products used in the plants; necessary precautions to prevent exposure; measures to be taken in the event of contact or inhalation; quality control for raw materials; control of storage levels of hazardous chemical substances; other special or exceptional hazards).

The operating procedures must be easily accessible to staff working in the plants and in maintenance, and must be reviewed with sufficient frequency to ensure that they correspond to the operations actually carried out, taking account of any modifications to processes, appliances and facilities in the plant. Specifically, in refineries, safety procedures for dangerous tasks must be drawn up and applied. These procedures must be followed by company staff and by sub-contractors. The entry of external workers into the plant (maintenance and laboratory workers, representatives of sub-contractors, etc.) must be regulated.

The plant manual mentions these activities, but does not normally explain them in an analytical way;

at times it is assumed that they are well-known. It is therefore necessary for these to form the first step in the education and training programme for staff. It is also necessary to draw up a complete list of these, to avoid dangerous omissions.

The procedures are set down in special manuals, known as operating manuals, issued by process and engineering companies in collaboration with the management of the refinery which is to use them. In addition, the manufacturers and suppliers of appliances also produce specific manuals.

References

- AALUND L.R. (1977) *Competition sparks refinery progress*, «Oil & Gas Journal», 75th Anniversary Issue, August, 339.
- GIAVARINI C. (1989) *L'industria della raffinazione del petrolio. Le origini e lo sviluppo*, «La Chimica e l'Industria», 71, 12.
- GIAVARINI C. (1990) *Gli anni del piombo*, «La Chimica e l'Industria», 72, 1027.
- GIAVARINI C. (1993) *L'industria della raffinazione del petrolio. Ambiente e innovazione tecnologica nello sviluppo attuale*, «La Rivista dei Combustibili», 47, 16.
- IADANZA P. (2004) *Per la 'dieselizzazione' generalizzata degli autoveicoli*, «La Rivista dei Combustibili», 58, 60-66.
- PARKASH S. (2003) *Refining processes handbook*, Amsterdam-London, Gulf.
- RUMBOLD C. (1971) *Raffinazione*, in: Eni (1962-1971) *Enciclopedia del petrolio e del gas naturale*, Milano, Colombo, 8v.; v. VIII, 372.
- SWATY T.E. (2005) *Global refining industry trends. The present and future*, «Hydrocarbon Processing», September, 35-44.

CARLO GIAVARINI

Dipartimento di Ingegneria Chimica, dei Materiali,
delle Materie Prime e Metallurgia
Università degli Studi di Roma 'La Sapienza'
Roma, Italy