Atmospheric distillation
of crude oil

The purpose of atmospheric distillation, which is carried out at slightly above atmospheric pressure, is to separate (fractionate) the feedstock (crude oil) into different products with characteristics aimed at satisfying the demands of the market for motor fuels (gasoline, kerosene and diesel), combustible fuels (LPG, kerosene, heating gas oil and fuel oil) and feedstocks for the petrochemical industry. The products obtained can be used as they are or, in the majority of instances, must be subjected to further processing in a refinery (isomerization, catalytic reforming, desulphuration, vacuum distillation, etc.) in order to make them usable as finished products.

In addition to hydrogen and carbon, hetero-atoms such as sulphur, nitrogen and oxygen may be present in the molecules making up the crude oil, along with organometallic compounds containing iron, vanadium, nickel, sodium, arsenic, etc. Moreover, even though the crude oil may be treated at the wellhead to dehydrate and stabilize it, part of the reservoir water still remains in it; similarly, when transported by ship the crude oil can be ‘polluted’ by the residual water remaining in the tanks. This is generally water containing salts (chlorides) which can cause problems of corrosion in the subsequent operations of heating and condensation. Finally, the crude oil may contain dissolved gases (hydrogen sulphide, nitrogen, carbon dioxide) in different percentages depending on the type of crude oil and the effectiveness of the stabilization treatment carried out, as well as on the method adopted for transportation (via pipeline or ship) from the production site to the place of use. Therefore, in addition to the distillation-based fractionating operations, special treatment processes must be carried out: for example, desalination is carried out when it is necessary to remove water, salts and sediment present in the crude oils. The dissolved gases, such as hydrogen sulphide, nitrogen and carbon dioxide, are separated by heating, while other gases (hydrogen chloride and hydrogen sulphide), which can be produced as a result of the heating and decomposition, must be neutralized in the condensation phase by the addition of special additives, in order to avoid problems of corrosion.

A crude-oil atmospheric-distillation (or topping) plant makes it possible to obtain distillates (made up of the overhead product and the side fractions) and the residue, by the physical separation of a mixture of homologous components. This separation, which makes use of the differing distributions of the components between the vapour and the liquid phases, takes place in stages operating in conditions close to equilibrium. A typical scheme for such a plant can be found in Fig. 1.

The separation of the various fractions of the distillate is achieved by fractional condensation of the vapours of the distillate, which is an operation requiring heat removal. In the case of a distillation column (or still) this heat removal is carried out by means of a series of refluxes: external reflux, consisting of part of the condensed overhead product, and intermediate refluxes, consisting of liquid withdrawn from the column and, after cooling, returned to it at a point above that from which it was withdrawn. Intermediate refluxes are commonly called circulating refluxes or pumparound.

The feed, coming from the storage tanks, is pumped to the heater, having been preheated with heat recovered, by means of a heat exchanger, from the overhead vapours, side fractions, intermediate refluxes and the atmospheric residue. After having been heated in the heater to the temperature required for the operating conditions, the feed is transferred to the flash zone of the atmospheric column by means of a transfer line, where the separation takes place into the vaporized fractions (equivalent to the total of the distillates) and the liquid residue.
Separation of the feed into the side fractions and the overhead product is carried out in the sections of the column between the flash zone and the column's overhead, by partial cooling and condensation. The side fractions and the bottom products are extracted from the column in the liquid phase while the top products are extracted in vapour phase and subsequently cooled, condensed and, in part, recycled to the top of the column as an external reflux (see below).

The side fractions are sent to the side stripping column (stripper), where the light components are removed by the injection of steam, in order to improve their flammability characteristics; the lightest parts are returned to the column. After being cooled by heat exchange with the feed and by means of available coolers, the side fractions are sent to storage or are used as the feedstock for downstream units. The circulating intermediate refluxes return to the column after having been cooled by heat exchange with the feed and by available chillers. The atmospheric residue is sent to storage, after heat exchange with the feed and on final cooling with available coolers, or else is used directly as feedstock for the vacuum distillation plant.

In stationary conditions, the enthalpy balance of an atmospheric distillation column reflects the parity of the inlet enthalpy with the outlet enthalpy. The inlet enthalpy is given by the sum of the enthalpy of the incoming feed and the enthalpy of the steam sent to the strippers. The outlet enthalpy is obtained by adding to the enthalpy of the distillates and of the bottom residue, the heat removed in the heat exchangers that are deployed in the circuit of the external reflux and circulating refluxes.

The vapours exiting from the top of the column are cooled and condensed in different ways depending on the number of overhead accumulators provided; a part of them constitutes the overhead reflux and a part is sent to the stabilization unit (Fig. 2). If there are two accumulators, there is an initial condensation and the liquid phase obtained is used as a hot reflux and sent to the top of the column, at an intermediate temperature between that at which it came out of the column and

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**Fig. 1.** Simplified layout of a crude oil atmospheric distillation unit. D-1, desalter; C-1, principal column; C-2-C-5, stripping columns; C-6, stabilization unit; D-2 and D-3, reflux accumulators; H-1, heater.
that maintained in the second accumulator. The residual vapours coming out of the first accumulator are subsequently condensed to obtain the top product and water. In the second accumulator condensation may be total or partial depending on the temperature and pressure conditions adopted and the nature of the crude oil being used. In fact, in the case of crude oils with particularly high contents of light hydrocarbons and in the presence of incondensables, total condensation may require temperatures which are too low to be achieved with the available cooling systems. Alternatively, the pressure in the accumulator would have to be increased with a consequent increase in the pressure profile of the entire column and the need to increase the outlet temperature level of the heater in order to obtain the required quantity of distillates. When a single accumulator is used, the vapours at the top of the column must be condensed in order to achieve condensation of the reflux, the top distillate and the water. The liquid hydrocarbon phase is in part used as a cold reflux, while the remaining part is sent as feedstock to the stabilization and splitter columns for fractionating into combustible gas, LPG, and light and heavy naphthas. The temperature in the final accumulator is generally between 40 and 50°C, to be compatible with the available cooling systems (cooling water or air).

Even in the case of a single accumulator it is possible to have partial or total condensation of the top product, depending on the operating conditions of the top product separator itself. The vapour phase, made up predominantly of light hydrocarbons (C_1-C_4) along with any incondensable gases such as nitrogen, hydrogen sulphide, etc., is sent to the blow down header and subsequently to the flare or, if required, is burnt as fuel or, alternatively, recovered by compression. The condensed water is generally sent for treatment to remove the polluting elements, in order to allow its reuse.

### 2.2.1 Desalination

Desalination of the crude oil is a process whose purpose is to eliminate the salts normally present in the water phase which is generally present within it.
The salt contents of certain crudes, expressed in terms of NaCl equivalents, are summarised in Table 1. The salts typically contained in crude are sodium, magnesium and calcium chlorides. The need for this processing is due to the fact that the salts, if not removed, could cause deposits to form within the equipment (for example, on the surfaces of the exchangers, reducing the efficiency of the heat exchange) and the forming of hydrogen chloride (HCl) by hydrolysis of MgCl₂ and CaCl₂, leading to corrosion, especially in the section containing the overhead product condensers of the atmospheric distillation column. Moreover, desalination treatment, which is performed generally in two stages (Fig. 3) to minimize the residual salt and/or solid content, is advisable in order to avoid problems in the downstream plant, in the event that the residue (atmospheric or vacuum) is to be sent for thermal or catalytic conversion processing.

The water and salt content in a crude is dependent on the characteristics of the reservoir and on the treatment which the crude itself has undergone at the wellhead (normally involving dehydration processes which reduce the water content to about 0.5-2% by volume). Water can also come from transport by ship, if ballast H₂O remains in the compartments used for transporting the crude oil. The water is present in the form of dispersed particles with varying dimensions of up to 1 µm in diameter. The characteristics of the water and of the crude oil (density, surface tension, chemical components) and the method of production determine the sizes of the particles and the stability of the emulsion, whose formation is assisted among other things, by the presence of natural emulsifying agents in the crude, such as asphaltenes, resins, paraffins, organic acids and particles of inorganic solids.

First of all, the desalination treatment requires the addition of water to the crude oil in order to form an emulsion of H₂O droplets dispersed in the oil. The water dissolves the salts contained in the crude, hence the greater the water dosage, the lower is the salt content of the output. Nevertheless, an excess of washing water can lead to crude being drawn into the water and vice versa. A typical amount is 5-8% of H₂O by volume with respect to the input crude oil.

The formation of the water/oil emulsion is assisted by the presence of a mixing valve which, by means of a pressure drop normally between 0.5 and 3 bar, ensures a close oil/water contact. This pressure drop caused by the mixing valve is the primary element in the correct operation of the desalter. The ideal value of this pressure drop is dependent on a number of factors, such as the type of crude oil, the operating temperature of the desalter, the oil/water mixing velocity, the presence of emulsifying agents in the crude and the quality of the washing water. Therefore, it is only through analysis of the actual operation of the desalter that the correct pressure drop can be determined. Nevertheless, it is important not to employ pressure drops in the mixing valve that are too high, since, when using excessive levels the removal of salt is drastically reduced due to the formation of a stable emulsion.

### Table 1. Salt content of some crude oils, expressed in terms of NaCl equivalent

<table>
<thead>
<tr>
<th>Crude Oil</th>
<th>Source</th>
<th>Salt Content (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Marlim</td>
<td>Brazil</td>
<td>100</td>
</tr>
<tr>
<td>Cerro Negro</td>
<td>Venezuela</td>
<td>655</td>
</tr>
<tr>
<td>Iranian Heavy</td>
<td>Iran</td>
<td>102</td>
</tr>
<tr>
<td>Rospo</td>
<td>Italy</td>
<td>388</td>
</tr>
<tr>
<td>Ural</td>
<td>Russia</td>
<td>72</td>
</tr>
<tr>
<td>Athabasca Bitumen</td>
<td>Canada</td>
<td>15-45</td>
</tr>
</tbody>
</table>

**Fig. 3.** Operational diagram for a two stage desalter: dLC, differential level controller; PC, pressure controller.
which hinders separation of the aqueous phase. The operating pressure of the desalter must be maintained about 2-3 bar above the pressure corresponding to the boiling temperature of the crude oil at values such as to avoid the formation of vapours which could prevent the desalter from operating properly.

Next it is necessary to break the emulsion formed in this way by sedimentation of the heavier discontinuous phase (the droplets of water). In conditions of free fall and in the absence of turbulence, the velocity of sedimentation follows Stokes’ law; hence the falling velocity increases (therefore encouraging the separation) if the particle size grows, if the viscosity of the continuous phase diminishes and if the difference between the densities of the two phases increases.

In order to promote an increase in particle sizes during the desalination treatment of a crude oil, the oil (non-conductive) containing the water (conductive) is subjected to the effects of an electrical field. This effect causes the conductive particles to aggregate together, because they are subjected to the influence of electrostatic induction and have a tendency to align themselves along the lines of force of the electrical field. Hence, as they attracted by the electrodes, they are subjected to forces of coalescence while in motion and form increasingly bigger particles, until they fall by force of gravity.

In a light crude (39ºAPI) the velocity of sedimentation of the water varies depending on the diameter of the droplets, as indicated in Table 2. A reduction in viscosity of the continuous phase, which takes place through an increase in operating temperature and which promotes coalescence and decantation, also improves the contact efficiency of the crude oil and the injected water. However, an increase in temperature causes an increase in conductivity of the oil, which becomes very rapid above 120ºC.

In the presence of particularly stable emulsions, it may be necessary to use a de-emulsifier which, by modifying the properties of the oil/water interface increases the ability of the stabilizing agents to dissolve in oil and reduces the surface tension of the water droplets, so as to enable them to coalesce. In this way the time needed for separation is reduced, enhancing the performance of the desalter.

In essence, a desalter consists of a vessel containing two electrodes (three in some configurations), one on the earthed side of the vessel, the other suspended on insulators; an electricity generator delivers a suitable electrical potential to the suspended electrode. The positioning of and the distance between the electrodes depend on the characteristics of the feed, the substances to be eliminated and the processing conditions. The alternate current system is based on the application of a high-voltage electrical field which generates an electrical charge on the drops of water present in the hydrocarbon phase, causing them to oscillate as they pass between the electrodes. During this oscillation, the drops are first elongated and then compressed by the alternations of the electrical field. Through the effect of this agitation the particles tend to aggregate together into particles of increasing size, until segregation under effects of gravity takes place and a water layer forms at the bottom of the desalter.

### Table 2. Rate of sedimentation of water, in a typical light crude, as a function of the diameter of the droplets

<table>
<thead>
<tr>
<th>DIAMETER OF THE DROPLETS (µm)</th>
<th>RATE OF SEDIMENTATION (cm/h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>0.033</td>
</tr>
<tr>
<td>10</td>
<td>0.813</td>
</tr>
<tr>
<td>30</td>
<td>7.366</td>
</tr>
<tr>
<td>100</td>
<td>82.55</td>
</tr>
<tr>
<td>400</td>
<td>133.10</td>
</tr>
</tbody>
</table>

2.2.2 Vaporization

After the desalination treatment, the crude oil must be heated up to the inlet temperature required by the fractionating column. This is performed by means of a series of heat exchangers, in which the heat of the hot streams coming out of the fractionating column is used to pre-heat the crude oil. Typically, this recovery enables temperatures of between 240 and 280ºC to be achieved. The remaining part of the energy is supplied by a heater which raises the feed entering the column to the temperature required to vaporize both the products which will then be extracted as side cuts and a part equal to about 10-20% of the bottoms product. This last fraction, after condensation in the trays of the column immediately above the feeding area (flash zone), forms the internal liquid reflux.

The liquid fraction leaving the heater and the internal liquid reflux are used to feed a steam stripping section, provided in the bottom of the atmospheric column, in order to remove the lightest components and hence to obtain a higher gas oil yield.

The required heater outlet temperature, to which a specific enthalpy corresponds, depends on the type of crude oil treated (light, medium or heavy crude) and, at a given pressure, is correlated to the yield of distillates required. The maximum permissible column feeding
The temperature depends, therefore, on the characteristics of the feed and normally it does not exceed 370–380°C. In fact, if this limit is exceeded, cracking can take place in the last part of the heater’s coil and coke can form, resulting in an increase in the pressure drop in the heater and a reduction in the overall performance of the plant. Whenever excessive deposits of coke occur, it is necessary to shutdown the plant and remove the coke which has been deposited (a decoking operation).

A variation of the traditional scheme involves the addition of a pre-flash vessel (see again Fig. 2) which, operating at a temperature of 170–200°C and at a pressure of 4–6 bar, removes the light part of the crude and sends it directly to the main fractionating column, while the liquid fraction is subsequently heated up to the temperature of the flash zone. As an alternative, a pre-flash column could be inserted which enables gas and non-stabilized light naphtha to be separated as top products. The bottom of the pre-flash column may be equipped with steam stripping or a reboiler heater. The bottoms product of the pre-flash column is further heated, by the use of exchangers and a heater, up to the temperature required for the flash zone. This solution is adopted when it is desired to reduce the diameter of the distillation column.

A key consideration for the vaporization section is that of maximizing the recovery of heat from the hot streams for heating the crude oil. The methodology commonly used to optimize heat recovery and at the same time to reduce the surface area of the heat exchangers thereby minimizing the investment cost, makes use of what is called **pinch technology**, which is a rigorous and structured approach to determine the minimum amount of energy necessary in a process, and which drives the design in this respect. In applications such as those being described, pinch technology is capable of establishing the most appropriate configuration of a series of exchangers, seeking to minimize the costs of the heating (fuel for the heater) and cooling (air and water) utilities. This aim is achieved by analysing the *composite curve* which, in the delta enthalpy/temperature representation of the streams, provides the graphical profiles of the energy available from the process (**hot composite curve**) and of the energy requirements of the system (**cold composite curve**).

**Fig. 4B** shows the construction of a hot composite curve, from two hot streams (1 and 2), where $CP$ (kJ/°C s) indicates the thermal flow rate of the stream, which is the product of the specific heat $C_p$ (kJ/°C kg) and the flow rate in weight $M$ (kg/s). A hot composite curve showing variations of enthalpy in time-temperature units, on the other hand, is shown in **Fig. 4A**.

Composite curves provide a counterflow representation of the heat exchange and are used to identify the minimum energy requirement of the system. It is obtained by trying to superimpose the hot and cold composite curves, until the minimum temperature difference obtainable in an economic way is reached. **Fig. 5** shows the degree of superimposition
which allows the greatest possible heat recovery, highlighting the residual parts of the heating ($Q_{H_{\text{min}}}$) and cooling ($Q_{C_{\text{min}}}$) which must be ensured by external fluids.

### 2.2.3 Fractionating

Fractionating is the basic operation carried out on crude oil in every refinery, from which the products are obtained which feed the downstream plant. Every hydrocarbon has a boiling point which, for the lightest compounds (from C$_1$ to C$_4$) at atmospheric pressure, is below 0°C, while for heavier compounds it can reach such high temperatures that it causes the molecules to break and cracking products to form. The crude oil which has been suitably heated to obtain a partial evaporation is sent to the bottom section of a column, in which, as a result of the effect of the material and heat exchange which takes place on the individual trays, a temperature profile is established which exhibits a decrease towards the top of the column. The material and heat exchange is caused by contact between the vapours which rise towards the top and the liquid at a lower temperature which falls towards the bottom or the cold liquid (reflux) sent to the top of the column. At each point of the column, mixtures of hydrocarbon liquids are collected whose boiling temperature at the specific pressure at that point corresponds to the temperature of equilibrium on the tray itself. The lightest products remain in vapour phase and continue to rise towards the top of the column. The temperature and pressure profiles corresponding to the theoretical stages in a fractionating column are shown in Table 3. The theoretical stage 1 represents the overhead condenser, while stages 30 and 31 simulate the stripping trays.

Fractionating is ensured by the presence in the column of devices (trays) which favour contact between the liquid and the vapour phases. In fact, a thermal and material exchange takes place on the trays of the column, between the vapours which are rising and the liquid which is descending and which, in the case of a theoretical tray, allows a condition of equilibrium to be reached between the vapours and the liquid coming out of an individual stage. In the material and thermal exchange which takes place, the vapours are enriched by the fractions with a lower boiling temperature which evaporate from the liquid and are depleted by the fractions with a higher boiling temperature which condense. In stable operating conditions it is therefore possible to recover, at different heights of the column, side cuts with the compositions and characteristics required by the downstream processes or which can be sent to storage.

**Table 3. Temperature and pressure trends for an atmospheric distillation column**

<table>
<thead>
<tr>
<th>Tray</th>
<th>Temperature (°C)</th>
<th>Pressure (bar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>127</td>
<td>2.2</td>
</tr>
<tr>
<td>2</td>
<td>150</td>
<td>2.22</td>
</tr>
<tr>
<td>3</td>
<td>166</td>
<td>2.24</td>
</tr>
<tr>
<td>4</td>
<td>174</td>
<td>2.25</td>
</tr>
<tr>
<td>5</td>
<td>178</td>
<td>2.27</td>
</tr>
<tr>
<td>6</td>
<td>181</td>
<td>2.29</td>
</tr>
<tr>
<td>7</td>
<td>184</td>
<td>2.31</td>
</tr>
<tr>
<td>8</td>
<td>187</td>
<td>2.32</td>
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<td>9</td>
<td>190</td>
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<tr>
<td>10</td>
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<td>11</td>
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</tr>
<tr>
<td>14</td>
<td>213</td>
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</tr>
<tr>
<td>15</td>
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</tr>
<tr>
<td>16</td>
<td>235</td>
<td>2.47</td>
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<td>2.70</td>
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<td>363</td>
<td>2.75</td>
</tr>
<tr>
<td>31</td>
<td>359</td>
<td>2.80</td>
</tr>
</tbody>
</table>

Typical cuts from an atmospheric fractionating column are:

- **Top product**: a mixture containing the lightest part of the hydrocarbons (up to C$_4$), light and heavy naphtha (in other set-ups, the heavy naphtha could constitute the first side cut).
- **First side fraction**: heavy naphtha or kerosene.
- **Second side fraction**: light gas oil (typically used as transportation fuel).
- **Third side fraction**: heavy gas oil (typically used as heating oil or fluxant for fuel oil).
Residue: product intended either to produce fuel oil, after the possible addition of a fluxant, or as feedstock for the vacuum distillation plant.

The boiling ranges of the different fractions and the topping operating conditions must be established *a priori*. To do this a number of combinations of yields are provided for, for which the plant must allow a certain degree of flexibility, such as to enable adjustments to be made quickly in line with the quality of the crude oil and/or the products demanded by the market. The starting point for determining the provisional quantity and characteristics of the products is the distillation TBP (True Boiling Point); based on the specifications of the finished products and experience, the yields and the principal characteristics of the fractions can be calculated by making an arbitrary assumption about the final boiling points of the products that could be obtained from the crude. These products are found between boundary zones which represent fractions common to two adjacent products. The boundary zones allow, when necessary, for the final points originally specified to be shifted, subtracting all or a part of a certain border fraction from this or that product and adding it to the adjacent product.

Once the characteristics of the desired products have been established, it remains to establish the efficiency with which the fractions are to be separated from each other; in the refining industry this is done using conventional methods, given the complexity of the composition of the mixtures involved. In practice, the starting point is the ASTM D 86 curve (see Chapter 2.1) of the fractions, noting the difference between the temperature at which 5% of a fraction has distilled and that at which 95% of the fraction with a boiling point immediately below it has distilled; if this difference is positive there is a gap and the fractionating is considered to be good, whereas if it is negative there is an overlap and the fractionating is deemed to be unsatisfactory. By way of an example, Fig. 6 shows that heavy naphtha and kerosene are well fractionated, that is, they are well separated from one another given that there is a gap of $+13^\circ$C; on the other hand, light gas oil and heavy gas oil are not well separated, as there is an overlap of $-42^\circ$C, since the light gas oil contains about 30% of product which should be part of the heavy gas oil, while the latter contains about 20% of product which should be part of the light gas oil.

Based on the value of the internal reflux ratio, which depends on other processing variables (characteristics of the fractions, overflash, intermediate refluxes), the number of theoretical trays necessary is defined so as to achieve the value of the product of the internal reflux ratio by the number of trays, which is, in turn, determined on the basis of the deviation from the ideal fractionating (Fenske, 1932; Gilliland, 1940; Colburn, 1941). The number of actual trays is determined by dividing the number of theoretical trays by an efficiency coefficient which depends on both the physical characteristics of the fluid in question and the typology of the trays selected (Gunnness, 1936; Ballast [... 1974).

Features of the contact devices

Fractionating trays

The most commonly used fractionating trays are the valve, sieve and bubble cap types.

Valve trays are based on the principle of the check valve (Fig. 7). When the vapour flow increases, the

![Fig. 6. ASTM distillation curves for petroleum fractions showing the fractionating efficiency through gap or overlap (Giavarini, 1999).](image_url)

![Fig. 7. Detail of a valve tray (courtesy of Koch-Glitsch).](image_url)
float begins to rise and the vapour passes through the valve. Some floats begin to rise at 20-30% of the vapour load and at 50-70% they are completely raised. This allows for a wide range of operating loads (high flexibility), while maintaining high efficiency of the tray. Valve trays require special attention when they are used in columns which operate under vacuum because in the event of pressure variations, the valves can become ‘stuck’ at the level of the tray or undergo erosion. Valve trays are not suitable for use in the presence of fluids which can cause scaling, corrosion or the formation of carbon residues. On the other hand, they are recommended in situations which call for high flexibility, not operating under vacuum. Some examples of their use relate to: vapour flow-rates which vary significantly and unpredictably in a section of the column; fractionating columns which are used in batch mode with feeding loads and compositions which can also vary markedly; and columns which can operate with wide variations of flow-rate, up to about 30% from the design value.

Sieve trays (Fig. 8) are characterized by their low cost, excellent efficiency, good capacity and reasonable flexibility (where flexibility is defined by the ratio between the maximum load that still allows satisfactory performance and the design load). Sieve trays can be used in almost all working conditions and are designed to operate satisfactorily in a wide range of operating conditions. The maximum capacity of a sieve tray is at least equal to, if not greater than, that of a valve tray; its flexibility can reach a maximum of about 3. They can also be used in the presence of fouling fluids provided that the holes have a diameter of 20-25 mm. Sieve trays are not suited to working conditions which call for high flexibility, for which bubble cap or valve trays should be used, even though they are more costly. At very low vapour loads (such as during start-up) sieve trays have difficulty maintaining a sufficient head of liquid on the tray and experience weeping to the point where they lose all of the liquid. Therefore, when a heated reboiler is provided and the liquid is collected into a seal pan installed below the downcomer of the sieve tray, it is necessary to ensure satisfactory feeding by installing an auxiliary line from the bottom of the column to the inlet of the reboiler, or else a chimney tray under the sieve tray, as a draw-off tray.

Bubble cap trays (Fig. 9) are particularly expensive, from 50 to 100% more than the cost of valve trays.
They should therefore be considered only when high flexibility is required and where there are problems of scaling or the formation of carbon residues.

**Packing**

Packing is used in a fractionating column for the same reason as trays, that is, to ensure good contact between the liquid and the vapour phases so as to permit a material transfer (Tsai, 1985; Oglebay Norton Co., 1987). From an economics point of view, trays are best used for processing large volumes of vapour and liquid.

Packing columns are normally considered for use with corrosive, but not scale depositing, fluids in the heat exchange zone, in columns which operate under vacuum (where a low pressure drop is called for) and in columns with a diameter of less than 1,000 mm, as an alternative to cartridge trays.

When choosing the best packing, the factors to be evaluated include capacity, efficiency, resistance to corrosion and cost. Fig. 10 shows some types of packing. Steel Pall rings should be considered as a first choice, since they offer the advantage of high capacity, are unbreakable and of all the various types of packing have the greatest flexibility. Packings using Pall rings are considered to have a very long lifespan provided there is no corrosion. Pall rings made from other materials are also available: aluminium rings can be used in pumparound zones for heavy hydrocarbons; plastic rings can be used at temperatures up to 120°C; while ceramic rings are preferable in corrosive environments but have a limited lifespan, even though in well operated columns they can last as long as ten years. Ceramic rings are resistant to acids, alkalis and solvents, with the exception of caustic solutions and hydrofluoric acid. In designing a fractionating column, consideration should also be given to the possibility of installing the structured type packing, illustrated in Fig. 11. Generally this type of packing is more expensive, but it is normally used when high separation performance with low pressure drop is required, for example in super-fractionating or vacuum columns.

**2.2.4 Stripping and stabilization**

In this section of the atmospheric distillation plant, the side and top cuts are treated in order to bring them up to the specifications required.

The cut that comes out of the top of the column, generally composed of LPG (Liquefied Petroleum Gas) and naphtha, is sent to a naphtha re-distillation column, that normally works at pressures of between 8 and 10 bar and at a temperature of about 180°C at the bottom. The temperature at the bottom of this column is dependent on the pressure and on the final point of distillation of the naphtha. In this column, those components that remained dissolved in the naphtha are eliminated: this operation is called stabilization. The mixture, composed mainly of methane and ethane, is obtained in a gaseous form and is sent to the refinery’s fuel gas network. Furthermore this gas stream contains minor quantities of propane and butane (normal-butane and iso-butane) with variable concentrations depending on the pressure of the overhead accumulator and on the temperature. A liquid blend is also obtained that is called LPG and is used domestically and as motor fuel.
LPG is liquid at ambient temperature and at a sufficient pressure that depends on the relative ratio of the concentrations of propane and butane. The naphtha coming out from the bottom of the stabilizing column can, in turn, be sent to a column where the various fractions (light, medium and heavy) are separated; this instance is what is referred to as a splitting column.

The side cuts of the principal fractionating column (kerosene, light and heavy gas oil) are instead each sent to feed a column containing 4 to 6 fractionating trays where, with the help of an injection of superheated steam, all traces of the lightest components are removed. The operation of treating with superheated steam is called stripping and, as already mentioned, the columns where it is carried out are called strippers. The fraction at the top of the stripper (strip out) is then sent back to the main column. This operation makes it possible to increase the flash point of the side cut. In some cases, especially for the kerosene fraction, it is difficult to obtain the required flash point value simply by stripping with steam: in this case a reboiler is used to treat the liquid at the bottom of the stripper. In other cases, for example for the gas oil fraction that is to be used as fuel for diesel motors, it is necessary to remove the traces of water, that are normally found dissolved in the fraction when stripping has been performed using steam. Elimination of traces of water to reach a residual value of a few tenths of ppm, is obtained by sending the product at the bottom of the stripper to a vacuum drying column. Alternatively, the gas oil fraction can be sent to a salt drier, followed by a coalescer. Once this refining has been carried out, the products are sent to their relevant tanks, after having been appropriately cooled. The operations of stabilization and stripping complete the processing of an atmospheric distillation plant.

Table 4 shows the yields and characteristics (density, sulphur content) obtainable by means of this process, when fed with a typical crude coming from the Middle East.

<table>
<thead>
<tr>
<th>Table 4. Yields and characteristics of the fractions obtained from the stripping and stabilization operations</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Yield (as % of volume of crude)</strong></td>
</tr>
<tr>
<td>Light naphtha</td>
</tr>
<tr>
<td>4.9</td>
</tr>
<tr>
<td><strong>Density (kg/dm³) at 15°C</strong></td>
</tr>
<tr>
<td>0.66</td>
</tr>
<tr>
<td><strong>Sulphur content (% by weight)</strong></td>
</tr>
<tr>
<td>0.02</td>
</tr>
</tbody>
</table>

2.2.5 Problems of corrosion and materials

In choosing the materials to use in an atmospheric distillation plant an evaluation must first be made of the quality and quantity of the corrosive components in the crude. A rough evaluation of the corrosive potential of the crude is provided by the total quantities of heavy acids present, of which an approximate indication is provided by the neutralization number, expressed in mg of KOH needed to neutralize one gram of crude. This value relates to the neutralization of all the acids present in the crude oil, organic and inorganic, strong and weak, of the sulphur containing compounds such as hydrogen sulphide, mercaptans and thiophenols, of hydrolysable esters, and of salts formed by strong acids and weak alkalis (MgCl₂). More specifically, the products present in the crude that influence the choice of materials are the salts, the sulphur and the naphthenic acids. In fact, the first two are always present in varying quantities.

Corrosion by salts

Depending on the reservoir from which it has come and the method of transportation, salts are present in the crude in varying quantities in the form of NaCl, MgCl₂, CaCl₂ and NaHCO₃ in a ratio more or less the same as that found in sea water. If the salt content is lower than 8.5 g/m³ the crude oil is not considered to be corrosive. The corrosiveness of salts is due to the decomposition of MgCl₂ and CaCl₂ that takes place in the heater coils at high temperature. In such a case HCl is produced, which is not corrosive at temperatures above the dew point of water, whereas it becomes extremely aggressive at lower temperatures. Corrosive phenomena appear when there is condensation of water (column overhead zone, condensers and collecting accumulators of the reflux and/or of the top product). Normally the salts are removed in the desalination section.

Corrosion by sulphur

Sulphur is present in the form of hydrogen sulphide (H₂S) dissolved in the crude or as organic sulphur combined in the molecules of the hydrocarbons; in the latter case it can appear as sulphide, mercaptanic sulphur and thiophenic sulphur. The sulphur content limit that separates a corrosive from a non-corrosive crude oil is between 0.5 and 1% by weight. Nevertheless, it sometimes happens that
crude oils with a sulphur content below 0.5% are more corrosive than others that contain more than 1%. This depends on the form in which the sulphur is present and the temperature at which the hydrocarbon fractions are found. The corrosion is caused by decomposition of the sulphur-containing molecule as a result of heating, with the production of H₂S; these molecules start to decompose at 260°C. The decomposition proceeds fairly quickly between 340 and 400°C and is almost complete at 480°C.

**Corrosion by naphthenic acids**

The definition of naphthenic acids in the petroleum industry includes all the organic acids present in the crude oil. Their name is derived from the first acids discovered in crude, derived from the structure of cyclopentane. However, crude oils contain a great variety of organic acids, that include both low molecular-weight acids, such as fatty acids, and saturated and unsaturated acids made up of single or multiple ring structures. Consequently, naphthenic acids include a vast family of hydrocarbon compounds that all contain the acid radical group — COOH. Generally, in atmospheric distillation these acids are concentrated in the cuts of heavy gas oils and residue; their corrosiveness shows up at operating temperatures above 240°C. Once the acid base of the crude oil has been established, a crude is considered aggressive if the neutralization number is greater than 0.5 mg KOH/g. The aggressiveness of these acids is apparent mainly where there is high turbulence, for example in centrifugal pumps, in heaters (especially in the bends of the coils), in the connecting line between the heater and the fractionating column and in the inlet section where the partially vaporized crude oil enters the column.

**Choice of materials**

The choice of materials for the following areas of an atmospheric distillation plant is critical: the vaporization section and the fractionation section.

In the hottest part of the vaporization section, above 250°C, where sulphidation of the material can take place owing to the presence of sulphur, steels with a high chromium content are used. The heater coils (high temperature and high internal velocities) are usually made of 5Cr-0.5Mo or of 9Cr-1Mo. In the case of naphthenic crude oils with a neutralization number above 0.5 mg KOH/g, the heater coils are manufactured from AISI 316L type stainless steel, at least for the end part where vaporization occurs and as a consequence, there are high velocities.

In the fractionating section the column is normally made from carbon steel with the lower part clad in 12Cr; when there are naphthenic acids present in the feed crude oil, AISI 316L stainless steel is used. In the sections in which the shell of the column is clad in 12Cr or in AISI 316L, the trays are also made of the same material. The top section of the atmospheric column is the part at highest risk of corrosion, due to the presence of HCl which concentrates in the condensing steam. Besides particular materials like monel metal, used both as cladding material for the shell and for the 3-4 top trays, provision is normally made for injection of corrosion inhibitors and neutralizing agents to ensure that the pH of the water, that is condensed and removed from the column overhead receiver, is kept between 5.5 and 6.5. The parts that are primarily subject to corrosion are made thicker. Moreover, corrosion tests are also carried out or ultrasonic measurements are taken to check that the remaining thickness is always above the safety limits.

**2.2.6 Operating variables**

For the correct operation of an atmospheric distillation unit it is essential to consider the effect on both the quality and the yield of the products obtained, and on the operating costs, of changes in the adopted values for the principal operating variables (described below).

**Temperature leaving the heater and entering the distillation column**

This variable must be precisely controlled because it determines the degree of vaporization of the crude and the amount of heat supplied to the heater. The input temperature of the crude into the column is correlated to the characteristics of the crude itself and the quantity and the quality of the fractions to be produced; because all the energy is provided through preheating of the crude oil, any variation in temperature creates a disturbance in the equilibrium profile between the phases and of the temperature throughout the column, such as to cause a variation in the characteristics of the products if no action is taken using the control systems.

A low exit temperature from the heater produces a smaller quantity of vaporized material and consequently a reduced quantity of distillates, while an excessively high temperature causes cracking reactions with the formation of gas and carbon deposits, in particular on the heater coils, making it necessary to shutdown the plant more often to clean/decoke the heater itself.

**Operating pressure of the distillation column**

Once the pressure in the overhead accumulator has been specified based on the characteristics of the crude, the conditions of the cooling systems (cooling water or air) and the possibility to obtain the greatest
degree of condensation to avoid loss of product, the operating pressure of the atmospheric column is determined by the quantity of vaporized material in the column.

The quantity of vaporized material, at a constant pressure, depends on the composition of the feedstock, the outlet temperature of the heater, on the degree of steam stripping injected in the bottom section, on the heat removed from the side refluxes (pumparound), by the flow rate of side fractions extracted from the column and the strip-out flow rates entering the column from the side strippers.

Whenever the temperature in the column is used as an indirect measure of the composition of the products, the pressure in the column must be checked carefully. Typical operational pressure values are 2.1 bar in the bottom section and 1.4 bar in the overhead section of the column. For the same production of distillates, higher pressures require a higher outlet temperature from the heater, and therefore a greater consumption of energy and leads to the possibility of formation of carbon deposits on the coils of the heater itself. In fact, working at higher pressures, other conditions being equal, the fractionating of contiguous fractions is more difficult. On the other hand, working at higher pressures reduces the volumetric loads, with the consequent possibility of reducing the diameter of the column.

Controlling the pressure in the overhead section of a fractionating column can be carried out using two principal typologies: partial condensation systems and total condensation systems. Some of the possible configurations of pressure control by means of partial condensation are shown in Fig. 12. The layout in Fig. 12 A applies to systems in which the top product is condensed but, because of the presence of inert gases or of significant quantities of methane and ethane, total condensation is not possible, so their continuous removal in the form of gas must be provided for so as to keep the pressure constant at the desired value. The layout in Fig. 12 B applies to columns where it is necessary to maintain a constant pressure at the top of the column, acting on the flow of uncondensed material that is present in the accumulator and that is sent to the unit downstream. This layout is applied mainly to stabilizing columns in which there is always a fraction of gas present as a product. The layout in Fig. 12 C, also called total reflux, is applied to columns in which the overhead distillate is present only in the vapour phase and the condensed liquid is used only as reflux. The pressure controller keeps the overhead pressure of the column constant, while a differential pressure controller, acting on the condenser bypass, also keeps the pressure constant in the overhead receiver.

There are several configurations in total condensation systems for controlling the operating pressure in fractionating columns without producing gas in the overhead section (overcooled or bubble point distillate). It is important, in choosing the most suitable system, to keep in mind the required flexibility of the system itself, the absolute value of the operating pressure, the availability of inert gas (for example nitrogen) at an adequate pressure, and the possibility of contamination due to the blanketing gas.

In the configuration shown in Fig. 13 (distillate at bubble point, that is at the temperature at which, in a liquid made up of two or more components, the first...
the column overhead rises, valve A opens and valve B closes; if the pressure goes down, the opposite happens. A hand control is also included in order to discharge any incondensable materials that might accumulate. This method of control is adopted to take account of the performance differences of the condenser caused by variations in the temperature of the incoming cooling water or air, according to the type of condenser used, and depending on the season of the year or the day/night cycle.

In the configuration in Fig. 14 (overcooled distillate, in other words, zero flow rate of vapour produced) the action of the pressure controller on the control valve has the effect of varying the flow rate through the condenser. If the pressure in the column goes down, the control valve is progressively closed and the liquid in the accumulator is brought back to the bubble point temperature with a partial flow of vapour through the equalizing line; the opposite happens if the pressure rises.

The configuration depicted in Fig. 15 applies when total condensation is required with overcooling of the liquid product; therefore the pressure in the accumulator must be maintained by sending in an incondensable gas (nitrogen), since the vapour pressure of the liquid produced would be lower than the pressure value to be maintained. The pressure controller operates the appropriate control valve if entry of nitrogen is called for to maintain the required pressure, or alternatively on the other valve, causing a discharge to the flare, if there is a tendency for the pressure to increase, following the accumulation of incondensables or of an increase in the level that would tend to compress the nitrogen present in the space above the liquid contained in the accumulator.

**Flow and temperature of reflux in the column**

The heat which is not removed by means of the products leaving the column must be extracted by removing the liquid in appropriate sections of the column and sending it back to the column after cooling. In an atmospheric distillation column, generally there are three intermediate refluxes present: overhead, kerosene and gas oil. Obviously the amounts of heat taken out by the pumparound system vary depending on the temperature of the liquid draw-off, the return temperature and the flow rate; these amounts of heat are determining factors for the heat balance of the column and for the assumed values of the flow rate of the liquid and the vapour in the various sections of the column itself. The distribution of the extracted heat along the column is determined by the degree of
fractionation required, as well as by the thermal level to which the heat is removed. In addition to the temperature, the flow rates of the various refluxes in the column also have an effect on the fractionating. High flow rates of reflux in the column can cause flooding of the return zone and weeping onto the trays below, thus causing a reduction in the efficiency of the trays themselves. Low reflux flow rates, instead, can induce entrainment of the vapour (blowing) towards the trays above the return point into the column, again causing a reduction in the fractionating efficiency.

**Stripping steam in the column**

Super-heated steam is injected into the lower part of the atmospheric distillation column in order to remove the lighter components from the bottoms product, that is those with a lower boiling temperature. The effect of the steam is such as to reduce the partial pressure of the hydrocarbon phase, in this way causing the components with a lower boiling temperature to pass from the liquid phase to the gas phase. A typical flow rate for these injections is 2% by weight, in relation to the flow rate of atmospheric residue coming out from the bottom of the column. A flow rate which is too low tends to leave a part of the light distillate in the bottoms residue, while a rate which is too high can cause the higher distillates to be contaminated with traces of heavy product.

**Flow rates of side draw-offs from the distillation column**

At each point along the atmospheric column, and especially at the extraction point on the column of a stream or a side cut, the temperature of the liquid reflects the boiling temperature of the liquid at that exact point. However, an increase in the flow rate of liquid extracted from the column leads to a reduction of the internal reflux; as a result, the liquid becomes richer in less volatile components and, as a consequence, raises its boiling temperature in the section concerned. Conversely, a reduction in the flow rate of the draw-off fraction causes more liquid to remain in the section of the column immediately below the extraction point, with a consequent reduction in temperature.

As a general rule it can be stated that, as the extraction flow rate is increased, the boiling point of the extracted liquid rises, whereas as it is reduced, the boiling point decreases, therefore causing it to become richer in the more volatile components.

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**PAOLO RICCI**

**ROMOLO MONTANARI**

Snamprogetti
San Donato Milanese, Milano, Italy