History of the upstream industry

The pre-industrial period. From ancient times to the mid Nineteenth century

Ancient times and the Middle Ages

Natural products containing mixtures of solid and semi-solid hydrocarbons were already known by the ancient civilizations in the Mediterranean area and in the Middle East, as confirmed by a number of archaeological testimonies, by various mentions in the Bible and by numerous Sumerian, Assyrian and Babylonian inscriptions. They were commonly used by the Mesopotamian and Persian civilizations as impermeable materials of construction. In ancient times, solid hydrocarbons (bitumen and asphalt) were much sought after, while the liquid ones (known as ‘naphtha’), which were less common, never became items of daily consumption. Lack of distillation techniques, necessary for removing the more easily inflammable light fractions, prevented the use of liquid hydrocarbons as sources of energy. In ancient documents, naphtha is always associated with its rapid inflammability, making its use impossible in lamps, and so it was little employed (apart from its use linked with its presumed medicinal properties, popular up to the early decades of the Twentieth century). This was until the Byzantines and the Arabs put it to use after some primitive distillation techniques had been developed, as a powerful weapon of war, in the preparation of what was called ‘Greek fire’, a sort of inflammable mixture used in incendiary projectiles.

From the medical literature of Ancient Egypt it is learnt that *petrol* (a term which however derives from the Medieval Latin *petroleum,* i.e. rock oil) was used as an ointment and in curative preparations for eye infections, while bitumen was used for embalmment. The Egyptians imported the latter from Palestine or Syria, and it was not until the dominion of the Romans that some oil springs along the coast of the Red Sea were exploited. Herodotus (*c.* 484 BC-*c.* 425 BC) states in his *Histories* that in Persia they excavated wells from which asphalt, salt and oil were obtained. Diodorus Siculus (*floruit* 49 BC) in *Bibliotheca historica*, Flavius Josephus (*c.* 37 AD-*c.* 100 AD) in *Bellum judaicum* and Vitruvius (First century BC) in *De architectura* tell of the peoples settled along the banks of the *Lacus Asphaltites* (today called the Dead Sea) collected material termed *bitumen judaicus*, and obtained great profits from selling it to the Egyptians. Strabo (*c.* 63 BC-*c.* 20 AD) in his *Geographia* recounts that this sea was full of asphalt, which erupted at the surface from the centre of the lake, as though the waters were boiling.

The fame of the Dead Sea continued as time went by: in the Seventh century AD Isidore of Seville (570-636) again wrote about it, at second-hand, in his *Originum, sive etymologiarum libri XX,* which, together with the preceding *Naturalis historia* of Pliny the Elder (23 AD-79 AD), influenced all compilations of natural history in the ensuing centuries.

In the Classical Age, the richest occurrences of hydrocarbons were in the Tigris and Euphrates valleys. The importance of this region is reflected in the writings of various authors, who mention the asphalt springs of Babylonia. Strabo describes the clear, light, highly inflammable oil and the dark viscous oil, not dangerous to handle, from which bitumen could be obtained by evaporating the light fractions. Deposits of bitumen and of asphalt rocks were also known in Turkey, along the southern coast of Asia Minor. In Europe important sources of supply were the island of Zante, in the Ionian Sea, and Sicily. Dioschorides (*c.* 40 AD-*c.* 90 AD), in his *De materia medica* and Pliny the Elder recall that at the river Akragas, near Akragantium (modern-day Agrigentum) there was a spring from which an oily liquid bitumen gushed and floated on water which the local inhabitants collected to use in their lanterns instead of olive oil, and also to treat animal scabies. In the Imperial Age, oil was imported from Parthia, from Mesopotamia and from Media. Pliny the Elder recalls that in the north-east of Iran there were wells that produced naphtha, and Plutarch (46-127 AD), in his *Parallel lives*, recounts that Proxenus, a Macedonian officer in Alexander the Great’s vanguard, discovered naphtha springs by the river Oxus (present day Amu Darya) in Turkmenistan.

In ancient history there is also mention of occurrences of natural gas, known as the ‘eternal fires’ of Persia, characterized by flames that required no supplies to keep burning. These, due to their size and continuity, were regarded with awe, and the followers of the Zoroastrian religion considered them to be sacred, transforming them into the symbol of their religion. Eternal fires were also found in the vicinity of Kirkuk, where they were called 'kirkuk baba' or the 'father of sound', because of the hissing that could be heard close to the emissions.

In the first decades of the expansion of Islam, after the downfall of the Persian Empire, there were fresh written testimonies of hydrocarbons. Arab authors bore witness to the fact that the ancient springs in the Middle East had not been forgotten, but were indeed exploited regularly, while others had been further explored, such as those of Baku in the Caspian Sea. The production of crude oil in Arab lands was considerable, to the extent that legislation was drawn up to discipline the concessions. The Sultan of Egypt imported oil from Persia and from Syria to supply the torches of his personal guard. In Medieval times, in Damascus, light oil distillates were produced, to be used for lighting, for cleaning silk and other textiles, or for uses in warfare. In fact, from the very earliest centuries of the Christian Age, first in Alexandria and then in Syria, various distillation techniques had been developed. In the following centuries, they started producing lighting and lubricating oil which they extracted from asphalt rocks, with a process called *destillatio per descensum*. The liquid that resulted was a mixture of hydrocarbons obtained through a process of roasting, distillation and cracking.

Distilling techniques in the real sense of the term were not finalized until the middle of Thirteenth century in the Mediterranean area under Arab influence, and they migrated slowly to the West thanks to the spread of the culture of alchemy; a century later, in Europe, the retort and the distilling flask were still more or less unknown outside of these laboratories. In the medieval West, knowledge of hydrocarbons and the tradition of their use were not entirely lost, and were revived by the contacts and the information brought back by merchants going to the East and by the Crusaders returning from the Holy Land, who told stories of burning fountains, of oil springs and of the use of Greek fire. The oil springs around Baku became known to Europeans about 1270, thanks to the descriptions of Marco Polo (*Il Milione*, 1298-99) and of one of his contemporaries, the German theologian and natural philosopher Albertus Magnus, who in *De mineralibus et rebus metallicis libri quinque* (*c.* 1260) described naphtha and bitumen and their properties.

With regard to the applications of these substances, liquid and solid, these continued to be numerous in medicine, agriculture and pharmacy. Medical manuals and the medieval pharmacopoeia, based on Dioschoride's *De materia medica* and on the *Liber canonis medicinae* of Avicenna (980-1037), repeat classical and Arabic knowledge on the virtues of petroleum and of bitumen, favouring the spread of and trading in these products that began to be actively sought after. In particular, the medicinal uses of petroleum developed, as witnessed from the Sixteenth century onwards by a vast amount of literature. Numerous documents testify that in Renaissance Europe various centres of production of natural liquid hydrocarbons were in activity; produced in small quantities, but to be found in every pharmacy. The main oil springs were found in the Emilian Apennines, and supplied the various varieties of *rock oil* or *oil of Modena*. Other localities famed for their springs were the Tyrol, the Tegernsee region in Bavaria and the mine at Pechelbronn in Alsace. Also known were the oil of Gabian (France) and that of Brunswick and Wietze (Hanover).

Over these centuries, petroleum products were used as a substance for lighting and for lubricating, in the preparation of paints and more seldom as a fuel. Due to their scarcity and their high cost of transport over long distances, the applications of this oil were concentrated on its medicinal virtues, which were often publicized, around the end of the Fifteenth century and in the Sixteenth century, also by means of the early forms of journalism, with printed newssheets distributed by merchants and travellers in the various courts, fairs and markets.

Concerning Emilian oil, the most ancient mention of the oil (*olleum petrollium*) of Montegibbio, a hill locality in the municipality of Sassuolo, dates from 1440, and is cited in the list of taxes on medicines of the city of Vienna. In 1462, Doctor Francesco Ariosto wrote a short essay on it, describing its medical virtues. This work remained in manuscript form until 1690, when it was finally printed by Jacobeus Holgher in Copenhagen: *De oleo Montis Zibinii, seu petroleo agri Mutinensis libellus.* However, the real distribution came with Doctor Bernardino Ramazzini's 1698 edition. Ramazzini, in fact, considered that this oil was effective as an ointment for skin complaints, as a cure for scabies and as a purgative. Between the Sixteenth and the Eighteenth centuries there is frequent mention of such terms as *rock oil*, *holy oil*, *oil of Montesibile*, *oleum Montezibini* and *oil of Santa Caterina*.

Important among the descriptions of the oils of the Emilian Apennines is the one by Georgius Agricola both in *De natura eorum qui effluunt ex terra lib. IV* (1546) and above all in *De re metallica* (1556), an important treatise on mineral and metallurgical techniques, in which oil and bitumen production and refining techniques are described, accompanied by splendid illustrations. Moreover, the German Jesuit Athanasius Kircher left many indications on natural fires in his *Mundus subterraneus* (1665). This is an important work as it analyzes Italian natural fires, while in his *China monumentis qua sacris et qua profanis* […] (1667) he describes Chinese *hydropyric wells*, obtaining descriptions of them from accounts of Jesuit missionaries. Italian oil is also mentioned in the treatise on the mines of Alonzo A. Barba, *El arte de los metales* […] (1640) and in the work by Pierre Pomet *Histoire general des drogues, traitant des plantes, des animaux et des minéraux* (1694). In 1671 Paolo Boccone published *Recherches et observations naturelles* […] in which the main occurrences of hydrocarbons in Italy, including those in the Apennines between Bologna and Piacenza, are described.

The Eighteenth and Nineteenth centuries

A milestone in the study of oil-bearing substances in the latter half of the Eighteenth century is represented by some entries in the *Encyclopédie* […] (1751-72) of Denis Diderot and Jean D'Alembert. The subject is subdivided into four sections *asphalt*, *bitume*, *naphthe*, *pétrol*, written by Doctor Louis De Jaucourt, who sets out with precision the knowledge of the time and places of production of these substances. Apart from the crude oil from the Middle East and Sumatra, in Europe mention is made of the oil produced at Gabian, in France, and in Italy, in the duchies of Parma and Piacenza and of Modena. Particular attention is paid to the efforts made in chemical analysis by Gilles-François Boulduc (1675-1742), Étienne-François Géoffroy l'aîné (1672-1731), William Homberg (1652-1715) and others. With regard to the nature and origin of petroleum, a subject hotly debated even after this, the hypothesis was that an underground fire distilled and sublimated the bituminous parts of certain rocks within the earth's crust, which, condensed on cold rocks, sprang out to the surface through fractured rocks.

The scientific study of hydrocarbons was given a considerable boost by M.E. Eirini d'Eyrinis, a Russian (or Greek) doctor who studied them in the early part of the Eighteenth century and applied them as waterproofing, construction and road paving material (*Dissertation sur l'asphalte ou ciment naturel, avec la manière de l'employer, et l'utilité des huiles qu'on en retire, découvert depuis quelques années au Val de Travers*, 1721). A few decades later, Alessandro Volta discovered a natural gas, methane, which he called *inflammable native marsh air*, distinguishing it from inflammable air, the hydrogen (*Lettere del signor don Alessandro Volta* […] *sull'aria infiammabile nativa delle paludi*, 1777). He, barely thirty years of age, started investigating the inflammable gases which bubbled up in a spring of San Colombano at Lambro, in the vicinity of Milan, and those emanating from the bottom of the reed beds at Angera, on Lake Maggiore. He also devised methods of collecting them and transporting them to the laboratory, where he conducted experiments on their combustion and inflammability in air and in oxygen, setting fire to them with electric sparks and recognizing that they contained carbon and that in the combustion process they released water. The discovery of a new type of natural *inflammable air* was a great success, and earned numerous recognitions for Volta by contemporary chemists. He also mentioned its origin, stating that it came "from plant and animal bodies decomposing in water", and he compared it with other analogous manifestations. Volta visited and studied the fires of Velleia (1784) and the "salse" (mud volcanoes) of Nirano, and deduced that the inflammable air issuing from them was identical to that released in marshes. Shortly afterwards these studies inspired also Lazzaro Spallanzani (*Viaggi alle due Sicilie e in alcune parti dell'Appennino*, 1792-97), who studied numerous occurrences of gas and oil in the northern Apennines, and for this inflammable air he coined the fortunate term of 'natural gas'; he considered it to be of inorganic origin, and used a different name to distinguish it from marsh gas, in contrast with Volta's more precise deductions.

With reference to the underground flow of oil and natural gas, it is recalled that specific studies were not carried out until the Twentieth century. Earlier, the only case studied, being then more interesting, was that of the motion of water in porous media, which provided the scientific and technological basis for subsequent studies on petroleum, as in the case of measurement of liquid flows through layers of sand. These studies date mainly from 1856, when the French civil engineer Henry Darcy, commissioned to construct the water supply system for the city of Dijon (*Détermination des lois* [...], 1856) hit upon the empirical law that explained the flow of water through sand layers, already used for some time as filters. The results were generalized in the empirical law which was named after him. *Darcy's law* correlates the rate of flow with the hydraulic gradient by means of a constant which he indicated with the term *permeability*, probably using the terminology already in use among contemporary hydraulic engineers. The validity of Darcy's law was confirmed by the experiments conducted on the most varied samples of natural and artificial porous materials, while subsequent studies revealed that it could be extended to also adequately describe the simultaneous flow of a number of phases (as in the case of hydrocarbons, in which there is often the simultaneous flow of oil, water and gas), although this was not discovered until the first half of the Twentieth century.

In particular there was a formidable transfer of knowledge from the extraction of water to that of oil regarding drilling techniques. In spite of the development of certain techniques of percussion drilling (or of other types) the majority of the wells (both water and oil) were excavated manually until the early part of the Nineteenth century. The places where oil was produced from excavated wells were the Pechelbronn mine in Alsace, the various sites in the aforementioned Emilian Apennines, the Baku area and the Far East. Major Michael Symes, the British Ambassador to Burma, visited the places of oil production in 1765 and counted more than 500 hand-dug wells.

Towards the turn of the Eighteenth century percussion drilling, at least in the West, began to be developed and to be accepted as the preferred technique for constructing wells more than about a hundred metres deep, when hand excavation started to become difficult. In this period percussion drilling changed from the spring pole method – in which just the elasticity of a pole held fast at one end was used to supply alternating motion to the drilling tool – to the drilling rig itself with beams and counterweights, more susceptible to mechanization, and then to the free-fall rope drawworks, a technique known as *free-fall drilling*.

The development of numerous drilling tools and rigs started in France: well known are the plates of the *Encyclopédie* [...] of Diderot and D'Alembert and the treatise on the drilling of artesian wells by François Garnier, *De l'art du fontainier sondeur et des puits artésiens* (1822), followed by the more famous *Traité sur les puits artésiens*, [...] (1826). A mining engineer and a student at the École Polytéchnique, Garnier pinpointed this discipline in modern engineering, studying the construction drawings of the various types of drilling rigs and tools, and defining a terminology still used to this day (*sonde, sondage, trepan, tige, curette*, etc.). In 1845, engineer Pierre-Pascal Fauvelle took 22 days to drill a well 170 metres deep at Perpignan using hollow rods in which water circulated to remove the drilling cuttings. The invention of the principle of rotary drilling with circulation of fluid is often attributed to Fauvelle, even though it is not certain if he actually caused the drilling rods to rotate. His system was probably one of percussion with circulation of water. However, it is certain that his was the idea to remove the sludge or cuttings by circulating a fluid and using a hollow drilling tool (Fauvelle, 1845). Amédée Burat, in his treatise on the art of mining, *Traité du gisement et de l'exploitation des minéraux utiles*, set out the scheme of a motor-driven percussion rig, already modern in its basic lines and in its operating principle (Burat, 1855).

In these decades one technological development of drilling followed another at a fast rate. In 1844 Robert Beart of Britain took out a patent for a rotary drilling method, while in the United States the earliest patent of the sort was assigned to S. Bowles in 1857. The technique of drilling using a diamond coring tool, devised by the French engineer Rudolph Leschot, also stems from these early industrial applications.

Throughout the Nineteenth century rotary drilling was considered less reliable than percussion drilling, which appeared more indicated for the analysis of productive strata. Even in the early part of the Twentieth century almost every drilling rig was of the percussion type, and in Europe the dominating models were those of Albert Fauck, patented in 1889, and of Anton Raky, both Hungarian engineers who used the Fauvelle system with water circulation.

In the United States, European technologies made slow progress. The need to drill deeper wells occurred in the early part of the Nineteenth century, during the ‘rush to the West’ of pioneers seeking their fortune and new lands so as to obtain a supply of salt extracted from the saline water present in the subsoil. The spring pole technique spread rapidly in the eastern United States and then further and further west, using a system of solid rods, eventually called the *Canadian method* (or the *Galician method* in Europe, from its spread in Galicia after the mid Nineteenth century), as opposed to the *Pennsylvanian method* using ropes, which was to become widespread within a few decades, and which later became the commonest method of drilling all over the United States. It is interesting to observe that the work of the producers of brine was often disturbed by the presence of oil which, not having any commercial value, was dumped in the watercourses.

In the United States the percussion drilling technology was developing autonomously with respect to Europe. In 1841 William Morris patented an articulated joint for percussion drilling (*drilling jar*), and in 1854 a well was drilled at St. Louis (Alabama) down to about 650 m to supply a sugar plant with fresh water. In 1858 a similar well was drilled at Louisville (Kentucky) in just 16 months. The technology spread also to Canada where in 1858, at Petrolia (Ontario), a water well encountered oil and was completed as such. But the real development of percussion drilling took place only after the drilling of Edwin Laurentine Drake’s famous well in 1859, which marked the beginning of the autonomous production of oil.

The age of empirical technology: from the mid Nineteenth century to the 1920s

The main events

At the start of the Nineteenth century the Industrial Revolution was in full swing. The demand for lubricating and illuminating oils was met almost exclusively by tallow and animal oils (above all whale oil) and processes were being developed for the production of illuminating oil by coal distillation. Soon, however, it was realized that for lighting purposes, oil was a better raw material than coal, but that unfortunately it was only a scientific curiosity, found in numerous localities but in small quantities. In the United States oil was known to and used by the native Americans long before ‘Colonel’ Drake drilled his well at Titusville in Pennsylvania, and was collected by skimming it off the surface of a number of springs. Documents exist drawn up by French missionaries in the Seventeenth century mentioning the production of crude oil west of the present State of New York, and in the Eighteenth century it is known that oil was sold at Niagara by the Seneca Indians (hence the name *Seneca oil*), who had settled to the east of Lake Erie, in north-west Pennsylvania. Soon the American colonists, too, started collecting oil and using it for medicinal purposes, as had already been done for centuries in Europe.

In the United States oil was produced and used in modest quantities also by the producers of salt water, and Samuel Martin Kier, a citizen of Pittsburgh (Pennsylvania), started bottling it and selling it as a medicine, obtaining it as a by-product of wells for the production of salt managed by his father at Tarentum in Pennsylvania. These salt waters were produced from formations some hundred or so feet deep, by means of wells drilled by the percussion method, a technique which in this area underwent strong development in the first few decades of the Nineteenth century. However, the oil produced together with the water was often very abundant and, not being able to be placed on the market, was burnt near the wells or dumped in the rivers. In those times, artificial lighting, which certainly improved the quality of man’s life and work, was still a luxury; the commonest form of lighting was the ill-smelling whale oil, which led to such intensive hunting that these cetaceans were on the verge of extinction by the first half of the century. Kier soon realized that if he had been able to eliminate the smoke and the bad smell that was produced when oil was burnt, he would have been able to sell it successfully for lighting purposes, as an alternative to candles and animal oils. After numerous attempts, in 1850 Kier finalized a rudimentary distilling apparatus and started marketing a product which he called *carbon oil*, more economical, safer and more efficient than other illuminating substances of the time. The use of carbon oil spread from Pittsburgh throughout Pennsylvania, and then to New York. Obviously, within a short time demand outstripped supply but the efforts made to try to increase production were in vain until August 1859, when Drake successfully drilled the first well specifically dedicated to the exploration and to the commercial production of hydrocarbons.

The path from Kier to Drake was a complex one and was taken thanks to the farsightedness and the initiative of courageous investors, open-minded speculators, bankers, scientists and adventurers. The adventure of the first oil well started at Titusville, where many occurrences of oil were known. In the early 1850s, a well-off inhabitant of Titusville who possessed a farm and land with numerous springs in which oil came to the surface, sent a sample of it to his son Francis B. Brewer, a doctor in Vermont, informing him that Kier sold it as a universal cure. Brewer showed the oil collected at his father’s farm to a number of friends and professors at Dartmouth College (New Hampshire), his university. This sample attracted the attention of two New York businessmen, George H. Bissel, a lawyer, and his partner Jonathan G. Eveleth, who in 1854 bought the lands where Brewer’s springs were situated and founded the Pennsylvania Rock Oil Company. To assess the economic value of the oil, in order to make it easier to sell the shares of the company, Eveleth and Bissel requested the advice of Benjamin Silliman Jr., professor of Chemistry at Yale University. Silliman carried out the fractionated distillation of the Titusville crude oil, comparing it with that produced in other parts of the world (including Russian, Burmese and Italian crudes), and in 1855 he wrote a brilliant report on its properties and the possibilities of exploiting it industrially: *Report on the rock-oil, or petroleum, from Venango County, Pennsylvania, with special reference to its use for illumination and other purposes*. Following this, the company was also financed by the banker James M. Townsend of New Haven, who, together with numerous other partners, engaged

Drake to explore the possibility of producing oil on an industrial basis from his company's lands.

Drake was not a cultured man, nor even a drilling expert (after a career as a general handyman, his last job had been that of conducter for a railroad company). He had a reserved character and could not manage to exploit the success of the enterprise he was about to undertake. Drake arrived at Titusville in 1857 to begin the operations on behalf of Townsend's company, illegally assuming the title of colonel so as to be looked up to in town. During the first year he limited himself to enlarging and deepening the old springs, with little success, until he decided to drill a well.

For this purpose he hired a salt-well driller, William A. Smith, who arrived at Titusville in April 1859 and amid many difficulties started operations. After some months' work, carried out with very limited funds, on 27 August 1859 Drake's well began producing crude oil from a depth of about 20 m, with a discharge of some ten barrels a day (the *barrel*, as a unit of measurement of oil, was not introduced until 1866, when the Pennsylvania association of crude oil producers fixed the volume of the barrel as 42 US gallons measured at 60°F). This news reached New York just two weeks later and was published in the «New York Tribune». Within the space of a few days the rush for black gold started: investors, drillmen, carters, coopers and adventurers descended on Titusville with even more enthusiasm than that of the first Californian gold rush which had taken place only ten years earlier. Fierce speculation started and every piece of land available was rented or bought at extremely high prices. By the end of 1859 three more wells had already been drilled, while a year later there were 74 wells in production at Titusville. Then enthusiasm increased even more in 1861, when some wells were drilled that produced some thousands of barrels a day (the Empire Well produced 3,000), inundating the oil market and causing prices to collapse tragically.

The wells were drilled with small percussion type rigs, which here found fertile terrain for their improvement. In the majority of cases the wells were a few tens of metres deep, seldom more than 100 m and were located without following any particular objectives. In those days it was thought that the oil came from cracks in the subsoil, and not until the end of 1870 was it realized that it could also be contained in porous rocks. One of the first instruments for conducting investigations in the well was a mechanical device called a *cervice searcher*, already in use from the early 1870s. Another innovation that revolutionized production of wells was the invention of the *torpedo*, a pipe filled with explosive, with a percussion detonator, lowered to the bottom of not very productive wells, to increase production by fracturing the reservoir rock. This first method of stimulation was devised by E.A.L. Roberts, an ex-colonel in the Federal army who, returning from the war of Secession, tried out his invention at Titusville, obtaining the patent in 1866. The first torpedoes used gunpowder, but it was later found that nitro-glycerine was more effective. Roberts, the patent holder, sold his well-site services at exorbitant prices, not appreciated by operators, who often carried out the operation on their own. For this reason many legal actions were taken for breach of patent, but in the end the United States Supreme Court ruled in Roberts' favour. Towards the end of the century Hermann Frasch developed a method of stimulating wells by injecting hydrochloric acid which, dissolving the calcareous rocks, widened the fractures through which the hydrocarbons flowed. Standard Oil patented the method in 1896, but it was not perfected until after 1930, with the introduction of corrosion inhibitors to protect the metal pipes and the wellhead separation apparatuses.

In the first wells the crude oil did not flow spontaneously to the surface, except in rare cases and for a short time, but was almost always produced by means of piston-operated hand pumps used in the water wells of nearby farms. The oil was collected at the well-head and stored in ditches; not until 1861 was it conveyed to storage tanks, large vats made of pine, cypress or sequoia wood (only later of riveted steel) of truncated conical shape, which also acted as separators, decanting the water from the oil and evaporating the gas, which vented into the atmosphere.

The first devices for recovery of the gas associated with the oil were introduced in 1863. These were rudimentary separators, simple closed containers mounted over the storage tanks, maintained at atmospheric pressure, the liquids issuing from the bottom and the gas at the top, piped to the points of use, normally inside the work site. Subsequently, the need to treat ever greater production flows, often under pressure, led to shifting the separator to ground level and providing it with control systems for the level of the fluids. In 1904 the first pressurized separator was introduced, able to operate at a pressure of 10 bars, and very soon it was observed that the amount of oil recovered was greater if the separator was placed upstream of the storage tank instead of conveying all the wellhead fluid directly into the tank. This was the start of the technology of surface processing plants.

During the first years of development of the oil industry, the transport of crude was a very serious problem. At first wooden barrels were used, transported by horse-drawn carts, by raft along rivers or by developing short stretches of railway. Between 1865 and 1866 Samuel van Syckel devised and developed transport by pipeline, at the beginning intended for transporting the oil from the wells to the railway loading stations, where before long the flatcars for transporting the barrels were replaced by primitive wooden tank trucks. The first oil pipeline, laid on the ground, consisted of a 2-inch diameter pipe 5 miles in length, able to transport 80 barrels of crude an hour. Shortly afterwards the railway network was also developed in an adequate manner, enabling the oil to be transported to the refineries in Pittsburgh or to the port of New York. By 1880 tank trucks of welded steel, very similar to modern ones, had already been designed and constructed.

In the decade after Drake's achievement, wells were drilled and brought into production without the use of well casings. Within a short time, however, to prevent the caving in of the well, a start was made on lining the superficial part of the well with a sort of conductor pipe. Following this, the pipe was extended down to the deepest formations so as to counter any collapse of the walls, or to attempt to isolate the aquifers above the layers that produced oil. For this purpose, even before the development of the well casing system, specific production tubes a few inches in diameter (*tubing*) were used, lowered to near the production interval, provided at their end with a sort of packer to isolate the overlying aquifers (a sort of expandable seal between the wall of the well and the pipe bringing up the oil). This device, called the *seed bag*, consisted of a leather sleeve fixed to the outside of the end of the pipe lowered into the hole and filled to a length of 10-20 inches with flax seeds mixed with gum tragacanth powder. The water present in the well made the mixture of seeds and rubber expand slowly, ensuring a reasonable seal. Towards the end of 1870 the practice of using well casing and production tubing became more or less standard, even though cementing the space between casing and well was not yet in use (it did not begin to come into use until the early part of the Twentieth century). The technique of using packers was then improved, with the introduction of elements of rubber and cloth which expanded by exerting an overpressure on the pipe. In 1880 Solomon R. Dresser obtained a patent for a cylindrical packer and founded a service company that was active throughout the ensuing century. Another pioneer of service companies was Byron Jackson, who in 1879 began producing submersible pumps for deep wells; his initials form the acronym by which this company, still active today, is known (BJ, Byron Jackson company).

From the completion of Drake's well until the end of 1880, the percussion drilling technology made great strides forward in terms of both mechanical equipment and technical ability. The first drilling service company (John Eaton) was set up in 1862, based on Oil City (Pennsylvania), a few miles from Titusville, supplying machinery and equipment. The company acquired a partner in 1869, and became the Eaton & Cole Company, specialized in percussion drilling rigs and developed in the present National Oilwell-Varco. Later, the technology of drilling machinery and rigs increased their size, forms and principles of operation, leading to the development of the big percussion rigs used until the first half of the Twentieth century. In their operating principles, the latter were substantially identical to the earliest rigs, except for small details in the machinery and the power generation system. From 1880 to 1930 standardized, mobile or semi-mobile percussion-type drilling rigs were developed, accompanied by all their equipment, and from the turn of the Nineteenth century rotary drilling began to become specialized and to exist alongside and strongly compete with percussion drilling. In the early 1930s the need arose to drill more rapidly and to be able to move more speedily the drill rigs from one place to another. This led to the development of rigs powered by modular internal-combustion engines, lighter than steam-driven ones, and it was possible to make numerous improvements thanks to the use of new types of steel of higher quality and power generation systems of adequate capacity, size and weight, which also considerably extended the maximum depth that could be reached.

The development of rotary drilling

Very little is known about rotary tool drilling prior to 1844, although it is most likely that the technique was already known and used in various parts of the world (in a basic form it seems to have already been used by Ancient Egyptian builders). As a curiosity, it is noted that in 1823, in the Proud'homme family plantation at Oakland (Louisiana), a French engineer bored several water wells more than a hundred metres deep, applying a rotary technique without any circulation of fluid. The drilling equipment and tools, particularly advanced in their design and construction, were made on the spot under the supervision of the engineer himself, and they can still be seen today. However, this remained an isolated fact, and the modern system of rotary drilling with hydraulic circulation was not developed in America until the last twenty years of the Nineteenth century, for drilling water wells in areas where percussion drilling could not be successfully applied.

In Europe, machinery and systems for rotary hydraulic drilling with diamond tools had already been patented by Leschot in 1863 and were used for mining. On 12 July 1844 the Englishman Robert Beart of Godmanchester obtained a patent for a rotary drilling method with hydraulic circulation and a kelly, while in the United States the first patent for a gear-driven rotary and percussion drill was assigned to L. Holms in 1865. A noteworthy technological improvement was made in 1866, again in the United States, with the patent of P. Sweeney for the construction of a small scale rotary drill rig. Sweeney's machine operated with a toothed disc tool, the precursor of the modern rotary bits, which enabled even the toughest rocks to be crushed; it was hand operated and drilled with water circulation. Shortly after Sweeney's idea, in 1869 the American J.F. Summers patented a drilling system using a rotary table, kelly and gear-driven winch. That same year T.W. Rowland patented a rig to be used in shallow offshore waters, a reticular metal structure with four legs standing on the seabed, fitted with an above-water platform for the drilling equipment; a precursor of the modern fixed structures still used today for offshore operations all over the world. From 1880 onwards numerous other patents were issued aimed at improving this technology which, in a more or less rudimentary form, included all the essential elements of current technology (for example, in 1883 the Baker brothers obtained a patent for a new system of rotation and circulation; in 1889 M.T. Chapman for an injection head and a twin-drum winch; in 1891 A.J. Ross for under-reaming equipment, similar to the present-day underreamer; S.W. Douglas for a core barrel, etc.).

The first rotary drill rig for oil exploration was installed in 1894 at Corsicana (Texas) by John Galey, and to this the Baker brothers gave a great boost by the improvement of numerous items of equipment. The success of these first attempts, with the discovery of new oilfields, caused the new rotary system to be more and more appreciated and developed. Again in Texas, in 1901 the first important oil well, the famous Spindletop, was drilled and completed with a rotary rig. Although percussion rigs continued to drill the majority of the wells also in the ensuing decades, rotary drilling started gradually to replace percussion ones in areas characterized by soft, unconsolidated formations. In the first decade of the Twentieth century the use of the square rod rotary table in its modern version became affirmed, and drill pipes were fitted with modern rapid conical-thread tool joints. In 1920 rotary rigs drilled almost all the wells in the coastal plains of the Gulf of Mexico, and they began gaining ground on the percussion drilling market in the areas of soft formations in Oklahoma, Kansas and northern Texas. This technology soon spread to Europe, too, and in 1881 the rotary drilling system was used at Pechelbronn, like at Baku, where the Nobel brothers were making their fortune.

In the first period of development of drilling for oil, they were reluctant to use drilling fluids for fear that they might contaminate the oil or displace it farther away, while in drilling water wells they were normally used to speed up progress. In 1889 M.T. Chapman applied for a patent for a rotary drill with a crown gear, and another patent for the composition of a drilling fluid, consisting of water mixed with clay, for the purpose of forming an impermeable lining on the walls of the well. Such was the birth of *drilling fluid* (or *mud*), essential for drilling deep wells; this, thanks to its constant circulation and control of density and viscosity, enabled the operation to be carried out continuously and safely, removing drill cuttings and counterbalancing the pressure of the formation fluids, preventing them from flowing freely into the well. In 1889 J.L. Buckingham proposed the use of oily substances instead of water, indicating mineral oil as the component of these muds, in anticipation of oil-based drilling fluids which, in the course of time, proved to be extremely effective in particular well conditions. The rational development of muds with a clay base, however, did not take place until the early part of the Twentieth century, with studies by J.O. Lewis and W.F. McMurray (Lewis and McMurray, 1916).

John Davison Rockefeller and the birth of the oil companies

During the first phase of development of the American oil industry, small private operators produced the crude oil and sold it at the rig site or free on rail. The problem of the transport, refining and distribution of the processed products – almost exclusively lighting oil in the first thirty years of the industry – thus became fundamental. This industrial sector was the background of the saga of John Davison Rockefeller (1839-1937), the first American magnate and future founder of the first oil company (Standard Oil), who built up his economic empire on the basis of oil. After an apprenticeship as an accountant, in 1859 Rockefeller, together with Maurice B. Clark, founded a commission business in Cleveland dealing in commodities. After having seen what was happening in nearby Titusville, in 1863 he organized the firm of Clark, Andrews & Company, entering the refining sector as a secondary activity. Two years later it was transformed into Rockefeller & Andrews and, with the help of his brother William, John Davison founded William Rockefeller & Company to manage a second refinery, also in Cleveland. In 1867 the two refineries were combined as Rockefeller, Andrew, Flagler & Company, which three years later was transformed into a share capital company, the Standard Oil Company of Ohio, with John Davison as president and its head office in New York at 140 Pearl Street, a stone's throw from the Stock Exchange on Wall Street. Under his presidency the company obtained control of the oil industry by means of mergers, favourable rail rates, rebates on the tariffs paid to the rail companies by other producers, and other share mechanisms (such as the making of a trust) which were not illegal at the time. In 1882 the Standard Oil trust controlled 95% of all American refining and 90% of the oil pipelines, and also had interests in iron mining, in the production of timber, in production plants and in transportation. Standard Oil held sway over the oil of Pennsylvania, or rather over American oil, and had absorbed, more or less openly, all the big refineries in Cleveland and Pittsburgh, dominating the sector of refining, transport and sale by 1877. In the port of New York it possessed a deposit equipped to receive the refined oil, to put it in barrels and to export it all over the world, from Mexico to South Africa, from Europe to Australia, to Argentina and even to China. Standard Oil became the first and the largest oil company in the world, and was the model for modern multinationals. Rockefeller soon looked upon it as a company integrated vertically, with the *upstream* phases (exploration and production) perfectly integrated with the *downstream* sectors (refining and marketing). In 1899 the Supreme Court of Ohio ruled that this trust was in violation of the Sherman Anti-trust Act, and Standard Oil was split up into 20 companies, with the ploy of founding a holding company named Standard Oil of New Jersey, active until 1911, when the Supreme Court declared this, too, to be unlawful.

In those years Rockefeller had already retired from business, and devoted himself to philanthropic works and charity, as a militant of the Baptist Church; he was a personality full of lights and shades. He contributed to the development of the great game of free competition, the basis of the capitalist system, with its advantages and its inconveniences: advantages for consumers, inconveniences for the less competent or less organized producers.

After Drake's discovery at Titusville, oil began to be actively sought also in other States of the Union, and soon other wells encountered formations of gas and oil, and the industry expanded into West Virginia, Tennessee, Ohio, Indiana, Kentucky and Alabama, and then California, Louisiana, Oklahoma and Texas, which, at the start of the Twentieth century, became one of the most promising areas in the whole continent. Shortly afterwards, important reservoirs were also discovered in Canada.

The explosion of the American oil industry drew attention to the small European fields, already exploited with small-scale techniques, and the industry slowly started up. Apart from the historical areas of production (the Emilian Apennines, Pechelbrunn, Wietze, etc.), where active prospecting began by means of drilling new wells using the techniques imported from the United States, very soon new fields were discovered in Galicia (in present-day Poland, then part of the Austro-Hungarian Empire), Romania, Austria, Croatia and Russia (especially in Siberia), the latter being the only one in which afterwards spectacular results were achieved. Particularly important was also the development of the Romanian oil industry, which started in the twenty years between 1840 and 1860 around Plojesti, in the Carpathians. German prospectors struck oil also in Persia, but at that time there were no entrepreneurs willing to invest capital.

In the Russian Empire the small oil occurrences around Baku (a region ceded by Persia in 1813), known for centuries, started to be developed, and soon led to unexpected results: oil and gas in abundance everywhere, at shallow depths, and the crude gushed out naturally, without any need to be pumped. In 1847, at Bibi-Eybat, in the vicinity of Baku, the Russian engineer F.A. Semenov drilled the first well in this area using a mechanical (percussion) rig. Following this, the monopoly for production was granted to an Armenian family, the Mirzoev brothers, who started an oil company in 1856 and built the first refinery on the Sourachany peninsula in 1859. Ten years later, at Baku there were over 20 refineries; had there not been transport problems, these products would have strongly competed against American oil.

Towards 1880 the brothers Alfred, Ludwig and Robert Nobel, of Swedish origin, who had numerous commercial contacts with the Russian Empire for the supply of arms, were attracted by Baku and by the possibilities of the profits they might be able to make there. Using the financial resources of Alfred, the inventor of dynamite, the Nobel brothers bought various areas of land and by the end of the decade they had acquired control of more than 40% of local oil production, from drilling to exportation. They imposed on the budding industry the stamp of their inventive genius, quite the contrary of the technical and cultural backwardness of the Russian Empire and of the other local operators, making up the lag of the Russian oil industry behind that of the United States. In the early 1890s, the Nobel's built a modern refinery at Baku, using the design of the great German chemist Justus von Liebig. In the same way as Rockefeller, the Nobel's triumphed above all in the transport sector. They developed transport by pipeline and by rail, first of all stimulating the construction of the famous Trans-Caucasian railway from Baku to Tbilisi in 1883 and, in the decade between 1897 and 1907, of an oil pipeline from Baku to Batum, on the Black Sea, which for the time was a world record: 833 kilometres in length, 20 inches in diameter and with 16 intermediate pumping stations.

Their revolutionary idea, however, was transport by sea, as they designed craft with the hull subdivided into compartments into which the crude was directly poured. The first oil tanker, the *Zoroastro*, with a steel hull and a cargo of 240 tons, began service on the Black Sea in 1878. In 1885 the *Glückauf*, a steam vessel of 2,300 tons, 100 metres in length and already with a twin-walled hull, was launched at Hamburg. Two years later, a Swedish shipyard supplied a prototype, also of 2,300 tons, for the Caspian Sea, plying between Baku and Astrakhan, where it discharged the oil into smaller tankers able to navigate the Volga and supply the interior of Russia. From the Black Sea other tankers served the Mediterranean and Europe, and the ports of Alexandria, Izmir, Naples and Marseilles opened up to the Nobel brothers' fleet, consisting of the *Moses*, the *Spinoza* and the *Darwin.* From the United States, Standard Oil observed the development of this technology. In 1881 it purchased the steamship *Vaderland*, equipped for the mixed transport of crude and passengers, and after that it experimented with an oil tanker under sail, the *Andromeda*, and then purchased the *Glückauf* from the Nobel's, so that this vessel then served the American oil industry. Subsequently Standard Oil had its own fleet, but in this technology it let the Russians move ahead.

In spite of the construction of the railway and the development of oil pipelines and tankers in the Caspian, transport prices strongly limited the development of the Baku area throughout the Nineteenth century, even if towards the end of the century the German bankers, the Rothschild's, invested a great deal of money, helping to upgrade the whole area. Nevertheless the great political instability and the social turbulence in this area, starting at the beginning of the Twentieth century with the tragic massacre of the Armenians by the Turks and continuing with the workers' struggles, seriously impeded industrial development. After the October Revolution in 1917, all the assets of the Nobel's at Baku were expropriated without even a minimum indemnity, and they were forced to take refuge in Germany. At the same time, a long period of almost eighty years began for Russian oil technology in which they lagged behind the West.

Calouste Sarkis Gulbenkian, an Armenian from Constantinople, visited Baku in 1891 and soon realized the economic potential of the local oil industry. Naturalized as a British subject in 1902, financial adviser to the Turkish embassy in London and himself a financier, he was a key person in the balanced development of production in the Middle Eastern areas of Mesopotamia, then under Turkish domination. In 1914 Constantinople granted to the Turkish Petroleum Company (founded by Gulbenkian together with the National Bank of Turkey) the concession for the whole area. Shortly afterwards, thanks to Gulbenkian, Turkish Petroleum was subdivided between the Anglo-Persian Oil Company (the future British Petroleum), Royal Dutch-Shell and Deutsche Bank (involved – among other things – in the construction of the Berlin-Baghdad railway), in exchange for 5% of the future profits.

At the beginning of the Twentieth century, simultaneously with the birth in the United States of the first independent companies (Exxon and Mobil, both derived from Standard Oil, Texaco, Gulf, Phillips, etc.), the first oil wars started to germinate. In 1908 the British Empire, urged on by Winston Churchill, converted the whole of its Navy from coal to oil, to gain an advantage in speed over the German fleet. But Great Britain did not possess any oil at that time and therefore it had to look elsewhere for it, and started providing military protection for access to the supply areas. Meanwhile, the Americans had found large fields in Mexico, and the British likewise in Persia (with Lord Julius de Reuters and William Knox d'Arcy, followed by the foundation of the Anglo-Persian Oil Company). Important discoveries were also made in the Dutch colonies in the Far East, which contributed towards the establishment of Royal Dutch. More precisely, in 1906 Marcus Samuel, the founder of Shell, met the Dutchman Henri W.A. Deterding, with a view to the agreement leading up to the new Royal Dutch Shell group; this colossus was backed by the British Empire and was able to stand up against Standard Oil, competing on the great Chinese market and preceding Standard Oil in Latin America thanks to the concessions obtained in Venezuela by Gulbenkian.

In 1907, Russia and Great Britain agreed to divide Persia into three sectors of influence: the North under Russian control, the South British, and the Centre neutral. Standard Oil was blocked in the race for India, but gained important positions at Baku. In Italy, with few energy resources, Standard Oil wanted to exclude Shell from prospecting. In 1927, the State oil company, the AGenzia Italiana Petroli, known as AGIP, was founded and carried out prospecting in national territory and in the colonies up to the outbreak of the Second World War, with limited technical equipment and little success.

As from the first decade of the Twentieth century, the history of the management of oil fields and the strategic importance of this raw material become a fundamental chapter in world geopolitical, economic and diplomatic history. Oil had become so essential for the economy of the nations that its value, apart from economic, was of a political nature, not subject merely to the mechanism of demand and supply, but also to those of the various strategies of national foreign policies, interwoven between wars, interests in colonial countries, affairs of the state and clashes between large-scale financial and industrial groups.

Spindletop and Captain Lucas

From the technological standpoint, immediately after the pioneering beginnings outlined above, the history of the oil industry reached a turning point on 10 January 1901, when a well erupted ("blew") at Spindletop, near Beaumont (Texas), with a powerful roar accompanied by a jet of oil more than

50 m into the air, visible from a distance of several kilometres. This well was not the first oil find, and Spindletop was not a big field, but it confirmed, beyond any possible doubt, that huge quantities of oil existed, spurring on free enterprise to seek it.

In Texas, the first oil discovery well was drilled in 1865 at Saratoga, but was not completed due to the inadequacy of the equipment; the first productive well was completed the following year at Nacogdoches. In 1894, at Corsicana, a water well started producing considerable quantities of crude, giving rise to a small-scale oil rush. In those years a citizen of Beaumont, Pattillo Higgins, joined in this venture and, against the opinions of the geologists of the Mines Office, he strenuously followed up his idea of drilling a well in the vicinity of some springs from which emanated sulphurous, inflammable gas around a small bulge in the plain, later known as Spindletop, to the south of Beaumont. Drilling of the first well came to an abrupt end as the equipment proved inadequate for the clayey, unconsolidated soils of the area. Higgins kept on with the attempt together with a Croatian mining engineer, Captain Anthony F. Lucas, who took up the technical and economic challenge offered by Higgins.

Lucas started a well in 1899 and found a small quantity of oil at a depth of just under 200 m; but, due to the strong pressure of the soil and the gas, the casing of the well collapsed very shortly. Lucas then acquired numerous mining rights around Spindletop, with two other investors in the sector, James M. Guffey and John Galey. On 27 October 1900 the drilling of a new well finally started, although until then no wells had ever been drilled through clayey, poorly consolidated formations, with strong formation pressure which tended to make the well cave in and made the equipment and the drilling methods available not very effective. On 10 January 1901, at a depth of about 330 m, the well had a violent blow-out and was transformed into an impressive jet of oil, estimated to have a daily discharge rate of around 100,000 barrels. The eruption continued out of control for about ten days, leaving on the ground a volume of more than 800,000 barrels of crude, and attracting crowds of onlookers and oil seekers who within a short time settled at Beaumont (whose population in just a few months went up from 10,000 to 50,000), and furious drilling activity took place near Lucas' well. On 26 March that same year, a second well blew and, by the end of 1901, there were some 180 wells that had behaved in more or less the same way.

The oil boom at Spindletop did not last long; already in 1908 the oil had to be pumped up from the wells, and the population of Beaumont declined to about 20,000. Despite this, the perception given was of enormous importance. Beaumont became a small industrial city where oil and drilling companies had their head offices, with a foundry and also a large refinery. Later, oil was discovered in numerous other places in Texas and Louisiana, and the industrial and economic world began to realize that oil was available in huge quantities, and could quite rightly be regarded no longer as just raw material for lighting, but also as becoming the main form of energy of the new century, usable in industry and for sea and land transport. The great amount of crude oil available favoured the development of the budding automobile industry, then strongly expanding precisely thanks to the ever increasing availability of a new fuel, gasoline, derived from oil.

The development of petroleum engineering and petroleum geology

Petroleum engineering and petroleum geology were somewhat slow in developing, compared with the rudimentary empirical technology used in the first drilling and production sites. For almost the entire Nineteenth century it was believed that oil deposits followed the alignment of the small water courses or creeks (hence the term *creekology*), and for this reason drilling was carried out further and further downstream, although, quite rightly, in choosing fresh sites great importance was attached to any surface occurrences of oil or gas and to paraffin and bituminous deposits. The theory of the accumulation of deposits under anticlinal folds was developed in 1861 by Thomas Sterry Hunt, but remained a dead letter for at least twenty years and was not correctly interpreted until the beginning of the Twentieth century (Munn, 1909). However, the opinions of geologists were not held in high esteem even by producers, and vice versa. The drilling of the Spindletop well, in fact, was strongly opposed by officials of the USGS (United States Geological Service), who considered it impossible to find oil and gas in the coastal areas of Texas.

John F. Carll has often been recognized as the first 'petroleum engineer'. During his fifteen years with the Pennsylvania Geological Survey, in 1880 he undertook the first prospecting activity organized in this sector. He devised drilling equipment, he understood that oil could be produced from porous sandstone, he defined the concept of *oil pool*, and he devised a method to estimate the quantity of oil in place and the importance of *waterflooding* for increasing the recovery factor. Moreover, he suggested the analogy with a keg of draught beer to explain the flow of oil and gas from deposits under pressure (Carll, 1880). He succeeded also in convincing the production companies of the need to have an assistant at the drill site to collect well data and to compile daily reports on activity for the use of the few office technicians. In 1877 more than 4,000 wells had already been drilled in the state of New York and in Pennsylvania; of all these, the drilling reports of fewer than 40 wells were conserved, while none was written in such a form as to be useful for any interpretation by the Geological Survey.

At the turn of the Twentieth century the industry started to entrust the solution of the complex problems connected with the production of crude to professional engineers. In 1907 the Kern Oil and Trading Company of California took on a number of geologists and mining engineers who had graduated from Stanford University, to study the conditions of the subsoil so as to protect the oil-bearing strata against the invasion of water and to improve production technology.

A decisive boost towards innovation and the engineering approach in prospecting did not occur until 1913, when the United States Bureau of Mines (USBM) was founded in order to study the country's resources and to suggest programmes for their rational development, under the guidance of Ralph Arnold (Arnold and Garfias, 1913). Four years later the Oil and Gas Division of USBM was organized. This office, together with its laboratories (the first one was established at Bartlesville, Oklahoma, in 1914), was the first one in the hydrocarbons industry to start scientific studies so as to understand the mechanisms of producing oil from its reservoirs.

The first course in Petroleum Engineering was begun in 1912 at the University of Pittsburgh and the first degrees in this field were conferred as from 1916. In Europe, this discipline arrived on the late side. In Italy, for example, the first degree course in Mining Engineering with ‘Hydrocarbons’ as a specialization was established in 1938, during the autarkic period, at the University of Bologna.

For the development of the oil industry the role of the American Institute of Mining Engineers (AIME), founded in 1871, proved fundamental. In 1913 AIME set up a committee for oil and gas, headed by Lucas, for the purpose of promoting and disseminating knowledge in the field of petroleum engineering. In 1922, with the increase in the number of affiliations, they set up the AIME Petroleum Division, then the AIME Petroleum Branch, finally transformed in 1957 into the Society of Petroleum Engineers (SPE). The Petroleum Engineering Division of API (the American Petroleum Institute) was founded in 1927.

Until about 1920, engineers, although concerned with plant design, were not employed in drilling and production, which used mostly empiric techniques. It was in the ensuing period that, above all in the United States, the various companies realized the need to rationalize drilling techniques and promoted the setting up of study groups under the auspices of AIME, API, AAPG (American Association of Petroleum Geologists) and lastly of AChS (American Chemical Society). In this way, a start was made on the application of modern engineering techniques in drilling, which enabled the growing demand for hydrocarbons to be met and led to the development of deeper and deeper oilfields, both onshore and offshore. In this regard, the first text on petroleum engineering was written by Paul M. Paine and B.K. Stroud (Paine and Stroud, 1913), followed by that of Roswell H. Johnson and L.G. Huntley (Johnson and Huntley, 1916) and shortly afterwards, in 1921, by the publication by John R. Suman (Suman, 1921). That same year, Walter H. Jeffrey published the first text regarding drilling (Jeffrey, 1921), while the first real treatise on the engineering of hydrocarbons, properly so termed, came out in 1924 by Lester C. Uren, Professor Emeritus of Petroleum Engineering at the University of California (Uren, 1924). In Europe, studies in this sector were few and far between, and therefore it was United States’ techniques that became most widespread in the world, except for the aforementioned behaviour of the autarkic USSR. However, it was not until the 1960s that new methods proposed by individual technicians were taken up and market planning of prospecting was adopted in order to meet the demand for drilling and development of fields in ever more difficult situations.

The systematic treatment of oilwell disciplines (from the 1920s to the end of the Second World War)

Drilling and production engineering

After the oil discoveries in Texas, rotary drilling underwent noteworthy development. The continuous improvements resulting from the necessity to complete deeper and deeper wells, in any type of formation whatsoever, transformed rotary drilling into the most effective, rapid and reliable technique.

Until 1910 this was carried out with fixed blade tools (fishtail bits with 2, 3 or 4 blades) or with disc bits, both effective only in extremely soft formations. The real revolution took place already in 1909, when the Texan driller Howard Hughes Sr. patented a roller cone bit also able to penetrate hard consolidated rocks, for which reason it was known as a *rock bit*. The first model proposed by Hughes was a bit with two interchangeable roller cones, with 166 cutters per roller, with a central hole for the regular circulation of drilling fluid. Very soon this was perfected with the production of a 3-roller bit which, at the beginning of the 1930s, conquered the drilling market. In those years the use of hard metal inserts also became popular, to protect the cutting structure. Similarly, in 1913 Granville A. Humason of Shreveport (Louisiana) patented the cross-roller bit based on a particular arrangement of cylindrical rollers with cutters, and this bit was very successful until the end of the 1950s, when it was abandoned in favour of the 3-roller bit. A further type of bit developed in these years was the pseudospherical single-roller rotating bit, with a skewed axis, known as *Zublin*, after the name of its inventor.

Towards the end of the 1920s, following the perfecting of the roller bits, which made it possible to extend the field of application of rotary drilling to hard and consolidated formations, percussion rigs rapidly began to lose ground. In the 1930s, following the discovery of the big oil fields in the United States, drilling became more and more competitive and the need to drill deep wells rapidly and reliably became a primary objective, achieved by developing the rotary technique and increasing the installed power of the rigs, traditionally supplied by steam machines similar to those used for percussion drilling. In 1925 the first diesel engine was applied to a rotary rig and in 1938 a depth of 4,500 m was exceeded, a record that was unbroken until 1947.

Although steam machines had undoubtable advantages for mechanical coupling with drilling rig equipment, in terms of characteristic curve, their greater bulk, the complicated management of the boilers and of the fuel and the frequent maintenance operations made them obsolete by the end of the 1930s, when they were finally abandoned in favour of internal combustion engines, easier to handle during the moving of the rig, being lighter in weight. The great technological developments in rotary drilling in the first three decades of the century meant that already in the early 1950s, percussion drilling had practically disappeared in oil well drilling.

The first drilling fluid was water which, mixing with the rock cuttings, form a natural mud. However, it was observed that using a mud of adequate characteristics, able to form a plastic lining around the well bore, the stability of the hole could be improved before setting the final casing. Shortly afterwards it was discovered that the density of the mud contributed towards hole stability, and was fundamental for controlling the formation pressure, preventing the uncontrolled outflow of formation fluids into the well. In the 1920s they started regulating mud density by adding ground barite (Stroud, 1925), and in the 1930s bentonite was identified as the clay material possessing the best characteristics for regulating viscosity (Garrison, 1939). The first additives to control viscosity (phosphates, tannin, quebracho) came into use in those same years. Again in this decade, with the establishment of specialized service companies, muds started to be studied in the laboratory and specific additives were found to improve their qualities and to control their rheology, establishing the first standard methods of measurement (Jones and Babson, 1935). Furthermore, oil-based muds (or ones with an oil-emulsified water base) were used industrially, both so as not to damage the productive formations, and to assist drilling in more difficult situations (deep wells, high pressures and temperatures, directional drilling, etc.). In 1938, for the first time, air or gas was used as a drilling fluid, but they did not come into common use until the 1950s and 1960s, together with foams or aerated muds.

Control of well verticality was a problem already known from the early part of the Twentieth century and often spontaneous deviation had led to interference with adjacent wells, trespassing or failure to reach the mining targets. The first rotary drilling operations were carried out without the help of adequate drill stems of heavy pipes and therefore the problem of well verticality became even more serious, also because the wells were getting deeper and deeper and there was the necessity to reach the mining targets with greater precision, respecting the limits of the concessions. Towards the end of the 1920s the practice came into use of using a string of drill collar placed at the bottom of the drill-stem to increase the weight on the bit and the stiffness of the stem, keeping the drill pipes always under traction. Shortly afterwards the use of stabilizers became widespread; these were placed in various parts of the drill string to increase stiffness and to have greater control over any spontaneous deviations of the hole. The first measurements of hole inclination were carried out at the end of the 1920s, by means of acid bottle clinometers. Compass and pendulum photoclinometers (of single-shot type) were developed in the 1930s by Eastman and led to the perfecting of directional drilling techniques. Nevertheless, an exact understanding of the mechanics of the forces associated with the drill string and with hole deviation had to wait until the 1950s, with the classic studies of Arthur Lubinski, which led to the development of the current practice of directional drilling (Lubinski and Wood, 1953, 1955; Lubinski and Blenkarn, 1957).

The drilling of deeper and deeper wells, where it is more likely to encounter anomalous pressures (often overpressures), shed light on another problem, well control and the techniques of intervening on wells in which uncontrolled blowouts are taking place. In the 1920s, James Abercrombie, a driller, and Henry Cameron, a workshop technician, designed, constructed and finalized a safety device to avoid uncontrolled blowouts during the drilling of the well, called BOP (BlowOut Preventer), fitted on the wellhead; this had already been in use in Texas and in California since the previous decade. The first commercial BOP was able to withstand a pressure of 3,000 psi in an 8-inch diameter hole. The device had enormous success and was developed in various configurations. In the 1930s, Louis Records identified the mechanisms that caused well blow-outs and drew up a safety procedure to bring up to the surface the fluids in overpressure that had entered a well, laying the foundations for modern well control techniques. At the same time, companies were set up that specialized in handling wells with a blow-out in progress, teams of highly skilled technicians and firemen who, at tremendous risk, tackled the wells in which accidents had occurred, under extremely dangerous conditions. Some of these technicians have become legendary, such as Myron Kinley and Red Adair. This experience led to the development of numerous safety provisions, both active and passive, still used today, especially in offshore fields.

Throughout the Nineteenth and part of the Twentieth century, the sole source of information on the rocks traversed in drilling derived from the visual analysis of the cuttings. In the 1920s the first mechanical core-barrels for oil wells were produced and the samples obtained started to be examined in the laboratory with the new techniques for measuring the petro-physical characteristics (porosity, permeability, saturation, etc.). In spite of this, due to the high cost of collecting samples, the technique of cutting analysis became increasingly more advanced. In this decade the technique of cutting analysis using ultraviolet light was perfected, to reveal traces of oil. After the introduction of shale shakers for improved separation of the cuttings from the mud, which took place in the 1930s, John T. Hayward started to develop the techniques known as *mud logging*, that is, the combined analysis of the cuttings and of the drilling fluid (controlling the liquids and the dissolved gases) as a function of the depth and drilling rate. In this way, they succeeded in reconstructing with a good degree of precision the lithology of the drilled formations and their oil and gas content. Moreover, the number of mechanical cores could be reduced to a minimum, thereby diminishing drilling costs. Simultaneously, drilling rigs were fitted with instruments for controlling the drilling parameters, such as depth gauges, indicators of weight on bit, rate of rotation, torque, mud flow and pressure, together with systems for continuous recording on paper. Measurements of this type led to the development of modern drilling engineering, and the advantages were soon discovered of optimizing mud flow and of the use of calibrated bit nozzles to increase the penetration rate (*jet circulation*), although these methods were not perfected until the 1950s.

The well casing technology had already been developed towards the end of the Nineteenth century, as well as some rudimentary techniques of cementing the casing to the well bore. Initially, the cement slurry was mixed by hand and fed by gravity into the annulus, where the casing was kept several metres above the well bottom; lowered to the bottom, the slurry rose through the annulus, guaranteeing a fair seal. Subsequently, small diameter pipes were used to inject the slurry at the bottom, in the clearance between the casing and the hole, and in the first decade of the Twentieth century in California the two-plug cementing method was developed. Between 1903 and 1907 R.C. Baker invented a cementing shoe for rotary drilling, and set up a service company specialized in cementing, which later became one of the largest service companies in the oil industry. In 1919 Erle P. Halliburton founded another service company at Wilson (Oklahoma) specialized in well cementing called the New Method Oil Well Cementing Company. In 1921 he devised a new cementing technique, far more rapid and above all effective, perfecting a method to mix the slurry rapidly and automatically using a jet mixer. In 1924 Halliburton became president of this company, now another of the biggest service companies, which attracted numerous investors, including various oil companies.

In the 1940s laboratory research showed that the setting time and the consistency of cement depended on its composition, on the pressure and on the temperature of the hole. Cement was therefore produced with characteristics such as to reduce the waiting time for it to set, making it possible to reduce significantly the rig time. Moreover, it was discovered that the main cause of unsuccessful cementing was contamination of the cement by the mud, and therefore more effective cementation plugs were developed and scratchers were introduced, placed around the casing to remove the mud cake and ensure a better seal.

With regard to the techniques of well completion in front of the oil-bearing layers and to the management of production, by the early part of the Twentieth century open-hole techniques or holes lined with a steel casing were adopted. In the latter case, casing perforation necessary to enable the productive layers to produce fluids at the surface, was carried out with mechanical pipe cutter tools similar to cutting arms, able to perforate the casing. This technique remained in use until the 1930s, when its place was taken by safer, more effective methods, based on firing steel bullets with an electrically triggered perforating gun lowered into the hole by cables (patented by Lane and Wells, 1932), which reduced the risk that the complex pipe cutter tool would get stuck or lost down the hole. After the Second World War, in addition to bullets, jet charges were used (patented by Muskat, 1949*,* owned by Gulf); these were far more powerful and penetrating than bullets, able to perforate even a number of concentric casings. As the production of layer fluids through the casing (cemented to the hole and thus unable to be substituted) could induce damaging by chemical corrosion, in the beginning of the Twentieth century a start was made on systematically producing oil and gas through tubing, which also made it possible to appropriately choose the rate of fluid production from the well bottom on the basis of fluo-dynamic considerations important in the case of two-phase gas-oil flow. At the same time, if production concerned loose or poorly-cemented formations, they began equipping the well section in correspondence with the productive layers with special filters or drains, in order to stop sand from entering the well, and to isolate the productive layers with tubing fitted with expandable packers.

In gas wells, the reservoir pressure guarantees spontaneous flow at the wellhead. In oil fields, on the other hand, spontaneous production is not always guaranteed, or usually ceases after a few months or a few years, according to the diminution of reservoir pressure. In this case, liquid production can only continue by supplying energy from outside. The oil from Drake's first well had already been produced by pumping, using a simple hand-operated piston pump similar to those used in water wells. Later, this system was mechanized with steam engines, but without introducing any particular improvements. Only the rods, once made of hard wood, were replaced around 1880 by steel bars. In the 1920s, modern pumps with rods and beams were developed, in view of the need to improve well productivity, while the wells were progressively deeper. In 1925, W.C. Trout, the owner of a small mechanical workshop at Lufkin (Texas), introduced the first pump with counterbalanced rods, fitted with a motor unit with a mechanical reducer to optimize the power used. Rod pumps are even now in very widespread use, and have substantially the same geometry as those designed in the last century. Improvements have been made in the field of materials (for example, light rods of fibre glass) and in control of performance both through the interpretation of dynamometric diagrams, and with interpretation of the elastic waves observed at the surface using mathematical models, sometimes even very refined ones.

In the 1930s, a new method was developed for the artificial lifting of hydrocarbons from wells, called *gas-lift*, based on the continuous or intermittent injection into the well of gas under relatively high pressure, in the space between casing and tubing. With this method, the injected gas becomes emulsified with the oil and makes it lighter, thus making production possible at the wellhead. In 1940, W.R. King introduced special valves called *gas-lift valves* which enabled the method to be rationalized and made it more flexible with the varied well conditions. In 1951, Harold McGowen and H.H. Moore developed a revolutionary type of side-valve that could be recovered by cable so that it could be maintained and repaired without having to extract the whole well completion.

Another method of artificial lift was developed as from the 1920s. In 1917 the Russian Armais Arutunoff produced an electric submersible pump of centrifugal type, suitable for the extreme conditions of a typical well for the production of oil. As a result of the Soviet revolution, he emigrated first to Germany and then to California, where he continued his study of this system and installed a prototype in 1921. In 1928 Frank Phillips (the founder of Phillips Petroleum of Bartlesville, Oklahoma) took an interest in this technology and financed its study by Arutunoff, leading to the development of commercial models. Presently, multi-stage electric submersible pumps are widely used, the most significant technological developments of which took place in the 1950s, with the application of new materials for the impellers, reliable packing, insulators for the electric engine and cables able to withstand high temperatures, up to the pumps of today, of great power and capacity. In the 1930s two other types of hydraulic pumps were produced which are still used today: submersible hydraulic pumps driven by a fluid under pressure, and jet pumps. Jet pumps, the principle and basic lines of which were already known in the mid-Nineteenth century, were patented in the petroleum field by W.J. McMahon in 1930, but came into common use only after 1970, with the development of automatic computing methods which permitted their correct use in this field. In the last thirty years progressive cavity pumps, i.e. Moyneau-type pumps (already known in the early Twentieth century, but scarcely applied) have been developed, made with materials able to stand the conditions of pressure, temperature and corrosiveness typical of oil wells. The principle of Moyneau pumps has led also to the subsequent development of the present PDM (Positive Displacement Motors) downhole motors, which are no more than Moyneau pumps with multi-lobe drive shaft made to operate as power machines.

With regard to the evolution of surface facilities, the rationalizing of production in oil fields led, in the 1930s, to the construction of ever more complex separation units. Three-phase separators were developed, fitted with devices to improve performance, and it was discovered that separation of the water could be improved by favouring the coalescence of the water drops on an inert medium with a high specific surface area (as wood chips or metal grids, in the case of gas-liquid). The difficulty was also recognized of treating emulsions of water in oil, often very stable, and it was discovered that they could be separated into their components by adding particular chemical additives, or by heating them. This contributed towards the use of field heaters and, more generally, towards devising real processing plants serving all the wells in a field or even of a number of adjacent fields. Although the first pressurized gas pipeline had been already constructed in 1891 between Indiana and

Chicago, by the end of the 1930s the increasingly more extensive marketing of natural gas led to the development of a growing number of gas fields and to the construction of the relevant processing plants. High-pressure horizontal separators and the first low-temperature separation units were introduced, in which the dehydration of gas from the associated water vapour took place, in order to prevent, as the temperature went down during transport, the formation of methane hydrates (in the presence of water in the free phase) which can clog the pipes. The problem of dehydration of the gas was already known in the 1920s, and was resolved at first simply with heaters which always kept the gas at a temperature higher than the point of formation of hydrates, and towards the end of the decade with the use of plants having a solid drying bed, although both methods were quite costly. In 1936 Thomas S. Bacon devised a method to dehydrate and sweeten natural gas by means of an amine solution. Later, in 1949, Laurence S. Reid developed a small field unit for dehydrating gas at the wellhead by means of injecting triethylenic glycol. This process was soon standardized and at present it still forms the basis of the industrial dehydrating processes of natural gas.

Reservoir engineering

In the first few years of the Twentieth century, the petroleum industry was occupied almost exclusively with the drilling and completion of wells, and until the 1920s they were at a higher stage of development with respect to knowledge and management of the reservoirs. A number of isolated studies were started at the end of the Nineteenth century on the application of Darcy's law to groundwater flow, with special regard to the single-phase flow of water, and on the physical properties of underground fluids. Concerning the first problem, throughout the Nineteenth century, with a few rare exceptions, they had only studied solutions relating to the stationary case, applied to the resolution of water filtration problems in the field of civil engineering and hydrogeology. In France, in 1863, Arsène-Juvenal Dupuit, a contemporary of Darcy, published his *Études théoriques et pratiques sur le mouvement des eaux dans les canaux découverts et à travers les terrains perméables* in which he elaborated on an expression equivalent to the empirical law of Darcy in a differential form (Dupuit, 1863). Furthermore, integrating the flow equation in a radial domain, Dupuit also obtained solutions for stationary flow both for confined aquifers and for unconfined ones. Shortly afterwards, the Austrian engineer Phillip Forchheimer was among the first ones to use the concepts of flow lines and of equipotential surfaces in studying the fluid flow in porous media. In 1898 he described the stationary flow in aquifers, recognizing the equation of Laplace to be applicable in that case (Forchheimer, 1898). In 1906, the German Gunther Thiem developed similar expressions, obtained independently from Dupuit's hypotheses (Thiem, 1906).

In the United States, apart from Carll's pioneering prospecting activity, as already mentioned, which in any case remained isolated, the first studies on the relations between pressure and fluid flow in porous media were carried out by Frederick H. Newell (1885), Franklin H. King (1899) and Charles S. Slichter (1899), who measured the discharge of air and water through consolidated and unconsolidated sands (King, 1899; Slichter, 1899). Slichter, a member of the University of Wisconsin and a collaborator of the USBM, did not know the results of Forchheimer's studies, and made an independent verification of the applicability of Laplace's equation. In 1924 Karl Terzaghi made an experimental study of the deformations in water-saturated clayey soils, and established the laws governing the relation between stress, deformation and fluid pressure inside porous media (Terzaghi, 1925).

As stated, in 1914 the USBM Petroleum Division Laboratories were established at Bartlesville (Oklahoma), for the purpose of studying the best techniques to increase the oil and gas recovery factor, thereby reducing the waste that often accompanied the production of the first oil fields. In 1904, questioned as to the rapid decline in production of the Spindletop field, Lucas recognized that too many wells had been sunk, and that "the cow was milked too hard, and moreover she was not milked intelligently". In those same years the industry started taking a systematic interest in the study of the physical mechanisms governing the production of hydrocarbons, seeking to identify – among other things – the importance of water pressure, the relationship between bottom pressure and production, and estimating the recovery factor. In this way, the new discipline of reservoir engineering slowly, but autonomously, began to develop. The first studies conducted by M.A. Brewster in 1925 regarded the increase in the recovery factor and optimizing the spacing of wells (Brewster, 1925). In 1920 the USBM started research on the flow of oil and gas in porous media, on measurement of well bottom pressures, on determining the physical properties of hydrocarbons, on estimating reserves and on waterflooding operations, even if the reservoir engineering did not start to become a semi-quantitative science until the mid-1930s.

A.W. Ambrose and J.O. Lewis were the first innovators in the USBM; in 1917 Lewis published an important study on relations between viscosity, capillary phenomena and quantity of gas in solution in oil (Lewis, 1917). Until 1928 research in this sector remained almost the monopoly of the USBM, even though some enlightened businessmen such as H.L. Doherty and E.W. Marland had already both started private research laboratories in Oklahoma at the beginning of the 1920s drawing researchers away from the USBM.

Doherty was convinced that the United States would soon be involved in another war, and that the supply of oil would have been fundamental in deciding the outcome; therefore he stimulated research, as well as attempting to persuade operators and legislators that it was necessary to exploit the reservoirs, which he considered strategic for national security, in the most prudent and most controlled manner possible. Marland, while less of an idealist than Doherty, encouraged the study of technologies to maximize the recovery of oil and in 1925 he opened a laboratory of production engineering, under W.V. Vietti, which was soon followed by laboratories dedicated to the study of gas saturation, of the oil shrinkage factor and well bottom pressure.

In 1925 Rockefeller and Universal Oil Products agreed to donate 50,000 dollars a year for five years, administered under the guidance of API, to support basic research in favour of the petroleum industry. In this context, the first studies started in 1927, under the name of *The fundamentals of the retention of oil by sands,* under the guidance of B.H. Sage and W.N. Lacey at CALTECH (the CALifornia institute of TECHnology), relating to the study of reservoirs under high pressure. Sage, Lacey and Schaafsma, in 1933, were the first ones to recognize the phenomenon of retrograde condensation in some high-pressure gas reservoirs, leading the way to studies on optimizing production in condensate reservoirs by means of gas cycling (Sage *et al.*, 1933). The great depression in the years 1930-31 caused the suspension of these research funds, but API managed to go on with its researches, albeit at a reduced scale, with various projects, the best known of which were *Project 37*, on the physical properties of hydrocarbons, *Project 27*, on surface and interface phenomena in hydrocarbon production, and *Project 47*, on mechanisms of oil displacement in porous media. Apart from these, API also financed research projects on the geology of hydrocarbon reservoirs. In these same years, in Europe, Jan Versluys, a Royal Dutch Shell hydrologist, also conducted studies on the physical mechanisms of oil production by natural porous materials.

In the 1920s, petrophysical studies were only just beginning, and the concepts of porosity and permeability were often still confused. A.F. Melcher, D.B. Dow and C.E. Reistle were among the first to begin studying the ways of measuring in the laboratory the properties of rocks and of the fluids contained in them. In 1920 Melcher finalized a method to measure the porosity and the density of some oil-bearing sands (Melcher, 1920) and in 1921 Ronald van Auken Mills studied the relations between flow conditions and structure of these sands (Mills, 1921). This research was continued in 1933 by G.H. Fancher of Penn State University. The study of fluid flow in porous media characterized research in much of the 1920s and was finally understood and codified in the early 1930s (Fancher, 1933). Among the most important scientists who contributed to the first studies on the flow of liquids and gases through porous media are F.G. Tickell, C.R. Fettke, C.F. Barb, P.G. Nutting, H.G. Botset and Morris Muskat (Tickell, 1928; Nutting, 1927, 1929 and 1930; Muskat and Botset, 1931; Tickell *et al.*, 1933). The research of these scholars also defined the concept of *absolute permeability* of porous media, separating it from the effects due to the viscosity of the fluid. In 1933 R.D. Wyckoff proposed a method for measuring permeability, subsequently adopted in the API standards published in 1935 (Wyckoff, 1933).

In 1937 Muskat, of Gulf, published *Flow of homogeneous fluids through porous media*, the first real treatise on the mechanics of hydrocarbon reservoirs, of fundamental importance for the future of research in this field (Muskat, 1937). In 1949, moreover, he published his *Physical principles of oil production*, a handbook which, together with his first treatise, formed the basic theoretical pillars of the engineering of hydrocarbon reservoirs, as it combined the fluid mechanics in porous media with the phase behaviour of hydrocarbon mixtures under reservoir conditions (Muskat, 1949).

In the 1930s further systematic studies were made on the petro-physics of reservoir rocks. In 1933 T.V. Moore, William Hurst and Ralph J. Schilthuis discovered the second-order differential linear equation which describes the non-stationary radial movement of compressible fluids within a porous medium. One year later they applied this to the calculation of the pressure variations in a reservoir and its effects on production capacity (Moore *et al.*, 1933). In 1936, G.L. Hassler introduced the concept of *relative permeability* as a function of saturation (Hassler *et al.*, 1936), and, again in 1936, Wyckoff and Botset discovered that this does not depend on the viscosity of oil but on saturation and in addition they tackled the study of two-phase oil-water and gas-water motion in unconsolidated rocks, later extended to all types of rock (Wyckoff and Botset, 1936).

In the same decade studies on flow under turbulent conditions (non-Darcy flow) were started, but not until the mid-1930s was the role of connate water evidenced in relation to the efficiency of oil displacement (Schilthuis, 1938). Until then, in fact, the watertable was regarded as a surface of clear separation between the aquifer and the reservoir, although petroleum geologists had already for some time recognized that the majority of hydrocarbon reservoirs had been deposited in a marine environment, and that the migration of hydrocarbons had taken place through porous water-saturated media. This mistaken idea greatly influenced the first estimates of hydrocarbons in place, the interpretation of the logs, the completion of many wells and the conducting of waterflooding operations. Afterwards it was demonstrated that in the majority of reservoirs water was present, in variable quantity, throughout the productive formation, in the form of a thin film between the rock and the oil, adhering to the rock, and as capillary water, also in those parts of the reservoir that produced oil only (i.e. anhydrous oil). This discovery confirmed the theories on the capillary behaviour of porous media, which had appeared shortly before, and which indicated a gradual passage from 100% of water at the base of the productive formation, to smaller values in the higher parts of the oil-bearing layers; this water was said to have occupied a "capillary fringe" above the completely water-saturated zone. The first measurements of capillary pressure were published by Hassler in 1943 (Hassler *et al.*, 1943) and research in this field was active throughout the decade, culminating in the work of W.R. Purcell (Purcell, 1949).

In 1940, M.C. Leverett and W.B. Lewis reported the results of the first researches on the three-phase flow of oil, gas and water (Leverett and Lewis, 1941). In the same period, the pioneers of reservoir engineering realized that to calculate the oil in place, it was necessary to determine the properties of the reservoir fluids as a function of its pressure and temperature. To this end, Schilthuis devised and described a bottomhole sampler and a method of measuring the physical characteristics of the samples obtained in 1935 (Schilthuis, 1935), while P. Comins and C.E. van Ostrand devised instruments for continuous recording in the well of pressure and temperature, respectively. Of the results obtained, relations between pressure, volume and temperature (known as *PVT measurements*) are important, as a function of the saturation pressure and the quantity of gas in solution in the oil, and of the consequent variation in the volume of the oil.

These findings made it possible to calculate the oil and gas present in the various situations, which enabled Schilthuis and D.L. Katz, in 1936, to introduce the equation of mass balance for bounded reservoirs, already proposed in an approximate way by Steward Coleman in 1930 (Coleman *et al.*, 1930; Katz, 1936; Schilthuis, 1936), later extended to water-drive reservoirs by Schilthuis (1936) himself and subsequently in a more satisfactory manner by Hurst (Hurst, 1943) and by A.F. van Everdingen and Hurst (van Everdingen and Hurst, 1949). The latter two researchers demonstrated the applicability and the validity of the mass balance equation to reservoirs with an aquifer of any size whatsoever. This method, later perfected by other authors (Tarner, Muskat, etc.), for a long time remained the basis for calculation of hydrocarbons in place as a function of the production data and for estimating production forecasts.

A fundamental step in the field of reservoir engineering was taken in 1941 by S.E. Buckley and Leverett, who presented a method of calculating the immiscible displacement of oil or gas by water (Buckley and Leverett, 1941). This method made it possible to calculate the recovery factor, clarifying the causes of the low recovery values observed in many reservoirs, and to identify the criteria for increasing them, appropriately exploiting the energy in place or supplying new energy by injecting gas or water. That same year, Leverett published two other fundamental studies on relative permeability and on the capillary behaviour of porous media (Leverett, 1941). In 1952 L.R. Kern extended Buckley and Leverett's study to the case of systems containing an initial saturation of displacement phase (Kern, 1952).

Prior to the Second World War, lastly, some different methods also started being studied for the improved recovery of petroleum. Mention has already been made of waterflooding and gas injection techniques, identified empirically and put into practice ever since the early years of the Twentieth century. In particular, at the end of the 1930s, research was started on displacement techniques with chemical substances (at the outset with alcohol, to displace the capillary water from the flooded zone) and on techniques of *in situ* combustion, developed above all in the USSR.

Seismic exploration and well geophysics

The developments in seismic, reflecting and refraction-type geophysical measurements have been fundamental (and they still are) for hydrcarbon exploration. Seismology started to develop in the second half of the Nineteenth century in concomitance with the beginning of the scientific study of earthquakes, following which John Clarence Karcher elaborated his theory of reflection seismics. In 1913, a Boston physicist, Reginald Fessendern, after using a sound-wave source for measuring the depth of the oceans, devised an instrument to measure the reflection and refraction of seismic waves in the subsoil, patenting a method and an instrument for locating mineral deposits in 1914. At the same time, the German scientist Ludger Mintrop invented a mechanical seismograph, subsequently widely used in the First World War to locate enemy artillery. Indeed, he observed that to improve the precision of the measurements it was necessary to introduce assumptions as to the type of formations present in the subsoil. At the end of the war, Mintrop overturned the problem, measuring the distances and interpreting the types of rocks traversed by the seismic waves. Moving to the United States, he patented this technique in 1923, and in 1924, in Brazoria county in Texas, the first oil field was discovered on the basis of structural images generated by seismic data.

In the first half of the 1920s, therefore, reflection seismics became established as an extremely precious method for the exploration of hydrocarbons, and in the early 1930s the first service companies for conducting seismic surveys were founded (the Geophysical Research Corporation, headed by Karcher himself, Geophysical Services, Petty Ray) and gave a great impetus to new prospecting in this field. After the end of the Second World War, Geophysical Services obtained a licence to make transistors (from which developed Texas Instruments, of which Geophysical Services became a subsidiary) which proved to be fundamental for making field seismic instruments lighter and more compact.

In the mid-1950s, the recording of seismic signals on magnetic tape started; until then they had been recorded on paper. This permitted the introduction of automatic data processing and the development of analog processors, which revolutionized data collection and treatment. In these years another basic step was the invention of *common-depth point data stacking*, devised by William Harry Mayne, which is still the main technique for improving the relationship between signal and noise. At the end of the decade the *Vibroseis system* was introduced; this is a vibrating or striking mass system with which it is possible to generate the waves necessary for seismic surveys, without having to resort to the detonation of explosive charges in the subsoil.

A definite improvement of knowledge of the characteristics of the subsoil and of formation fluids came about with the introduction of geophysical well logging, conceived by the brothers Conrad and Marcel Schlumberger in the early Twentieth century. This was when geophysics was just beginning to develop and the first applications of magnetic and gravimetric methods were being studied to investigate the internal structure of the Earth. The idea of Conrad Schlumberger, at the time professor of Physics at the École des mines in Paris, was that measurement of the electrical conductivity of rocks could be adequately used to study the form of mineral deposits. The first experiments, conducted in 1911 in Caen, in France, and aimed at mapping equipotential curves in an aquifer, confirmed that these measurements were not only able to detect metalliferous deposits, but also to reveal the form of the structures of the subsoil. The basic technique consists of lowering special instruments down the well, which reveal the easily measurable physical characteristics of the traversed layers and transmit these by cable to the surface, the data then being processed with appropriate calculation models. In 1921, Marcel Schlumberger carried out measurements of electrical resistance in a hole 820 metres deep, to verify whether such measurements were able to assist in the interpretation of surface seismic measurements. Soon it was realized that the interpretation of measurements of this type was extremely precious for investigating the characteristics of the rocks and fluids in the subsoil, and in fact, for this purpose, the Schlumberger brothers founded the Société de Prospection Électrique. The first geophysical measurement made inside an oil well was recorded in 1927 by Henry Doll in a 500 m deep well in the Pechelbronn field in Alsace, using a technique for measuring resistance developed by the Schlumbergers. Obviously, this first equipment was rather rudimentary, but nevertheless measurements were carried out at intervals of 1 m along the well profile.

At the end of the 1920s electric logs were already being used in Venezuela, in the USSR and in the East Indies; in the United States they were used for the first time in 1932 by Shell in California. In the mid-1930s there were already 12 teams operating in the various continents using the Schlumberger method; in 1934 the Schlumberger brothers founded an important subsurface prospecting enterprise, the

Schlumberger Well Surveying Corporation
(later Schlumberger Well Services, and even later the Schlumberger Wireline & Testing Corporation).

Downhole geophysical measurements soon started to expand and to become specialized: the first spontaneous potential log was recorded in 1931, while in 1938 came the first radioactive neutron log, designed by R.E. Fearon and perfected in 1941 by Bruno Pontecorvo. In the 1940s there was a decisive turning point in the field of log interpretation, a discipline that from being purely qualitative started to be also quantitative. In 1941 G.E. Archie published a famous paper, *The electrical resistivity log as an aid in determining some reservoir characteristics*, in which he analyzed the relationships between electrical resistance and water saturation of the formations, starting a fruitful field of research on the analysis of logs for calculating the basic properties of hydrocarbon reservoirs, such as porosity, permeability, saturation, etc. (Archie, 1941).

Drilling control and the integrated study of reservoirs (the post Second World War period and modern technologies)

By the early 1940s, research in the petroleum industry was gradually extended from public research agencies to private companies and to university laboratories. Furthermore, by the 1930s both the oil companies and the companies supplying goods and services were convinced that progress and the development of the petroleum industry were closely linked with the development of technology. Moreover, they were convinced that technology could be developed only with research and that, in view of the ever greater complexity of the problems and of knowledge, such research could be conducted effectively and in a competitive manner only by strong, numerous research groups, formed by specialists in various fields, and could certainly no longer be developed by individual experts, as had been done hitherto. For this reason, as of the end of the Second World War it is very difficult to connect each new basic research project or the development of a new technology to a single researcher, as the majority of studies were assigned to complex research groups, often very numerous. Moreover, more and more often progress in the scientific and technical field was protected by industrial patents owned by small or large companies, which thanks to them became successful on the market and were to make their commercial fortune.

Well engineering

From the 1950s onwards, rotary drill rigs have been increasingly improved, both regarding the automation of the various components, as well as in terms of modularity and ease of transport (for example, in mobile rigs derricks were replaced by reticular structures called *masts*, which were easier to transport). Steam engines, used until the 1940s, were replaced by internal combustion engines (diesel or gas), coupled with the main users (mud pumps, hoists and rotary tables) via mechanical transmission systems with gears and clutch (compound), subsequently substituted by electric transmission systems. The latter were first driven by direct current (with Ward-Leonard type regulation) and afterwards by alternating current (with silicon rectifiers or with the modern frequency converters, to make them more flexible to use and to set up on the worksite).

In this period, the continuous search for new fields made it necessary to drill deeper and deeper wells. In 1947 the depth of 4,500 m, already reached in 1938, was exceeded and two years later, in 1949, the depth of 6,000 m was also surpassed. This record was unbeaten until 1958, in which year a well was drilled to a depth of 7,700 m in Texas. In the 1960s and 1970s, there was a veritable rush to drill deeper and deeper wells: the 9,000 m threshold was passed in 1974 in Oklahoma with the Bertha-Rogers 1 well of 9,580 m. Following this, apart from experimental boreholes for geological and geophysical exploration (such as the in the Kola Peninsula, in Russia, which reached a depth of 12,260 m, and the KTB, Kontinentales TiefBohrprogramm) around Bayreuth in Bavaria, of 9,100 m), the deepest commercial oil well – the one at Wytch Farm, M11 – was drilled in England in 1998, with an extended horizontal path, which reached the measured depth of 10,650 m.

At the end of the 1940s, important technology was developed, when the Soviet Matvej Alkumovich Kapeljushnokov produced an original tool to be applied in rotary drilling with a hydraulic turbine (turbodrill), which remained practically unknown in the West until the early 1950s. The turbodrill, perfected and tested by Yakov A. Gelfgat of the Moscow Institute of Drilling Research, revolutionized the rotary technique, making it less dependent on the surface equipment. With this technology, the rotating movement of the bit is generated at the bottom of the drill string, directly over the bit, and thus drilling can go on even in the absence of any rotation of the string.

Simultaneously, Soviet technicians studied a different type of bottomhole motor, trying to adapt a high-power electric motor to the restricted geometry of the drill string. However, the great technical difficulties and that of reliability, linked to the possible methods of supplying electric motors, limited applications just to experimental type rigs, and the technology never reached commercial level. In the West, drilling with downhole motors gradually came back into use and a different type of downhole motor was developed, of hydraulic type. Onwards from the end of the 1950s, the study was resumed of a hydraulic machine already known at the beginning of the Twentieth century, the progressive cavity (or positive displacement) pump (otherwise called the *Moineau pump*, from the name of its inventor René Moineau, 1930). This machine, made to operate as a motor, i.e. feeding pressure to get torque at the drive shaft, can well be used as a volumetric power motor, adequate for drilling requirements. Currently downhole motors of this type (the already mentioned PDM) are used everywhere, and are indispensable in directional and horizontal drilling.

In the field of rotary drilling, a further innovation was the introduction of the top drive (power swivel), which enabled the rotary table to be eliminated. The first fully hydraulic string rotation tool was already produced in 1953, but it was not until the 1980s that the majority of the new drill rigs were fitted with a top drive (driven by a hydraulic or an electric motor). The top drive provides numerous advantages, both operative, in terms of safety and speed of operations, as well as of size, enabling the Kelly, the rotary table and the swivel to be eliminated, freeing the rig floor of many items of equipment. The top drive, together with downhole motors, represents the most significant evolution for oil drilling rigs in the last fifty years and probably the next step will be in the direction of rigs fully controlled by oleodynamic or pneumatic systems.

As far as directional drilling is concerned, the development of downhole motors, together with the theoretical and applied studies on the behaviour of the drill string subject to compression, conducted by Arthur Lubinski towards the middle of the 1950s, led to the development of extremely sophisticated and precise techniques. The control of the well path was performed by precision tools for the measurement of gradient and direction of the hole, with many electronic components, leading in the latter half of the 1980s to the introduction of a revolutionary system of measurement and control of the drill path in real time. This was the MWD (Measurement While Drilling) system, very soon coming into common use in all directional drilling, generating a continuous and rapid refinement of the methods, the precision and the technology used, as well as reducing service costs. The control method includes telemetric recording, through the mud pumped into the hole, of pressure impulses generated by a device placed inside the string, close to the bottom of the hole, which measures the angle and the direction of the hole in real time by means of solid-state electronic components.

In the first half of the 1980s, moreover, innovative methods were developed for directional drilling, combining with the MWD system, a particular PDM-type of bottomhole motor, appropriately tilted, such as the *Steerable* systems developed in 1984 by the Norton Christensen company. These systems are able to carry out the entire directional path (including any course corrections on the horizontal plane) without having to trip-out to change the geometry and the rigidity of the drill string. The advantage, apart from improved path control, resides in saved rig time, something that has become particularly sensitive in the last few decades (at present the rates for hiring large offshore drill rigs can exceed € 200,000 per day). In the 1990s, the finalizing of special systems to record certain logs in the drilling phase (called LWD, or Logging While Drilling, see below) contributed to the development of innovative systems of combined measurement, commonly called *Geosteering*. These are applied in directional drilling which, together with the possibility of guiding the well path in real time, conducts a series of measurements near the bit, making it possible to drill directional wells no longer solely on the basis of the geometrical path defined in the design stage, but following the targets on the basis of the geometrical and lithological data acquired instantaneously. These systems have now been further improved, with the introduction of Steerable motors, fitted with expandable stabilizers which allow extremely precise control of the path (automatic control of the well path) and may also be used for drilling almost perfectly vertical wells (system for verticality well control), useful in making modern hole configurations known as *slim profiles*.

As already mentioned, oil-based drilling fluids became more common from the 1950s onwards; these were devised for drilling the reservoir, as they do not damage the oil-bearing formations. Muds able to stand high temperatures were then introduced, or ones that could tolerate strong salt water contamination, or that of large volumes of drilled clay, while the specialization of additives such as lignosulphonates and polymers, for the stabilization of rheological properties, became accentuated. Furthermore, drilling systems using gas, air, foams and aerated muds were developed; these being useful for drilling through layers with abnormally low pressure and for geothermal drilling. At the end of the 1970s, with increased sensitivity towards problems of safeguarding health and the environment, in the choice of drilling fluids, environmental problems were taken into consideration, as well as those of cost and performance. Therefore, from the 1990s onwards, muds with a mineral or synthetic oil base, and, in general, those with a base of environment-friendly liquids of low toxicity, have been studied.

Regarding developments in drilling tools, it is recalled that in the 1950s the theoretical foundations were laid for the hydraulic optimization of drilling. Following this, roller bits were modified with the introduction of calibrated nozzles to force the drilling fluid out at high speed (jet circulation) so as to keep the cutting structure clean and increase the penetration rate (Nolley *et al.*, 1948; Bielstein and Cannon, 1950). Also in this sector, laboratory systems were devised to simulate drilling conditions with small-scale rigs which, combined with the theoretical and practical development of rock mechanics, enabled many phenomena regulating drilling to be understood, such as, for example, the differential pressure connected with the penetration rate (Cunningham and Eenink, 1959; Garnier and van Lingen, 1959).

In 1951 the first carbide insert roller bits or TCI bits (bits with Tungsten Carbide Inserts) were introduced, able to drill hard, abrasive formations, with limited wear and tear of the tool, and in the 1970s the first experiments were conducted using sealed bearing bits, first with roller bearings and then with friction bearings.

Bit technology reached a turning point in the early 1970s, when a new type of material was tried out, called PDC (Polycrystalline Diamond Compact). This new material, far more resistant to abrasion than tungsten carbide, made it possible to produce fixed-blade monobloc bits on which small cutting cylinders of PDC are mounted. The first PDC bits immediately proved that they could compete with roller bits due above all to their intrinsic reliability, since they have no moving parts (which can wear out, become loose and remain at the bottom of the hole) and thus could be coupled with bottomhole motors. From the mid-1990s onwards, PDC bits have been a valid alternative to roller bits, and currently they are the type most commonly used in the drilling industry. Experiments have since been conducted on new materials – always using synthetic diamonds – such as TSP (Thermally Stable Polycrystalline diamond) and cutters with an impregnated diamond matrix.

Numerous improvements have been made in recent decades in the evolution of well completion techniques. After the Second World War, in addition to steel bullets for perforating the casing, shaped charges were used, able to perforate even a number of concentric casings. This technology is still the one most widely used, and has been improved with the design of perforating guns able to contain a high charge density with precise angular separations. Then, from the end of the 1950s onwards, to reduce damage to the formation, the technique of casing perforation in *underbalanced* condition was finalized.

In the case of a well penetrating a number of mineralized layers containing fluids which are not mutually compatible (either because of their different composition, or due to their different physical or chemical characteristics), production can be obtained by separating the various layers with appropriate packers which seal the casing-tubing annular space and by equipping the tubing with valves able to be opened at the surface. This makes it possible to bring productive layers into production in a selective manner, in accordance with programmes drawn up on the basis of reservoir studies. In the early 1950s (and perhaps even earlier) multiple completion came into use, permitting the simultaneous production of a number of layers, leading to the development of ever more sophisticated packers in terms of design and materials used as well as setting technique. From the 1980s onwards, the term *completion* has come to indicate no longer the mere installation of hydraulic insulation devices and tubing, but the optimizing of well production, including numerous technologies to limit sand production from productive layers.

Finally, at the beginning of the 1990s, wells were drilled with a number of sub-horizontal branches (multibranch or multilateral wells) enabling production to be improved in the presence of multiple thin oil-bearing layers. The productive zones of these wells are often difficult to complete, and the relevant technique is in the process of rapid evolution.

Lastly, to increase the permeability around the well, various techniques have been developed. On the one hand, matrix stimulation techniques or the injection of acid solutions into the formation, and on the other hand various new methodologies of hydraulic fracturing (Clark, 1949; Clark *et al.*, 1952). The main improvements have been in the field of developing fracturing fluids, to obtain longer and larger fractures, additives to reduce losses of fluid in fractures, and techniques to make multiple fractures. As an interesting fact it is pointed out that in 1957, to increase the permeability of a gas field, nuclear energy was resorted to (Gasbuggy Project), but the gas produced was radioactive.

Still on the subject of well engineering, an important new contribution to drilling came with the technique of horizontal drilling, developed commercially in the last two decades of the Twentieth century, used to increase well productivity and the recovery factor, thanks to an increase in the drainage area. This is employed above all in fractured formations and in discontinuous reservoirs or ones of small thickness.

The first technological developments relating to the drilling of horizontal wells took place at the beginning of the 1940s, when John Eastman and John Zublin perfected short-radius equipment for increasing the productivity of some wells in California, which in some way anticipating the modern technology of multilateral wells. This equipment, basically flexible extra-heavy pipes with hinged joints able to rotate, could drill paths with radii of curvature of between 60 and 100 m, with horizontal sections up to 150 m long, and they enabled numerous lateral branches to be drilled in one and the same well, in a single formation, in various directions around the well. According to the United States Department of Energy (DOE), the first horizontal well was drilled at Texon (Texas) in 1929, followed in 1937 by the Yarega well in the USSR. In the 1950s, again in the USSR, more than 40 horizontal wells were drilled, but then this technique was abandoned, as with the technique of the time it was deemed too costly compared with the productive benefits resulting from it. A certain success was obtained – once more in the USSR – also by a number of multi-branch wells, drilled with a technique developed by Alexander Grygorian, foreseeing the use of bottomhole turbines; the first well was drilled in the Bashkortostan field in 1953, followed by several others. In the mid-1960s horizontal drilling techniques were also developed in China, but there, too, the technique was considered anti-economical.

Only twenty years later, in the United States, further research in this field started. In the early 1980s, the evolution of numerical modelling of reservoirs brought out the effective nature of short-radius multilateral wells, which gave a further boost to trying out the industrial applications of this technology, and between 1979 and 1981, in New Mexico, twelve horizontal wells were successfully drilled. This experience led to the perfecting of the modern technique known as *medium radius* curvature (about 150 m), developed using bottomhole motors and the first MWD systems. The first horizontal well drilled with this technique was in 1985, and by the end of the decade in North America there were more than 300 wells of this type. Parallel experiments were being carried out also in Europe. In France in 1977 studies and projects were started which led in 1980 to the construction of a *long radius* horizontal well, with an inclination of 90°, drilled without the help of downhole motors, in the Lacq field (southern France). Following these technological successes, in 1982 the first offshore horizontal productive wells were drilled in Italy in the Rospo Mare field, in the southern Adriatic. In spite of these first positive results, the industry did not thoroughly develop the horizontal well technology until the ensuing decade, which was its real golden era, with more than 3,000 wells drilled in the United States alone (between 1990 and 1998).

Of great importance was also the development of modern systems of well workover and of drilling systems without the assistance of the classical rig, a technology known as *coiled tubing.* Conceived for war purposes in England, to lay a small-diameter pipe rapidly under the English Channel, in order to supply petrol (gasoline) to the Allied troops who were landing in Normandy (the PLUTO project: PipeLine Under The Ocean), it was subsequently developed industrially by Bowen together with California Oil and placed on the market in 1962 for the workover of productive wells. Following this the coiled tubing technology was considerably modified (at present there are several dozen companies supplying this service) and in 1990 Eastman Christensen also introduced it in the field of drilling. The drilling rig and the drill string are replaced by a continuous pipe a few inches in diameter, coiled round a drum a few metres in diameter. The pipe, which acts as a drill string, is unwound and rewound on the drum with the help of special systems of traction, which continuously limit and control its deformations. It is interesting to observe that in this technology, the steel of the pipe is subject to tensile forces that often exceed the limit of elastic deformation (yield point) of the steel. Mention is also made in this field of the recent applications of tubular material whose diameter can be expanded in the well (expandable tubular material), useful for resolving numerous technical problems concerning the complex architecture of modern wells.

To conclude, it is also worth mentioning the modern technology of *casing drilling*, in which the drill string is substituted by the casing itself which is used to line the well; in this way it is possible to achieve closer tolerances between the casings, as well as reducing the rig time for tripping the drillstring and the casing.

Offshore drilling

The first offshore well was drilled in 1897 from a pier near Santa Barbara, in California. In the attempt to follow a number of coastal fields continuing towards the open sea, it was thought on the one hand of constructing wells in the sea, positioning the rigs on strongly-built piers projecting into the sea for about a hundred metres, and on the other hand of drilling wells from the seashore, directed beyond the coastline.

In the first decades of the Twentieth century various wells were drilled in protected waters (for example, marshes, swamps, lagoons and bays in the Gulf of Mexico), placing the rigs on platforms or drilling barges which allowed drilling to take place in very few metres of water, with the hull of the vessel resting on the bottom. Towards the end of the 1940s offshore drilling began on an industrial scale, using platforms on piles embedded in the seabed or submersible bottle platforms which could be used as mobile drilling rigs. Subsequently, to limit the high costs necessary to built these submersible platforms, which were made larger and larger, self-elevating drilling platforms, commonly called jack-ups, were devised, able to stand with their legs on the bottom and to operate over several tens of metres of water depth. The first commercial *jack-up* entered service in 1954 and at present there are plants with 150 m long legs, capable of drilling in water depths of more than 100 m.

The need to drill in deeper and deeper waters led, at the end of the 1940s, to the development of the first drillships, converted hulls (usually old colliers, whalers or cruisers) in whose hold an opening was made over which to install the derrick with the relevant equipment. At the same time, from the end of the 1950s onwards, semi-submersible drilling rigs were developed; these consisted of a triangular, rectangular or pentagonal shaped platform connected with submerged hulls by means of large columns.

With the rigs standing on the seabed, the drilling technique is the same as that used in onshore rigs, and the wellhead is placed at the surface, whereas in drilling operations with floating rigs (drill ships or semi-submersibles), not rigidly connected with the seabed, the wellhead and the Blow Out Preventers are placed on the seabed and are connected with the drill rig by means of a special risers for the return of drilling fluids. Floating rigs are kept in position by means of hooring systems (at depths of down to a few hundred metres) or by means of dynamic positioning systems, through the thrust of impeller systems (first developed in 1961 with the famous *Mohole project*, which proposed drilling through the ocean crust for geophysical explorations up to water depths of 6,000 m). Currently, with these dynamic positioning systems, it is possible to drill in water depths of about 3,000 m.

In Europe, the first offshore well was drilled in 1959 in an oil field off Gela, in Sicily. In 1960 the development of gas fields started off the Ravenna coast, where the first European offshore gas well was drilled. In the early 1970s, the discovery of the big fields in the North Sea and in the Gulf of Mexico gave a final boost to the development of increasingly more refined technologies for exploration and production of offshore hydrocarbons. Fixed production platforms exist at present in depths of more than 350 m, whereas with floating production rigs the technological limit for the development and the production of an offshore field is in the region of 1,800 m water depth (in 1997 it was only 800 m). This limit is in a phase of rapid growth, as technological innovation in this sector is extremely active and numerous ‘marginal’ fields can therefore be brought into production, connecting them with existing platforms or utilizing Floating Production Storage and Offloading units (FPSO).

For this purpose, the development of subsea completions is a sort of flower in the buttonhole of hydrocarbon engineering, as the technologies concerned are extremely refined and among the most complex ones ever attempted by man. The first subsea completion was installed in 1961 in United States waters in the Gulf of Mexico (West Cameron Block 192), in 16 m of water. This was followed by other completion works in California (Conception field). Since then more than 1,100 wells have been completed, using the most varied technologies, and two-thirds of these are still in operation. In the 1960s the maximum depth in which subsea wellheads were installed never exceeded 190 m and TFL (Through Flow Line) technologies were developed, making it possible to send production control and regulation devices down to the bottomhole through the production lines. In this way well production could be managed in an optimal manner, eliminating costly workovers in deep waters.

In the 1970s and 1980s, the development of subsea completions essentially concerned the safety of fixed structures (some of them were embedded in the seabed) and systems that could be installed diverless (i.e. without divers), while the distance of wells isolated from the fixed platforms, and the laying depths (which at the end of the 1980s had reached 220 m), increased. In 1971 the first subsea completion was installed in the North Sea at a depth of 70 m (Ekofisk field). At present the North Sea has more than 40% of such completions, the most complex of which are installed in Norwegian waters. 1975 witnessed the construction of the first FPSO (Floating Production, Storage and Offloading) system, situated in the Argyll field, in the British sector of the North Sea, where the Buchan field was also developed in 1981, as well as the Balmoral field in a depth of more than 120 m in 1986. In the mid-1990s in the Norwegian sector the Snorre and Åsgard fields came into production, the latter being particularly difficult, including 59 subsea completions. In 1997 the Mensa field in the Gulf of Mexico was brought into production, situated 150 miles south-east of New Orleans (Canyon block 687), in deep waters, in which three satellite wells produced with a head pressure of 700 bar and sent the oil to a platform over 100 km away. That same year production also started in the Troika field, again in the Gulf of Mexico, with its wellhead located at a depth of 820 m. In the 1990s horizontal wellheads were introduced, and on these it is easier to carry out workovers and maintenance operations; and submarine completion systems were developed for high-pressure fields, which are now able to handle pressures in the region of 1,000 bar.

Since the end of the 1990s, the technological frontier of the development of subsea completions has shifted to the Brazilian offshore, where numerous record depths have been reached. In the Campos basin the first subsea completion was carried out in 1977 at a depth of 117 m, in the Enchova field, while in 1999 a wellhead in the Roncador field was laid at a depth of 1853 m. Again in the 1990, the development started of the multiphase pump technology operating at the seabed, often indispensable for conveying to the treatment plants the fluids produced at the wellhead of remote fields situated in deep waters.

Reservoir engineering and the developments of seismics and geophysics

The systemization and the mathematical studies of reservoir engineering started in the 1930s, continued in the period after the Second World War and could be considered almost completed by the beginning of the 1950s. Subsequent developments have been aimed at an ever more marked optimization of the various technologies towards their global, integrated management, with the use, in the field of reservoir study, of the numerical modelling that developed side by side the greater possibilities offered by automatic calculation.

The mass balance equation for bounded reservoirs and the method of calculating the water encroachment as proposed in 1949 by van Everdingen and by Hurst were further refined in the ensuing years in the case of the application of the mass balance equation to under-saturated oil deposits, also taking account of the compressibility of the porous matrix. Simplified methods were also proposed for computing oil and gas recovery (Welge, 1952).

In the 1950s the analytical and practical study of the behaviour of well pressure during well testing in a transitory regime was concluded thanks to the studies of C.C. Miller, A.B. Dyes and C.A. Hutchinson Jr. (Miller *et al.*, 1950) and D.R. Horner (Horner, 1951), and to the development of the methods of determining the average pressure in bounded reservoirs (Mattews *et al.*, 1954). Also, Darcy's empiric law, applied for over a century to the study of the flow of fluids in porous media, was theoretically justified by Marion King Hubbert in 1956, referring it to the basic theorems of hydrodynamics (Hubbert, 1956).

The optimization of well spacing and distribution, a more and more pressing problem for increasing the recovery factor, called for the study of the advance of oil displacement fronts by gas and above all by water. These studies were first tackled with the use of analog models, based on the formal analogy of water flow in porous media, according to Darcy's law, and of the flow of electricity in conductors, based on Ohm's law. For this purpose, two-dimensional analogue models of stationary flow were initially introduced, using blotting paper or gelatine, or electrolytic tanks. Later, more refined models were excogitated, with resistance networks (Muskat, 1949). Analog models with blotting paper or gelatine enabled the advance front of oil to be determined by measuring the rate of advance of the hydroxyl ions (OH^-) which, in the presence of an electrolyte with a phenolphthalein base, evidenced – at least as a first approximation – their advance in time, while in the electrolytic tanks and in the resistance network models the advance was calculated on the basis of the distribution of the electric potential. Electrolytic tanks or gelatine models were also produced to simulate the variation in permeability of productive layers, varying their thickness. The simulation of production problems, however, required the study of transitory flow which it was possible to simulate only with analog models with resistance networks and condensers (Paschkis, 1942). Gulf, one of the first companies to use these techniques, constructed complex models with water drive and with a partial gas cap.

While determination of the oil in place and forecasting of production, effected by applying the a-dimensional mass balance equation, consider the global reservoir and give the water encroachment as a radial or a linear flow in the aquifer, the analogue model permitted the discretization of the phenomenon and, therefore, also the local study of pressure distribution. Nevertheless, the analog model showed many limitations and was hardly flexible and very costly. To overcome these limitations, as soon as the development of digital (numeric) computers and their greater potential so permitted, instead of elaborating analog models, numeric models were used, based on the discretization of the differential equations that govern the flow of fluids in the reservoir, resolved with methods of finite differences, or finite elements, or else with other more and more sophisticated numeric methods developed over time. Numeric models immediately proved to be more effective, economical and flexible in terms of carrying out production forecasts, also called *simulations*, introduced at the beginning of the 1960s.

Within certain limits, defined by the precision with which the petro-physical characteristics of the reservoir and those of the fluids contained are known, calculation models can address problems of multiphase flow in two or three dimensions. This is to simulate the behaviour both of the reservoir, and of every single well, under various operative conditions (transitory flow, multiphase flow in heterogeneous porous media, etc.). The enormous economic interests linked with the improvement of production management, with their pressing demands for precision, have decisively contributed to the development of automatic computing instruments.

Numeric computers and the progress made in numeric computing have led to the decisive refinement of calculations. Initially, the limits were the capacity of the computer and its cost. Computers now have the capacity to tackle any practical problem, and the sole limits are the precision with which the input data are supplied (characteristics of the reservoirs and of the aquifers, properties of the fluids, laws governing the fluid flow, even multi-phase, and fluid behaviour with variations in pressure and temperature, etc.). After the first studies in the 1950s of W.A. Bruce, D.G. McCarty and J. Douglas Jr., relating to two-dimensional fluid flow (Bruce, 1952; McCarty and Barfield, 1958; Douglas Jr. 1959), in the 1960s saw those on three-dimensional multi-phase flow, mainly limited to the two cases of gas-liquid two-phase flow and gas-water-oil three-phase flow (Coats *et al.*, 1967; Briggs and Dixon, 1968), developed after this right up to the compositional models of the 1980s.

In the 1970s, in a period of high oil prices, a start was made on more complex technical studies, in an attempt to increase the oil recovery factor, known also as EOR (Enhanced Oil Recovery), such as miscible displacement, displacement of chemical substances, the injection of CO_2, stimulation with steam and/or hot water, and *in situ* combustion. Currently, recovery factors of 30-40% are regarded as more than good, and therefore more than half of the oil in place remains trapped in the pores underground and is not recovered. Hence, even small increases in the recovery factor of a reservoir make a strong impact on its economic management.

This research was developed both at theoretical level and with models in the laboratory, and, lastly, also carrying out certain field tests. The first pilot plant for the injection of miscible gas into a reservoir was started in the early 1950s, injecting propane, nitrogen and carbon dioxide, spaced by appropriate water cushions. In the 1970s, particular attention was devoted to recovery processes improved by the injection of chemical substances, such as polymer solutions or alkaline fluids containing micellar suspensions of polymers, both acting on the interfacial tension of the reservoir fluids. Generally speaking with this method, the increase in the recovery factor is produced by the decrease in interface tension between water and oil, which induces greater mobility of the oil in the reservoir. Lastly, systems of stimulation with the injection of steam (continuous or discontinuous) and the more economic method of *in situ* combustion, were also finalized, both these methods being fairly widespread in numerous deposits of highly viscous heavy oil (high temperature, in fact, causes the viscosity of the oil to diminish, accelerating its flow to the productive wells).

From the 1990s onwards – although some studies on the subject had already appeared in the 1970s – I. Grant and Y. Schildberg introduced the integrated study of the reservoir, known also as *reservoir management*, into industrial practice. This type of study incorporates and attempts to use, by integrating them, all the information and knowledge available (in particular of a geological and geophysical nature) to arrive at a detailed description of the reservoir, borne out by numeric models, on which to conduct the necessary engineering calculations and in every phase to optimize its exploitation; in the last few years, this approach has become increasingly more complex and inter-disciplinary (Grant *et al.*, 1990; Schildberg *et al.*, 1997).

Regarding the development of seismic exploration, the equipment for performing seismic surveys at sea with dedicated vessels started to be developed in the mid-1950s. The second revolution in the field of seismic surveys, after the introduction of solid-state electronic devices and of recording on magnetic tape, occurred in the early 1960s, with the advent of digital technology. In 1961 the Geophysical Services started to use the first field seismic instrumentation including a digital data recording system and a computer to process the data. The development of information technology and of the interpretation of seismic surveys took place alongside this. In 1963 IBM introduced its famous digital computers of the 360 series, marking the beginning of the commercial use of this new type of processing instrument. Thanks to the increased computing power, in the 1960s it was also possible to put three-dimensional seismic surveys into practice; they were already known and theoretically studied from the outset of this discipline's studies but had never been developed due to the difficulties linked with recording great masses of data, and the lack of adequate computing instruments for their interpretation. The first 3D seismic survey was carried out near Houston in 1967.

Meanwhile, the discipline of seismic surveys had been provided with numerous instruments for interpreting the data, including single-channel and multiple-channel processing, the techniques of deconvolution, migration, inversion, noise reduction, filtering, etc. In 1972, in the Bell Lake oil field (New Mexico), a powerful campaign of 3D seismic surveys was carried out, supported by six large American oil companies, which confirmed the revolutionary effectiveness of this technique in subsurface exploration (just one month was necessary to acquire the data, and two years for their processing). The 3D images produced by 3D seismic surveys supply, in fact, clearer and more accurate information than the traditional 2D seismic surveys. At present 3D seismic surveys, together with the continuous improvements made in the techniques of data acquisition, processing, interpretation and above all three-dimensional data display in special projection rooms, can supply not only precise structural details of the formations, but also stratigraphic information and direct indicators of the presence of hydrocarbons. Obviously, this technique was immediately adapted to the requirements of surveying at sea, and improved with OBC (Ocean Bottom Cable) techniques.

Among the most recent innovations in this field, two seismic-type technologies should be pointed out:

- Four-dimensional (4D) seismic surveys consisting of 3D seismic surveys repeated in time (which constitutes the fourth dimension), useful for monitoring the variations in the properties of the reservoir (velocity of the fluids, temperature, pressure, etc,) during its productive life, making it possible to optimize the pattern of the production or injection wells, to speed up the production capacity and improve the recovery factor.
- Crosswell seismic surveys, in which a signal is generated in a well and the propagation of the seismic waves inside another well is recorded. This is a system of extremely high resolution, the only one able to show in detail the presence of faults, discordances and stratigraphic limits, variations of porosity, systems of fractures etc.

Since the Second World War all the techniques of wellbore geophysical measurements have developed enormously. In 1940, an independent company in Oklahoma, Humble Oil, developed the *gamma ray log*, thanks to the researches of Wynn Howell and Alex Frosch, together with a research group at Tulsa, later called the Well Survey. In 1946 Doll finalized the *electromagnetic induction log* and in 1948 M.R.J. Wyllie produced the quantitative interpretation of the *spontaneous potential log*, while the first *sonic log* was recorded in 1954 by R.A. Broding and his collaborators, jointly with the *density log* introduced by Lane & Wells. Simultaneously, the Schlumberger Well Surveying Corporation introduced, between 1949 and 1951, the *microlog*, the *laterolog* and the *microlaterolog*. These measurements were further perfected in time by a growing number of researchers, and new techniques have been used to make the information more and more reliable; for example, in 1966 the *formation density log* was introduced; in 1963 the *dual induction laterolog*, in 1970 the *spectrometry gamma ray* (developed by Lane & Wells) and the *dual laterolog*, while magnetic resonance measurements, although studied for this purpose from the end of the 1950s (Brown and Fatt, 1959), only date from the 1990s.

The last two decades have witnessed the development of ever more sophisticated methods of well logging, aimed above all at the indirect acquisition of images of the hole and of estimates of the permeability of the formation, a problem in part still unresolved. At the same time, numerous methods have been developed for the recording and transmission of logs in real time, that is, acquired and transmitted to the surface in real time during drilling operations. These technologies, known as LWD, are gradually replacing the classical wireline measurements, carried out at the end of drilling of every single section of the well. In this way considerable rig time reductions are obtained and in better management of drilling operations, enabling the first basic assessments of the reservoir to be made as soon as it has been drilled.

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A century of downstream activities

The first experiments in refining crude oil were carried out in the second half of the Nineteenth century (Eni, 1962-71; *Petroleum* […], 1959). They consisted in rudimentary separation by evaporation in retorts loaned from coal technology. The activity of such refineries is known in many parts of the world, from Mexico to Borneo, from Italy to Romania and from Russia to Curaçao. But the origin of the present downstream sector should more appropriately be linked to the activities developed in the United States in the first decade of the Twentieth century. Starting from these activities, the evolution of the main refinery processes and products up until the beginning of the Twenty-first century will be described below, from a broadly speaking chronological standpoint.

Desalting of crude oil

In the deposit, crude oil is almost always in contact with water which is to some extent salty, in a dispersed state or as an emulsion. Part of this water is eliminated before the crude reaches the refinery, while a more stable, emulsified, part has to be eliminated in the refinery before starting the distillation of the crude, as the salts dissolved in it are problematic in the plants, being deposited on the heated surfaces. Moreover, some chlorides become decomposed at the temperature of the processes, producing hydrogen chloride, which is corrosive for the plant parts. In the crude tanks in the refinery, part of the water may already separate spontaneously and then settle, and can therefore be discharged through the bottom outlet. This is not however sufficient to eliminate all the water present in the crude to begin processing. In relation to the quality and the provenance of the crude, the water will be more or less saline (the salts most commonly present are sodium, calcium and magnesium chlorides). For this reason the first process to which the crude is subjected in refineries is *desalting*, and to achieve it various methods have been applied: washing (dilution with fresh water and decantation or filtration); heating under moderate pressure and subsequent decantation; and treatment with chemical demulsifiers. As from the 1930s, the method that has progressively gained ground (and which is still applied) consists of diluting and heating the crude, and then treating it by means of an electric field. The crude is preheated in heat exchangers of the distillation unit, after which fresh water is added and a water-in-oil emulsion is formed, and is subsequently fed into the desalter, i.e. in a container under moderate pressure (5-10 bar) in which there is a high-voltage electrostatic field (10-30 kV). The water, which is separated by gravity, is discharged through the bottom outlet, while the desalted crude can be sent for distillation (Dunstan *et al.*, 1938-55, I; Eni, 1962-71).

Physical separation in the refinery: distillation and extraction with solvents

In the early days of the oil industry, the downstream sector essentially used physical separation processes based on the different boiling points of the components (distillation at atmospheric pressure for components not subject to thermal decomposition, distillation at reduced pressure for the residue). These processes were carried out in continuous flow plants, more or less like the distillation apparatuses of the same type invented (and patented) around 1880 by Alfred Nobel.

At the beginning of the Twentieth century, therefore, the processing of crude was limited to its fractional distillation, with the production of distillates (on average 10-12% between gasoline and kerosene or lamp oil) and of a residue (including everything left over after distillation). The most easily marketable and the most sold of these distillates was lamp oil, while gasoline was almost a ‘dead loss’, as the age of Henry Ford and of the great success of the motor car had not yet arrived. In those days it also happened that unscrupulous or dishonest dealers left part of the gasoline in the more remunerative lamp oil, which often led to accidents in offices and houses where it was used for lighting purposes.

However, by 1913 more than half a million automobiles were produced in the United States and the consumption of gasoline outstripped that of lamp oil (Remsberg and Higdon, 1994). Since at that time the requirements of the supplier were placed before those of the user, the quality of the gasoline was that determined by the quality of the crude, and as yet there was no talk of antiknock value or of the Octane Number (ON).

Distillation at atmospheric pressure was carried out in boiler plants: the preheated crude was introduced into the first of three or more boilers; from this the vapour of the light gasoline was led out at the head and was then condensed and possibly corrected; through an exchanger, the remainder went into the second boiler, from which the vapour of the subsequent fraction was let out, and so on, until a residue with a high boiling point was discharged (*Petroleum* […], 1959). Since the first experiments had already shown that it was not appropriate to apply a distillation temperature of more than approximately 400°C, because of the incipient thermal decomposition of the more sensitive molecules, the solution of conveying the residue from distillation at atmospheric pressure to a vacuum distillation plant (for example, 300 torr or less) and/or to distillation in a current of steam was quickly reached. In this way, one or two gas oils could be obtained and/or in the most favourable cases, depending on the quality of the crude, a base for lubricating oils. The 'residue of the residue' was destined for use as fuel oil, as an alternative to coal (ACS, 1951; Lucas, 2000).

After the plants with a number of boilers and a number of distillation columns, significant progress was made by carrying out the distillation in a single column (subsequently improved and substantially unified in what is still called the 'topping' process): the preheated crude was introduced through the top of the column where it partly evaporated. The residue was discharged through the bottom outlet and the distillate conveyed to a series of fractionating columns, each of which condensed an intermediate distillate, and from the last column the gasoline fraction was recovered (ACS, 1951). The progressive refinement of distillation technologies was also helped by the progress achieved in the materials used for constructing the plants and by the development of the connected equipment (furnaces and exchangers, pumps, valves, etc.).

The development of distillation theory did not precede its practical application, but rather accompanied it. The first studies on multi-component systems, of great interest for the petroleum industry, in fact date from the 1920s and 1930s. In 1925, for example, after the mathematical studies in 1922 by Warren Kendall Lewis applied to the design of fractionating columns, Warren Lee McCabe and E.W. Thiele presented a paper to the American Chemical Society, describing a new method for calculating the number of trays theoretically necessary for the separation of the components of a binary mixture in a rectification column. The contribution of McCabe was a great stride forward in the scientific design of distillation units up to 1936, when the new cracking systems came to the forefront.

The modern method of the primary (Straight-Run; SR) distillation of crude is based on a column with trays, first using 'bubble cap' contact devices and then, since the 1950s, using 'valve' devices, thereafter repeatedly modified in design. In many cases it was preceded by a head pre-evaporator column, provided with as many strippers as the fractions separated and leading off from the main column (Hengstebeck, 1959; Noel, 1959; Normand, 1963; Wuithier, 1965; Borza, 1993; Lucas, 2000; IFP, 1995-2002). Once preheated, the crude usually enters the column about one-third up its height; the fractions of the crude topping plant are the head gases – known as 'incondensibles' – followed by C_3-C_4 (LPG, Liquefied Petroleum Gas), by one or more fractions of C_{5+} (light gasoline and feed for reforming), kerosene and/or jet fuel, one or more gas oils, in relation to the connected plants (desulphurization, etc.), and residue. The latter can be sent to the vacuum distillation unit, and the resulting distillate (vacuum gas oil) can be suitable for the processing of lubricants. In its turn this 'vacuum residue' can be treated to obtain bitumen, or sent to the $CO+H_2$ gasification unit.

The early refiners realized that the crude could be treated not only on the basis of the boiling points of its components, but also according to the chemical groups that it contained. The application to oil of extraction with solvents, especially for separating aromatic hydrocarbons from the aliphatic compounds, probably started in this way. Much later, the quality of the crude lost part of its importance with respect to the applicability of the processing systems.

Extraction with solvents came to be used in the refinery very early on (between 1910 and 1925), above all for the production of base oils for lubricants from residues and heavy gas oils – eliminating entirely or to a large extent the asphaltic and aromatic part – but also for improving the medium and the heavy distillates. The first process chronologically speaking, due to Lazar Edeleanu in 1907, was extraction with liquid SO_2 (BP, 1958; Shell, 1980), applied first so as to remove the aromatic hydrocarbons from kerosene in order to diminish smokiness in lamps, and then to produce white oils and lubricants from gas oil and from the residues. Very soon after this came processes with liquid solvents at room pressure and temperature, less problematic in terms of corrosivity and difficulty of handling (phenol 1908, nitrobenzene, furfural 1925, dichloroethyl ether or Chlorex 1934), and then with mixed solvents (propane-phenol-cresylic acid or Selecto 1933; Dunstan *et al.*, 1938-55). Extraction with solvents also used innovative apparatus, such as, for example, rotating extractors RDC (Rotating Disc Contactors), patented in the United States by W.J. Podbielniak.

The need to increase the yield of gasoline as opposed to the part of the crude having a higher boiling point or which could not even be distilled acted as a stimulus to operators in the petroleum industry, and in this way thermal cracking came into being. The chemical expertise on which this process was based had, however, already been acquired.

The chemistry of the downstream sector

In so far as the kinetics of the reactions are concerned, in 1889 the physical chemist Svante August Arrhenius (1859-1927) had already formulated the law that bears his name, that is: $k=Ae^{-E/RT}$, where k is the constant or coefficient of the reaction rate, A is the frequency factor, E is the activation energy, R is the universal constant of gases and T is the thermodynamic temperature.

But, more generally, at the moment of development of the downstream industry, chemical knowledge or, in a broader sense, the necessary scientific foundations were already all available. In fact, it was sufficient to have a few notions of thermochemistry and of thermodynamics, general notions of organic chemistry, and little else, to lay the foundations for a good level of technological development. After this, downstream activities received increasing impetus from the know-how of the operators or the specialists. Lastly, it is evident that, also and above all in the passage from basic scientific knowledge to large-scale industrial successes, the history of the downstream sector has abundant confirmations of the fact that without research there is no real innovation. In 1924, T.A. Boyd had already observed that no other industry of the dimensions and the importance of the oil industry was based on such a great amount of fundamental chemical knowledge (ACS, 1951).

Many basic research results by universities and research centres laid the foundations for the practical developments in the industry, the most significant of which have been due to researchers of United States companies dedicated to research as their institutional objective (such as, for example, UOP, Houdry, Hydrocarbon Research, Lubrizol, Octel, etc.) as well as the big multinational corporations (BP, Esso, Mobil, Shell, Sinclair, etc.). The latter dedicated considerable resources to their units engaged in scientific research. Among the foremost chemists who have contributed towards developing basic knowledge and to applications of the science of hydrocarbons, the following should be noted: Vladimir Nicolaevi Ipatieff, Gustaf Egloff and Herman Pines, who produced hundreds of publications and patents, above all on the subject of catalytic processes and reactions.

Chemical treatments have been used from the very start of the refining industry, for instance with solutions of sodium hydroxide or with sulphuric acid, to eliminate impurities such as hydrogen sulphide and the mercaptans (from gasoline and from kerosene) or with oxidizing treatments using sodium plumbite or with sodium hypochlorite (sweetening process), to transform them into less disagreeable substances, for example to transform mercaptans into disulphides. Later, the importance of such treatments diminished to a certain extent for environmental reasons, given the difficulty and the cost of disposing of their residues.

Chemical compounds and mixtures of them have been used to eliminate groups of objectionable substances from fuels and lubricants. Chemistry entered the refinery also through the introduction of additives (often supplied by external business-to-business companies): scale removers for boilers and heating circuits; cleaning agents for reservoirs; additives for improving performance in relation to the particular uses of the products, especially of gasoline (antiknock additives, surfactants, antioxidants, deactivating substances for metals, anticorrosive and antistatic additives) but also of diesel fuel for motor vehicles (pro-cetane, flow point reducers, scale removers, detergents-dispersants, smoke preventers), of heating gas oil (flow point reducers, anti-foamers), or of lubricating oils (detergents, viscosity improvers, oiliness improvers, inhibitors, thickeners, anti-wear agents; Owen, 1989).

Thermal cracking

Thanks to the advent of the automobile and of electric lighting, the production of gasoline as a fuel became a priority in comparison with lamp oil (or kerosene) and an earlier hypothesis of ‘breaking’ by thermal means the chain of the heavier hydrocarbons, in order to obtain lighter fractions, i.e. ones having a shorter chain, became topical again.

From the very earliest days of modern chemistry, for that matter, it was ascertained that by heating any substance or material at an increasing temperature, the bonds between the atoms forming the molecules (or the macromolecules) break up, forming pieces – later called ‘radicals’ – in their turn liable to recombine forming other molecules. The first process based on a number of chemical reactions of hydrocarbons and of other components of crude, therefore, could not have taken place except by thermal cracking, the first plant for which was patented and constructed in 1891 in Russia.

In 1913, the chemist William M. Burton (1865-1964) of the Standard Oil Company of Indiana and manager of the refinery at Whiting (Indiana), after a series of difficult experiments with pilot plants, constructed a commercial plant for increasing the yield of gasoline from the distillates having the highest boiling points. The process consisted of heating the feed (a gas oil) in a steel boiler under moderate pressure, in that way obtaining a product able to contain up to 50% of boiling hydrocarbons in the field of gasoline distillation and thereby almost doubling the yield in gasoline from a crude. Obviously, being a rather drastic process, the composition of the gasoline obtained by cracking was very different from that of the first distillation. Moreover, and this might seem strange today, Burton’s boiler was heated by burning coal (*Petroleum* […], 1959).

Meanwhile, other protagonists entered the scene, including Jesse A. Dubbs (1855-?) and above all his son Carbon Petroleum Dubbs (1881-1962). The Dubbses were businessmen with interests in the production of bitumen, and the father, in 1909, had invented a process to demulsify a heavy Californian crude oil from such stable and viscous emulsions that they prevented the separation of the water and hence the processing of the same crude. The process consisted of heating the crude in a coil furnace, under moderate pressure, followed by evaporation and condensation of water together with light fractions, with a final residue of fuel oil. The process caught on, but subsequent events brought about the economic collapse of the Dubbses and of their companies.

The process whereby Dubbs Senior demulsified crude had some analogies with thermal cracking, to the point that a clever and crafty lawyer, Frank L. Belknap, alleged that Burton had violated Dubbs Senior’s patent, predating by three years the one for the process applied in the Whiting refinery. The controversy ended with an agreement: Dubbs Senior surrendered his patents to the Standard Oil Company of Indiana with adequate compensation (after which he continued his laboratory research). Within the very complicated framework of the claim, Belknap involved Jonathan Ogden Armour, the canned meat king, who was starting to be interested in investments in the field of bitumen and oil. In conclusion, the Dubbses benefited from this involvement, to the extent that when it was decided in 1914 to found the National Hydrocarbon Company (which in 1915 took the name of the Universal Oil Products Company, UOP), 300 of the 1,000 shares in its capital were assigned to Dubbs Senior (Remsberg and Higdon, 1994).

Gasoline obtained by cracking was not immediately successful: it was yellow instead of colourless like SR gasoline, it gave off a nasty smell and it was unstable, as part of the unsaturated hydrocarbons constituting it tended to react by forming rubbery substances. Cracking gasoline was sold at a lower price than that of SR gasoline. Considered in the light of present-day knowledge, the two processes differ considerably and it seems odd to say the least, that it was possible to deem the Dubbses right and to have penalized Burton. Among other things, the reactors patented were different: the Dubbs one was tubular, and thus different from Burton’s ‘boiler’ type.

Obviously, it was already known that by heating oil fractions with a high boiling point, or the crude oil itself, to above 450-500°C, the larger molecules decompose also forming hydrogen, methane and hydrocarbons that boil in the temperature interval of the distillation of the gasolines. This is due to radical reactions of pyrolysis of the C—C bonds, of dehydrogenation and of recombination of the hydrocarbon radicals as unsaturated compounds, as well as of desulphurization. All of which, as stated, formed part of the prior store of knowledge earlier elaborated by chemistry.

Very soon it was ascertained that the process parameters characterizing thermal cracking are temperature and residence time, while pressure is less decisive (in the industrial versions it was limited from the equivalent of atmospheric pressure to one of just a few bar). From the early years of the second decade in the Twentieth century, after the Dubbses and Burton, numerous technologists and many companies proposed, patented and constructed processes variously modified both in their basic parameters (i.e. temperature, pressure and residence time) and in the structure of the plants (Eni, 1962-71). In fact, other thermal cracking processes were very shortly patented by an array of inventors: E.M. Clark, the brothers Walter M. and Roy Cross, Joseph H. Adams, R.C. Holmes and F.T. Manley. Finally industrial plants were constructed in several United States refineries (*Petroleum* […], 1959).

Among the subsequent developments in thermal cracking – as of the years just after the First World War – the most significant ones were visbreaking and coking, which are still used. The former consists of a moderate treatment of heavy gas oil or of the residues, to lower the viscosity and improve flow at low temperatures, while the second one is based on a very severe treatment to obtain coke as the main product, in addition to gases and distillates.

All these processes were stimulated by the necessity to use crudes of poor quality (with high viscosity and density, a high C/H ratio and a high content of compounds containing heteroatoms of oxygen, nitrogen and sulphur) and by the progressive loss of interest of the refineries and of the market in residual fuel oils, the demand for which was declining, causing their price to drop. In fact, fuel oil could not compete with coal for uses common to them both, such as thermoelectric plants and gasification (Kobe and McKetta, 1958-65). There was an opposite trend in the development of the production of diesel fuel especially in the early 1950s, when in the United States steam locomotives were progressively replaced by locomotives burning gas oil, and more and more trucks were produced with diesel engines instead of internal combustion engines (Otto cycle).

The quality of diesel fuel is one of the main factors of particulate emission, such as what are known as ‘fine particulate matter’. Determination of the relations between properties of diesel fuel and engine emissions is fundamental for the refining industry and for the automobile industry, as it determines the technological choices and the consequent investments.

Visbreaking has also been coupled with thermal cracking of heavy gas oil; coking, instead, has not found particularly numerous applications and has been used in various versions: *delayed coking* (with coke storage chambers), *contact coking* and *fluid coking*, with the sub-type *flexicoking*. In the last three versions the coke formed can be partly gasified in a special section of the plant.

Improvements of SR gasoline and of gasoline from thermal cracking

The quality of SR gasoline is linked to its combustion characteristics in spark-ignition combustion automobile engines (Otto cycle, 2 or 4 stroke). Hence, from the very beginning of the downstream industry, the need arose of improving it and adapting it in step with the progress made in engine design and construction. At this time, thermal cracking, apart from doubling the yield in gasoline from a given crude, already produced a better fuel than SR gasoline. The problem thus arose of improving SR gasoline, and this was resolved above all with combined processes of aromatization-isomerization of hydrocarbons (known as reforming, at first only thermal, then with catalysts). In 1920 Thomas Midgley observed considerable differences in combustion in internal-combustion engines with gasoline of different origin and provenance; the following year Harry Ralph Ricardo dealt with the antiknock power of gasoline, and Midgley and Boyd, in the General Motors research laboratories, proved the high antiknock effectiveness of certain substances such as lead tetraethyl, tin tetraethyl, selenium diethyl, tellurium diethyl and numerous xylidines. Research, proposals, discussions and diatribes followed as to the action mechanism of antiknock substances both in the United States (G.L. Clark and W.C. Thee), and in Great Britain (Hugh Longbourne Callendar, R.O. King), as well as in France (Henri Muraour) and in Italy (Raffaele Ariano).

Gasoline ‘ethylated’ with lead tetraethyl (*ethyl gas*) was introduced in the United States in 1923, but in 1925 its use was suspended by the health authorities due to the toxic nature of the additive; it was finally readmitted in 1926 with a limit on the concentration of the latter (Eni, 1962-71). The use of lead tetraethyl gained ground in Europe and in the rest of the world in the immediately ensuing years, followed by that of mixtures of lead tetraethyl and lead tetramethyl. In the 1950s to 1960s other antiknock additives were proposed, with alternating fortune, such as methylcyclopentadiene manganese tricarbonyl and tricresyl phosphate, which were especially used as coadjuvants of lead-alkyls. Furthermore, experiments were also made with numerous aromatic amines, which however, did not have any important applications (Eni, 1962-71).

In 1927, Graham Edgar proposed assessing antiknock power by determining the ON. In this case, it was not a question of a real measurement, but of the result of experimentally comparing the gasoline concerned and a mixture of isooctane (2,2,4-trimethylpentane) and *n*-heptane, that is with hydrocarbons attributed the ON of 100 and 0, respectively. This comparison was carried out in the well-known CFR (Cooperative Fuel Research) motor, still in use, consisting of a single-cylinder engine, at a constant number of revs and a variable compression ratio, under conditions defined by means of special standards (the Motor Method-MM, and, since 1936, the Research Method-RM). In the years 1931-34 W.G. Lovell and some of his collaborators in the Ethyl Corporation experimentally determined the knocking characteristics of numerous hydrocarbons, pure and added in sample gasoline (Dunstan *et al.*, 1938-55). In 1933, at the first World Petroleum Congress held in London, one of the themes in the downstream session was the assessment of knock in automotive and aircraft gasoline. Starting in 1937 the subject was intensely dealt with in the United States by NACA

(National Advisory Committee of Aeronautics), the forerunner of NASA (National Aeronautics and Space Administration), with the determination of the antiknock characteristics of hydrocarbons and ethers (including MTBE, methyl-*tert*-butyl-ether), as they are of interest for aircraft fuels.

Thermal reforming appeared in refineries shortly after the First World War, and catalytic reforming in the 1930s; the latter developed in parallel with catalysts, first natural ones (clay, bauxite, alumina) and then metal or metal oxide based on a support of alumina or silica-alumina (ACS, 1951). The first catalytic reforming was patented in the 1930s by Kellogg (hydroforming) and was applied in the United States during the Second World War, especially for producing gasoline at an extremely high ON for fighter planes and toluene for explosives. This process used a catalyst with a molybdenum oxide base (MoO_3) on alumina, in a fixed bed, and with a number of chambers in a cyclic system of reaction-regeneration of the same catalyst. A derived process is *fluid hydroforming* by Eger V. Murphree of Esso in 1950.

All catalytic reforming at that time derived from the purchase in 1929 by Standard Oil of New Jersey of the patent rights of the German I.G. Farbenindustrie to the hydrogenation of coal and refining processes, including catalytic reforming (*Petroleum* […], 1959). The reforming process with a bauxite catalyst, called *cycloversion*, was used as of 1943, above all for treating gasoline from cracking in order to obtain fractions at a high ON for aviation fuel for military use. As the conditions for the various versions of reforming are favourable to the transformation of distillates from C_7 to C_{10}, and less so to the increase of the ON of the head fraction of the reformed product, first the *n*-paraffins C_5-C_6 (with a low ON) were separated from the heads, after which the latter were isomerized by catalytic processes in the presence of hydrogen (*isomer*, *isosiv*, *penex* and others).

As mentioned, the two original rival processes of thermal cracking and the successive ones produced a fairly similar gasoline of the same poor quality, above all because of the relative abundance of unsaturated hydrocarbons – the cause of the formation of rubbers – and of evil-smelling and very reactive sulphur compounds. Over of the years, processes were started and made operative to improve the quality of this gasoline, with treatments on earths in the vapour phase, as in the *gray clay* process (1924), and to increase the quantity obtainable in the refinery. In fact, it was immediately evident that more gasoline could be obtained from thermal cracking than from first distillation, but that its poor quality, in particular its yellowish colour, would mean that it would have to be sold at very low prices, since in the early 1920s, for reasons of commercial acceptability, gasoline 'had to' be colourless and odourless. Only after the introduction of lead tetraethyl as antiknock additive, did the highly toxic nature of said additive induce the refineries in the most advanced states, from 1925 onwards, to colour the gasoline containing it (ACS, 1951).

Changes in the processes induced by catalysts

From the early 1930s, with the success of the transformation of light olefins obtained by cracking so as to produce good quality gasoline, the refineries quickly adopted the use of the catalytic processes first with polymerization and then with alkylation. Although thermal cracking and visbreaking remained among the most widespread refining processes (and in their most modern versions they still are) for a long time, precisely from the end of the 1920s cracking processes began to be developed using catalysts, the application of which in industrial plants marked another important stage in the development of downstream technology.

The application of catalysis to produce fuels by cracking medium-heavy petroleum fractions was tried out for the first time in France by an engineer, Eugène Jules Houdry (1892-1962) between 1925 and 1930, although his research on the production of synthetic gasoline by catalytic means from lignite date from the beginning of the 1920s. Houdry, in fact, carried out systematic research on the effect on the cracking of hundreds of catalysts and, in 1927, he achieved his first positive results. He had invested a large part of his personal fortune in this research, but soon the scale of the research became such as to require the plant engineering experience and the capital of a large company. Not finding any such support in France, Houdry emigrated to the United States where he was invited to move by H.F. Sheets of the Vacuum Oil Company with which, in 1931, he formed the Houdry Process Corporation. In that same year the Vacuum Oil Company merged with Standard Oil of New York, forming the Socony-Vacuum Oil Company (later the Mobil Oil Company). Houdry's process operated at 450-500°C, under moderate pressure, using an 'acid' catalyst with a silica-alumina base, on a fixed bed; the catalyst was rapidly covered by a carbonaceous deposit, which was burnt with air under controlled conditions. This was a cyclic catalytic 'reactions-regeneration' process favoured by the resistance of the catalyst (supported iron oxide) under both reaction and regeneration conditions.

It was clear right from the beginning that the Houdry process could be perfected as it was a semi-continuous process, and the 'threat' of this innovation was such that in 1938 a group was started up, called Catalytic Research Associates, which coordinated research efforts in the field of catalysis applied to cracking petroleum of such 'giants' as Standard Oil of Indiana, Standard Oil of New Jersey, Shell and Texaco. The group developed the important process with a fluid-bed catalyst, inspired by a patent of W.W. Odell in 1929 (*Petroleum* […], 1959).

The first industrial plants applying the Houdry process were built in the United States in 1937, but they were very soon surpassed by other versions based on the same premises. Nevertheless, the concept of 'catalytic cracking' in its various versions chalked up great success, to the extent that in 1937 in the United States the production of gasoline by cracking exceeded that of SR gasoline as the main automotive fuel (Remsberg and Higdon, 1994; Lucas, 2000). The Houdry Process Corporation developed the subsequent versions of the process (*thermofor*, *houdriflow* and *mobile-bed thermofor*), as well as more efficient synthesis catalysts than those of natural origin.

The first experts in catalytic cracking realized that the underlying chemical processes were quite different from those of thermal cracking (Kobe and McKetta, 1958-65), which also manifested itself in the different composition of the product, especially in its gaseous fractions (more C_3-C_4 instead of H_2-C_2) and in light gasoline (higher isoparaffins/*n*-paraffins ratio).

As a first approximation, the primary reactions of the main classes of hydrocarbons present in the input may be represented as follows:

paraffin → paraffin + olefin

alkylnaphthene → naphthene + olefin

alkylaromatic → aromatic + olefin

Research on catalytic cracking stretched over some decades, above all with broad-based experiments on pure hydrocarbons, and with interpretations of the results not altogether compatible with each other, due to the different structure of the hydrocarbons studied compared with the input of the refinery plants (heavy gas oil or the residue of various crudes). However, these interpretations were confirmed by subsequent experiments on fractions obtained from the inputs of the big plants.

Particularly significant was the research of Heinz Heinemann of the Houdry Process Corporation (and subsequently of Kellogg and of the Mobil Oil Corporation) on catalysis and petroleum; of Gustav Egloff and collaborators of UOP (from 1939) on the catalytic cracking of cetane and of cetene; of B.S. Greensfelder of Shell (1945-50) on the mechanism of the reactions of hydrocarbons in catalytic cracking; and of Pines (1945-1950) on the mechanism of the reactions of isomerization (ACS, 1951; Eni, 1962-71). In Germany, as far back as the 1920s, attempts were made to apply to bitumens, to tars and to the heavy residues of petroleum both the coal hydrogenation technologies started by Friedrich Bergius in 1913, and the process elaborated and patented by Franz Fischer and Hans Tropsch in 1922 for the conversion by synthesis of coal gases into hydrocarbons and alcohols, with partly satisfactory results, called the 'Fischer-Tropsch process' – or 'synthesis' – (F-T). The experiments conducted in the German plants of Gelsenberg, Wesseling, Scholven and Weinheim – damaged in the Second World War and repaired in 1949-50 – concerned distillation residues and the residues of cracking and of heavy crudes. The technologies applied in these plants – loaned from the experiments on fossil coals – differed in part from the current ones in the United States. With the joint participation between I.G. Farbenindustrie and Standard Oil of New Jersey and using technologies patented by the former concerning fuels, hydrogenation of oils, syntheses based on coal and on the gasification of coal, lignites, etc., the contracting companies jointly declared their intention of granting licences to third parties for the application of their processes, for the purpose of promoting the expansion of the world petroleum industry.

The conclusion, which is still considered valid, of the comparative research carried out on thermal and catalytic cracking is in keeping with the diversity of the main mechanism of the reactions, which is radical-based for the thermal process and ionic for the catalytic process, the latter mechanism being applicable to *n*-paraffins, to isoparaffins and also substantially to naphthenic and aromatic hydrocarbons. Other studies concerned olefins, well known to be absent in crudes but formed in all hydrocarbon cracking processes and hence in contact with the catalyst and undergoing a number of secondary reactions. In conclusion, the primary products of the processes being compared are very similar (apart from the composition of the gases), whereas in catalytic cracking the secondary reactions are more important, being induced by the various carbon ions (primary, secondary and tertiary) and by the reactivity of the olefins produced at the start of the reaction, in the presence of the strongly acid catalyst. Indeed, one of the chief aims of the research to improve the results of catalytic cracking was that of opposing the secondary reactions, which removed part of the gasoline produced and increased the yield in gas (Kobe and McKetta, 1958-65; Lovink and Pine, 1990).

Because of the repeated variants made in the United States to the industrial process as of the years 1940-42, the modern versions of catalytic cracking and the relevant plants differ considerably from the original ones. Designated as TCC (Thermofor Catalytic Cracking), FCC (Fluid Catalytic Cracking) and RFCC (Resid Fluid Catalytic Cracking), they operate with a mobile or fluid-bed catalyst.

A real revolution in catalysis applied in the refinery occurred as of 1956, with the introduction, first by Linde, of zeolites, then variously modified and associated with metals. These materials, selective with regard to the structure of hydrocarbons, very soon proved to be far more effective in terms of the yield in distillates of catalytic cracking processes and of the quality of the gasoline fraction (more ON points than those reached with traditional silica-alumina catalysts). The distribution of the products of cracking was progressively improved; also the management of the coke deposited on the catalyst was optimized, enabling plants to operate in a profitable manner. In modern FCC plants, with such catalysts, the contact between input and catalyst takes place in a riser-type reactor, which operates at temperatures of around 500°C or slightly higher, at a pressure of 2.5-3 bar, with a contact time of 2-4 s. The catalyst is separated from the cracked product and is sent to the regenerator where the coke deposited is burnt off in an air stream at about 650°C. The regenerated catalyst then returns to the cycle; the cracked product is conveyed to the fractionating section (distillation) from which the following are obtained: a gas that cannot be condensed or *fuel gas* (used as a fuel in the refinery), a C_3-C_4 fraction rich in unsaturated hydrocarbons, gasoline, one or two gas oils and a residue also containing particles of the catalyst (Borza, 1993; Lucas, 2000).

In the management of FCC plants with gas oils and/or residues containing sulphur as the inputs, a very serious problem arose, namely that of sulphur dioxide emissions (SO_x) by the gases discharged by the regenerator. To resolve this, as from the mid-1970s recourse was made to Sulphur Transfer Agents (STA) with a metal oxide base (Ogden, 1991).

The progress of the subsequent versions of catalytic cracking, in plant engineering as well as in catalysts, induced researchers of various institutes and companies, not only in the United States (Chevron, Mobil R&D, W.R. Grace & Company, Filtrol Corporation), but also in France (CNRS-Conseil National de la Recherche Scientifique and universities, IFP-Institut Français du Pétrole with Total), in the USSR (Doben process), Spain (CSIC-Consejo Superior de Investigaciones Cientificas), Holland (Shell, Akzo Nobel), Finland (Neste Oy), Austria (OMV-Österreichische Mineralölverwaltung Aktiengesellschaft) and elsewhere, to reiterate the studies on the behaviour of the single hydrocarbons, their mixes or selected inputs of different crudes (Lovink and Pine, 1990).

Hydrocracking, in different versions, is applied to heavy gas oil for the production of gasoline, jet fuel and diesel fuel, with a metal (palladium) catalyst, or with nickel and molybdenum or wolfram oxides on zeolite, nickel-wolfram sulphide. The plants are of traditional fixed-bed type and are called in various ways: *isocracking* (California Research/Chevron), *sovafining* (Socony Mobil), *unicracking* (Union Oil), *lomax* (UOP), and others. There is also a fluid-bed type known as H-Oil (Hydrocarbon Research). At the end of the 1950s only the isocracking and lomax plants had been applied practically in a number of United States refineries, while other isocracking ones were being designed. In the 1970s more than 60 industrial hydrocracking plants in various versions (isomax, unicracking, Shell, BP, etc.) were in operation, under construction or being designed.

All these processes have been used for different purposes, given that, in any case, the hydrogenation reactions, in the various conditions in which they occur, enable intermediate and/or improved products to be obtained, even from heavy inputs considered to be poor due to the presence of organic impurities (sulphur and nitrogen compounds) and minerals (such as nickel and vanadium; Lucas, 2000). The demand for hydrogen in these processes generally exceeds its availability from catalytic reforming plants, and so its production is necessary by way of regasification (usually the conversion of hydrocarbons with steam, known as *steam reforming*).

The gasoline reforming processes were also very soon modified by the advent of catalysis: a catalyst with a molybdenum oxide base (MoO_3) on alumina was already adopted in 1940 (Kobe and McKetta, 1958-65). Catalytic reforming, including aromatization reactions, made considerable quantities of hydrogen available to the refineries, which opened up the way to new processes of treating the inputs to the reforming units (hydrotreating), to remove sulphur, nitrogen and oxygen heteroatoms, which were in various ways harmful to the catalysts and to the quality of the gasolines.

The first improvement process for gasoline obtained by cracking (at first thermal cracking, then also catalytic cracking) was desulphuration, brought about by simple passage over adsorbent-catalytic masses of minerals (natural bauxite, clay, alumina). This was followed by HDS (Hydrogen DeSulphurization), on catalysts of various composition, and by isomerization of the head fractions (C_5-C_6). In parallel, laboratory studies were carried out on catalytic processes – subsequently successfully applied in industry – for the transformation of the condensable gas fractions (C_2-C_4) into components of gasoline, in particular the polymerization of the olefins and the alkylation of the paraffins with olefins (ACS, 1951; BP, 1958). In fact, the more volatile fractions in the cracking processes have an excellent ON, but are not suitable to be formulated directly in commercial gasoline, since they would increase its volatility beyond the specified limits.

Thermal polymerization – in reality limited to dimerization and to trimerization – of gaseous olefins to gasoline components was adopted in refineries in the early 1930s. Catalytic polymerization was patented in the United States in 1934 by Ipatieff and was immediately successful, first in a refinery of Shell (a company with shareholdings in UOP), and subsequently in other plants, but mainly in the United States (ACS, 1951). The process was partly abandoned in favour of alkylation, above all because of the higher yield of this reaction in fractions with high ONs, and the consequent enhancement of the gasoline formulated for marketing (BP, 1958).

The alkylation of paraffins is a reaction that combines an olefin from C_2 to C_5 with a paraffin, to form a branched paraffin with a higher boiling point than that at the outset. Applied to unsaturated hydrocarbons obtained by thermal or catalytic cracking, this reaction gives rise to gasoline components which improve both its ON and its susceptibility to lead tetraethyl. These reactions of polymerization and alkylation were studied and explained in 1938 by Frank C. Whitmore (ACS, 1951). The polymerization of the lower olefins was relaunched in the years 1976-77 with the Dimersal process (Yves Chauvin, IFP), applied in numerous plants, also for elaborating products of petrochemical *steam cracking* (Lucas, 2000).

Alkylation, in its specific application (Alkazid UOP process since 1940 and others) was obtained with acid catalysts, first with aluminium chloride-hydrogen chloride ($AlCl_3$-HCl) and then with sulphuric acid (H_2SO_4) or with hydrogen fluoride (HF) and carried out in numerous refineries worldwide. The success of the process with HF catalysts – very important during the Second World War for the air forces of the Allies, thanks to the aircraft fuel having an extremely high antiknock power that was produced – had initially to deal with the highly toxic nature of HF, tackled courageously by the researchers Aristide von Grosse and C.B. Linn of UOP, engaged in the first experimentation and on developing the process (Remsberg and Higdon, 1994).

In practice, exploiting alkylation in the refineries was limited to the alkylation of isobutane paraffin with the olefins propylene, butene, pentene and mixtures of them. Alkylation processes with ethylene were also developed, but had limited applications, as the alkylation of isobutane to 2,2-dimethylbutane (neohexane) and to 2,3-dimethylbutane (bi-isopropyl). The catalysts for all the refinery processes were supplied by numerous specialized firms, such as Davison, Humphrey & Glasgow, Johnson Matthey, Engelhard, Hershaw, Ketjen and Degussa (Aalund, 1984).

The use of platinum in the refinery

Although the catalytic properties of platinum (Pt) were very well known, its possible industrial applications were not taken into consideration because of its high cost. In fact, the use of this metal as a catalyst were looked into as far back as the beginning of the Nineteenth century by such important scientists as Jöns Jacob Berzelius, Humphry Davy and Michael Faraday. In the Twentieth century, an important contribution on the subject came from Russia, which was a large-scale producer of this precious metal. In this regard, the research of the organic chemist N.H. Zelinskij should be recalled. In 1922 he published a paper on the catalytic dehydrogenation of cyclohexane to benzene, with platinum/coal and nickel/alumina catalysts. At the time Zelinskij's results did not arouse any interest at industrial level, also because benzene was liberally available from the coal industry, whereas cyclohexane was a laboratory curiosity. It could at most be remarked, in the light of knowledge acquired later, that Zelinskij would have done better to support platinum on alumina rather than on coal.

Subsequently, research on the behaviour of hydrocarbons having a boiling point in the range of gasoline showed that metals of the platinum group (platinum, rhodium, iridium) were very effective in converting *n*-paraffins and naphthenes into isoparaffins and aromatic hydrocarbons, under conditions compatible with the requirements of the refining industry.

The process called platforming (finalized by UOP, see below) was the first use of platinum in the petroleum industry, which afterwards demanded greater and greater quantities of it, confirming the well-known argument that in the passage from productions and uses in the chemical industry itself, to those of energy, the order of magnitude of the systems and the materials used changes.

Although the original catalyst contained less than 1% of platinum, and those proposed subsequently had even less, catalytic reforming has become the most important user of this metal but not the most important consumer, as platinum is recovered from the exhausted catalyst to be reused in the new catalyst.

In the 1930s, in the USSR, experiments were conducted on the behaviour of numerous hydrocarbons from C_5 to C_{10} in the presence of catalysts having a metal and a metal oxides base (N.I. Shuikin, R.A. Kazanskij, A.F. Platé and others). Ipatieff, already mentioned several times, played a foremost role in affirming catalysis in the petroleum industry. Already famous in Tsarist Russia between the Nineteenth and the Twentieth centuries, after the 1917 Revolution he held prestigious posts including political ones. In 1930, in Berlin for the second World Energy Conference, he met Egloff who invited him to visit the UOP research laboratories in Chicago. It is actually most likely that Egloff had gone to the conference partly in order to recruit some leading researchers for UOP, of which he was research director. In fact, in addition to Ipatieff, he also persuaded Tropsch, already famous as the joint inventor of the celebrated Fischer-Tropsch reaction, to move to the United States (Tropsch, however, in 1935 returned to Germany, where he died shortly afterwards of a heart attack). Ipatieff, therefore, was taken on in the UOP laboratories and became a professor at Northwestern University. Other emigrants from the USSR to the United States in 1930 were the family of the young Vladimir Haensel, who in 1935 obtained his BS (Bachelor of Science) degree in Engineering precisely at Northwestern University, and then in 1937 his Master's degree in Chemical Engineering at MIT (Massachusetts Institute of Technology). Immediately taken on by UOP to work under Ipatieff on catalytic reactions of hydrocarbons, Haensel continued his studies at Northwestern University for a PhD in Chemistry, again with the guidance of Ipatieff.

In March 1949, UOP announced at a congress of the WPRA (Western Petroleum Refiners Association) the discovery and development of a new gasoline reforming process, in the presence of hydrogen and at a relatively moderate pressure (30-35 bar), using a bivalent acid platinum-alumina catalyst, baptized platforming by UOP, and patented by Haensel. The main reactions, which permitted a considerable increase in the ON of straight-run gasoline, are the aromatization of naphthenes and the dehydrocyclization, together with isomerization and partial hydrocracking, of the *n*-paraffins, and lastly partial desulphurization (ACS, 1951; Kobe and McKetta, 1958-65; Wuithier, 1965):

$$n\text{-}C_6H_{14} \rightarrow C_6H_6 + 4\ H_2$$

$$n\text{-}C_6H_{14} \rightarrow \text{cycle}C_5H_{10}\text{-}CH_3 \rightarrow C_6H_6 + 4\ H_2$$

$$CH_3C_2H_4SH + H_2 \rightarrow H_2S + CH_3CH_2CH_3$$

Characteristic of the original process – conducted in plants with three reactors in series, interspersed with furnaces and exchangers – was the separation between the main feedstock conversion reactions: in the first reactor chiefly the aromatization of the *n*-paraffins took place (a quick, endothermal reaction which produces hydrogen), while the outflow was taken up to the optimal temperature for the other reactions (isomerization and hydrocracking) carried out in the two following reactors.

The application of the new process was extremely rapid. In fact, six months later, at the Old Dutch Refinery situated in Michigan, a plant based on it came into operation. That refinery was followed by many others, to the extent that within ten years UOP had set up more than 100 platforming plants in the United States and abroad. UOP's striking success stimulated numerous petroleum and plant engineering companies so that within a year there was a proliferation of imitations and patents: Atlantic proposed *catforming* (U.S. patent of F.G. Ciapetta, in 1951) with two reactors in series instead of UOP's three and a catalyst of platinum on silica-alumina (water resistant) different from UOP's; the Houdry Process Corporation patented *houdriforming*, with a certain number of fixed-bed reactors and a catalyst of platinum on alumina, with the addition of silica in the form of silicon tetrachloride; Socony Mobil patented *TCR* (Thermofor Catalytic Reforming) with just a single reactor and a catalyst with a base of chromium and molybdenum oxides that could be regenerated *in situ* (ACS, 1951; Kobe and McKetta, 1958-65); and Standard Oil of Indiana patented *ultraforming*, at low pressure with cyclical regeneration. Soon after, more patents were taken out, and among them Esso's *powerforming* had a certain success, with a platinum catalyst and three reactors, plus a fourth one as stand-by, which made it possible to regenerate the catalyst by inserting and removing from the process one reactor at a time without having to stop the plant.

The proliferation of processes and plants was accompanied by research on the behaviour of single hydrocarbons under process conditions. In the early 1950s, researchers of the United States oil companies and of the firms owning patents – directly or through universities and laboratories of associated companies – tried out different feedstocks, especially in the presence of the 'proprietary' catalysts (platinum/alumina/halogen, molybdenum and chromium oxides, wolfram-nickel sulphides, etc.). Apart from achieving useful results, they contributed towards increasing and refining knowledge of the mechanisms of hydrocarbon reactions. UOP proposed *rexforming*, a combined process of reforming on Pt, selective extraction of the reforming product and recycling of the paraffinic portion with a low ON. In 1955 the capacity of UOP's platforming plants was about equal to the sum of the capacities of all other types of catalytic reforming plants.

As the practical interest of the process lay in increasing the ON of the product with respect to the feedstock and in the susceptibility of the product to lead tetraethyl, at the time used as antiknock agent, not much interest was initially taken in by-products, such as incondensable gaseous hydrocarbons and hydrogen sulphide. However, UOP and other companies in the sector soon found adequate solutions to satisfactorily resolve the final presence of such substances. It did not take long for the problem of the action of sulphur on the catalyst to be resolved by supplying the plant with desulphurized gasoline, first with hydrogen-free processes (gray clay, Perco) and, as from the 1950s, by means of hydro-desulphurization (hydrofining, unifining, ultrafining and others) using the excess of hydrogen from the reforming processes.

Other catalytic reforming proposals were drawn up by IFP, such as the continuous process based on a mobile catalyst between the reactors and ‘internal’ regeneration, and by UOP itself which in 1968 developed and finalized CCR platforming. This operated at a pressure between 3 and 5 bar, with continuous regeneration of the catalyst (now bimetallic: platinum/rhenium, UOP, Chevron), with the three reactors on top of each other in a single structure, and a number of furnaces and exchangers between them to optimize the temperature of the individual reactors.

In 1974, 25 years after the first industrial plant, of seven catalytic reforming processes, platforming was the most entrenched one, with 500 plants in operation, under construction or planned. After almost sixty years, platforming, also in its new forms, is still the catalytic process most commonly used in refineries throughout the world.

It is more or less impossible to dwell on the countless actions for infractions of patents and for priorities which, especially in the United States, have concerned almost every innovation, from thermal cracking to catalysts, down to lubricants for engines and the mechanical details of the plants. Important companies have been involved in them, including Esso (later Exxon), Mobil, Shell, Texaco, Chevron and ARCO, which however ended up by reaching agreement, arousing the interest of the Federal Government of the United States which, suspecting cartel arrangement, intervened on the basis of the Sherman Antitrust Act. The controversy dragged on from 1924 until 1931, ending with the companies being acquitted by the US Supreme Court, finding that the licences had been liberally granted also to third parties, both in the United States and abroad.

To give an idea of the costs of using platinum catalysts, suffice it to say that in 1986 platinum cost about 26.000 £/g (16.25 $/g) and, given that a platforming plant required between 20 and 100 t of catalysts with 0.5% platinum (that is, between 100 and 500 kg of platinum), the metal immobilized corresponded to a value in Italian lire at the time ranging from 2.6 to 13.0 billion for each single plant (that is, from 1,625 to 8,125 million dollars).

Processes alongside cracking and reforming

The success of platforming, as of the other catalytic reforming processes, also meant introducing new processes into the refinery. In fact, seeing as catalytic reforming involved a significant increase in the ON of gasoline, it also meant – and it could not have been otherwise, given the process conditions – the formation of *n*-paraffins C_5 and C_6, whose low ON worsened that of the total reformed product and that of commercial gasoline. The need therefore arose of isomerizing these paraffins, producing better hydrocarbons from the ON standpoint.

The reaction of isomerizing *n*-paraffins had been known since 1933 thanks to the work of the Romanian chemists Costin D. Nenitzescu and A. Dragan. Not many years after the affirmation of catalytic reforming, numerous oil and plant engineering companies proposed industrial processes for the catalytic isomerization of *n*-paraffins, such as the butamer process for *n*-butane, UOP’s penex process for pentane, Esso’s liquid phase process and Shell’s isomer process for C_5-C_6; the separation of *n*-paraffins/isoparaffins in the product was largely based on the use of molecular sieves (zeolites), in various configurations and hence with different separation selectivities (Kobe and McKetta, 1958-65; Wuithier, 1965; Aalund, 1984; Ogden, 1991).

The maximum expansion of isomerization occurred during the Second World War; it was applied above all to *n*-butane, to obtain isobutene to be subjected to alkylation, so as to supply very large quantities of ‘100-130 grade’ aviation gasoline for the Allied Air Forces.

In a similar way the success of cracking (both thermal and catalytic) stimulated the development and the application in the refinery of processes to obtain hydrocarbons with a high ON from light olefins (from ethylene to butenes). This led, as a refining process, to the alkylation of *n*-paraffins C_3-C_4 with olefins. This process was developed in various versions and, although alkylation can come about at a high temperature without catalysts, the two industrial processes that became affirmed operate at a low temperature, in the liquid phase, with acid catalysts (sulphuric acid and hydrogen fluoride), obviously patented by those with the idea and the linked know-how (Kobe and McKetta, 1958-65; Aalund, 1984). There are numerous sequential and parallel reactions that form a multi-component product, i.e. a vast range of branched paraffins from C_5 to C_{12}.

In the early 1950s, reforming catalyzed by noble metals was already associated with separation processes of aromatic hydrocarbons (BTX, together or singly) by means of selective solvents: first with ethylene glycol (Udex Dow/UOP) then with sulfolane (Shell), N-methylpyrrolidone (Arosolvan/Distapex Lurgi), dimethyl sulphoxide (IFP, Elf-Union) and others. The aromatic hydrocarbons obtained come more and more often from the downstream sector itself and pass to petrochemicals, even though – in some large refineries – plants are constructed for the dealkylation of toluene to benzene, for the synthesis of cumene from benzene and propylene, and yet others. The dearomatized refined paraffin product was used in various ways, including the formulation of kerosene for jet planes, namely jet fuel.

Alongside these processes, to improve the quality of light distillates chemical treatments were developed aimed at removing small quantities of unwanted components, extracting them or transforming their molecules into other less undesirable ones (for example, less evil-smelling, non-corrosive, innocuous to catalysts). From the very beginning, these treatments have been carried out under discontinuous conditions (batch). Such was the case with the washing of SR gasoline with caustic soda (elimination of mercaptans) and for the oxidation of mercaptans to disulphides (a treatment known as *doctor*, with soda, sodium plumbite and sulphur):

$$Na_2PbO_2 + 2\ RSH \rightarrow (RS)_2Pb + 2\ NaOH$$

$$(RS)_2Pb + S \rightarrow PbS + RSSR$$

For the same purpose, the oxidizing treatment with a solution of copper chloride has also been applied, as in Phillips' *copper sweetening* process (W.A. Schulze, and numerous United States patents between 1934 and 1941):

$$2\ RSH + 2\ CuCl_2 \rightarrow RSSR + 2\ CuCl + 2\ HCl$$

$$2\ CuCl + 2\ HCl + {}^1/_2\ O_2 \rightarrow 2\ CuCl_2 + H_2O$$

$$2\ RSH + {}^1/_2\ O_2 \rightarrow RSSR + H_2O$$

The removal of mercaptans has also been achieved by extraction with an alcohol solution of sodium hydroxide (UOP's Unisol process), with alkaline isobutyrrate (Shell's Solutizer process) or with other selective solvents (the Pure Oil Company's Mercapsol process).

Minor products between gasoline and gas oil

Between the ranges of distillation of gasoline and gas oil there are a number of products for special uses: mixed solvents such as 'white spirit' or single ones such as hexane for stain removers. Next, at intervals of distillation, but not of importance, there are turbo fuels, derived from the progress of air propulsion from internal combustion engines to prop-jet engines and lastly to turbojet ones. The latter call for particular care because of the severe conditions of use of the aircraft (high altitudes and low temperatures). Civil and military jet aircraft still run on kerosene not very different from the lamp oil of the past. Strict IATA (International Air Transport Association) specifications and military ones such as those of NATO (North Atlantic Treaty Organization) qualify various subtypes, above all for safety purposes, and prescribe antistatic, anticorrosive, de-icing, as well as other additives (Lucas, 2000).

Gas oil for diesel engines

The technological and economic structure of the downstream industry has been oriented towards favouring the overall yield of gasoline for motor vehicles and improving its quality. As already stated, this has been done as from the years immediately prior to the First World War, with the start-up of the mass production of motor vehicles in the United States, largely concentrating on private automobiles equipped with internal combustion engines. The development of the processes, too, has been conditioned by the evident desire to maximize the yield and the quality of the fuel for this type of use. Thermal cracking, the catalytic processes aimed at demolishing the residual fuel oil and the gas oil itself as far as is possible and convenient, and even the attempts to use the tails of the gasoline + kerosene fraction in the best way penalized the yield and the motor qualities of diesel fuel. This system, in essence, generated the subsequent problems of using gas oil in diesel engines, given that for a good motoring quality of gas oil – in terms of 'ignition delay' expressed with the Cetane Number (CN) – *n*-paraffins and linear olefins are preferable, whereas the majority of the processes for obtaining quality gasoline (a high ON) transform said hydrocarbons into gas and aromatic hydrocarbons.

It may be assumed that the attitude in favour of gasoline and opposed to diesel derived from the fact that in the United States diesel engines have been reserved for heavy transport (railway locomotives, trucks, etc.). The subsequent progress of fast diesel engines for cars – especially in Europe and the Far East – has led to improved performance and reduced consumption, to the point of inducing users, at the turn of the Twenty-first century, to buy more cars with diesel engines than with gasoline engines.

So as not to upset the general organization of production, the refineries formulate different gas oils for summer and winter use and make use of more additives to obtain diesel fuel of satisfactory quality under the different conditions of use: 'pro-cetane' amyl nitrate and nitrite, to improve combustion; detergents to avoid clogging of the injectors; smoke reducers to improve emissions; substances able to improve performance at low temperature, and others (Owen, 1989).

The use of residues

The quality of the residue of atmospheric distillation and at reduced pressure is obviously linked to the quality of the crude processed. While, at present, in the majority of cases, the tendency is to minimize the production thereof, good quality residues (those of crudes containing *n*-paraffins and isoparaffins, naphthenic hydrocarbons, aromatics and small quantities of compounds containing heteroatoms) are suitable for the production of lubricants. Processing residue to produce lubricants, however, entails a series of operations, processes and plants, the costs of which are carefully weighed up by the refineries. Very often, what is termed the 'residue' also contains, apart from what remains after atmospheric and vacuum distillation of the crude, components from the residues of thermal and catalytic processes, including coke and metals. Consequently, there are many possible treatments, often based on a number of hydrogenating-cracking reactions (as, for example, Union Oil's hydrocracking). It must also be recalled that until the early 1920s, lubricants from petroleum were not widely used, and indeed, the engines of the aircraft used in the First World War were lubricated with castor oil.

As lubricating mineral oils have to possess common qualities (viscosity and high viscosity index, lubricating power, behaviour at low temperature) independently of their specific use, their production from base oils of petroleum origin involves a selection of the components, for example the elimination of the asphaltenes and the resins (deasphalting) and of the paraffin waxes (dewaxing).

In the industrialized states, at the beginning of the Twenty-first century, residual fuel oil as such remains for feeding the burners of medium-to-large furnaces and, often mixed with cracking oil, the diesel engines of ships with a gross tonnage of more than 2,000 t (Lucas, 2000). In this last use the possible inconveniences (carbonaceous deposits and damage to internal parts of the engines) are accepted given the significant gap between the costs of this residual fuel oil (bunker) as opposed to gas oil for automotive engines. The pollution at sea connected with the use of bunker fuel should improve thanks to the MARPOL (MARine POLlution) regulations, derived from the International Convention for the Prevention of Pollution from Ships, adopted on 2 November 1973, and to the new European legislation on the allowed sulphur content in fuel oils for ships.

Another destination of residues (not only those from distillation and from thermal and catalytic treatments) is gasification to carbon oxide + hydrogen ($CO + H_2$), by means of one of the now consolidated processes, loaned from coal technology (for example, the partial oxidation processes of Shell, Texaco, Lurgi and others). Another use of this synthesis gas obtained from residues is the generation of electric energy with the Integrated Gasification Combined Cycle (IGCC).

Processing residues to produce lubricants necessarily means an associated production of bitumen and of paraffin waxes.

Processing to obtain lubricants from heavy gas oil (vacuum) and residues dates from long ago. In the 1920s-1930s processes were already applied for the extraction of base oils for lubricants using selective solvents, such as the already mentioned propane (Kellogg), phenol (Kellogg), furfurol (Texaco) and nitrobenzene (Atlantic). In the main deasphalting process, recourse has mostly been had to hydrocarbon solvents, such as *n*-paraffins from C_3 (*propane deasphalting*, 1934) to C_6 or to fractions of SR gasoline. The input, usually heavy gas oil or vacuum residue, is mixed with a large excess of solvent in one or more extractors: the oil, having lost its asphaltenes and resins, is passed into heat exchangers where the solvent is removed and is then recycled. In relation to the quality of the original crude, the oily phase of deasphalting consists of base oil for lubricants, or else as feedstock for catalytic cracking or hydrocracking. The bitumen obtained from the deasphalting stage, heated in a furnace, is freed of the solvent residues and is used as a fuel in the refinery or else treated according to the destination of the bitumen obtained (Eni, 1962-71; Le Page *et al.*, 1992). The presence of *n*-paraffins with a high molecular weight or paraffin wax in the base oils, which raise the pour point, can be remedied with dewaxing processes, for example with such solvents as acetone, methyl isobutyl ketone or mixes of ketones and toluene (Texaco, *dilchill* of the Exxon R & E Company). The first industrial petroleum dewaxing process has been attributed to F.X. Govers, who developed it in 1933 in a cooling/pressing plant. Among the successive processes, crystallization with solvent followed by centrifuging has been applied industrially. Dewaxing has also been carried out with catalytic processes which involve cracking and isomerization reactions (Lucas, 2000).

To obtain the vast range of lubricants intended for various applications (oils for machine tools, for turbines, for compressors, for motors, for gears and differentials, etc.), whose quality is subject to rigorous specifications, in addition to the processes mentioned there are other treatments, including the addition of additives (to improve the viscosity index and the pour point, to combat the formation of sludge and corrosion of supports and bearings), looked after inside the refinery so as to place on the market high-quality products in conformity with the specifications.

It is not easy to define the composition of lubricating oils in general, in view of the wide range of possible applications. It can be stated that the oils produced in the greatest quantity, that is, those for motor vehicle engines, have an average composition of 80% hydrocarbons of petroleum origin, of the various classes (from C_{16} to C_{50}), and the remaning synthetic components – polymers such as polymethyl metacrylate and the co-polymers ethylene-propylene – and various additives. From the fractions with high boiling points and from the residues, insulating and diathermal oils and oils for applications in agriculture and wine-making are made, as well as paraffin waxes. This part of the downstream sector is less important in terms of quantity, but it is demanding in terms of quality, and is used by numerous companies even further downstream than the oil industry itself.

In 1905 Charles F. Mabery was the first to prove that paraffin wax is for the most part formed from normal paraffin and weakly branched between C_{25} and C_{29}. His discovery was preceded by the recovery of wax from United States oils used for the manufacture of candles, similar to those obtained from stearine and from spermaceti. The semisolid material (petrolatum) obtained by dewaxing in the production of lubricants, deoiled by means of solvent, can be treated to obtain solid paraffin, to be made to conform with the specifications for various types of commercial product (raw paraffin, in flakes, macro- and microcrystalline) obtained with various processes and techniques: repeated filtration, crystallization from different solvents, and treatments with hydrogen (Lucas, 2000). For many years, the main use of solid paraffin was in the production of paper, cardboard and oilskins (ACS, 1951; Eni, 1962-71); today it is put to yet further uses in the food, pharmaceutical and cosmetics industries.

Sulphur obtained from oil: from resource to waste

The catalytic desulphurization of downstream intermediates – first LPG and gasoline, then kerosene, jet fuel and gas oil – has progressively made conspicuous quantities of hydrogen sulphide available to the refineries. Among the most successful processes, Phillips' Perco, which was in use in the 1930s to the 1950s and used a catalyst consisting of bauxite or alumina, was able to achieve partial desulphurization together with an improvement in the ON and in susceptibility to antiknock lead alkyls. The processes used to recover hydrogen sulphide from natural gas (methane) were also successfully applied to petroleum gases and light gasolines.

From the end of the Nineteenth century it was known that with the process developed by C.F. Claus (patented in Great Britain in 1882 and 1883) excellent quality sulphur can be obtained by the oxidation of hydrogen sulphide, according to the following reactions:

$$H_2S + 1/2\ O_2 \rightarrow 1/n\ S_n + H_2O$$

Part of the feedstock is burnt:

$$H_2S + 3/2\ O_2 \rightarrow SO_2 + H_2O$$

The SO_2 obtained is caused to react with H_2S on a number of catalytic beds of activated alumina, giving sulphur and water:

$$SO_2 + 2\ H_2S \rightarrow 3\ S + 2\ H_2O$$

Thanks to this process, and with progressive improvement in technology, the conspicuous and increasing availability of H_2S, both from the refineries and from the desulphurization of natural gas with a high content of this acid, sulphur of any other provenance was rapidly ousted from the market (the last sulphur mine exploited with the Frasch process was closed down at the end of the Twentieth century). Indeed, at first, it represented a profit in the downstream balance sheet, stimulating the construction of Claus plants in the refineries (Kobe and McKetta, 1958-65). The commercial value of sulphur however drastically declined with the increase in its production – practically obligatory – in processing crude and natural gas, to the extent that it is today regarded more as a waste product, in view of the difficulty in disposing of it. The situation, already difficult, risks becoming critical in the short term.

Research and technology

Three institutes have greatly contributed to the scientific culture of the petroleum industry in general: the American Petroleum Institute (API), the Institute of Petroleum (IP) and the Institut Français du Pétrole (IFP). Apart from providing various incentives for research in universities and public and private bodies, these institutes have constantly provided useful information for the development of processes. In the United States, API, with its research projects on hydrocarbons, on sulphur and nitrogen compounds of oil, the Bureau of Mines and later the Department of Energy, have conducted research in which industry has been directly concerned. Furthermore, they have freely publicized the results of fundamental and applied research (Harold M. Smith, John S. Ball and numerous others). In France, the IFP, apart from conducting original research, has established companies and branches to which it has entrusted the marketing of 'proprietary' petroleum and petrochemical processes as well as the construction of plants. In the United Kingdom, IP has produced some important results from research into sulphur compounds present in crudes of various provenance (Stanley F. Birch, Ronald A. Dean and others). In the United States and in the United Kingdom, the chemistry laboratories of numerous universities – from the prestigious MIT, Caltech and Stanford to the universities of many States of the Union (Pennsylvania, Texas, Louisiana, California, Colorado, Oklahoma, Ohio and others) – distinguished themselves in research of considerable interest to the refining and petrochemical industries.

The United States oil companies, both directly in their productive units as well as in their big corporate research centres, worked intensively, and by the beginning of the 1950s they had spent more than 100 million dollars a year on research (ACS, 1951). They also financed publishing initiatives of common interest to the industry. Research regarding refinery processes and plants were conducted in many other countries: USSR, Japan, Germany, Spain, Italy, Mexico, India, and more recently, China and the countries of the Near and Middle East.

The evolution of markets and processes

In the early 1960s, two apparent novelties interested the petroleum industry, and the refineries in particular: the announcement of the production of proteins from oil and/or from paraffin-rich fractions, first at pilot plant scale and then at industrial scale (Alfred Champagnat, BP France), and subsequently the opening of a new market for virgin naphtha and for residual oils to be used in the gasification processes for production of combustible gases, above all to gases interchangeable with natural gas. These processes (Segas, ONIA-GEGI, M.S.-Gaz de France, UGI-CCR and many others) were used especially by companies in the sector of gas generation for household use and in the heating sector.

The production of proteins from petroleum was soon abandoned for hygienic and health reasons connected with the ban on their use in the food industry for human and animal consumption. The other novelty, gas generation, while initially successful above all in Europe, where there was an insufficient supply of natural gas, as time went by failed to be of interest in view of the massive imports of natural gas from the USSR and from the countries of North Africa.

Mention must also be made of the progressive increase in the processing capacity of the individual refineries, and the extensive automation of the plants, making it possible to reduce the number of workers. The adoption of linear programming in the early 1950s and the application of miniaturized electronic instruments for the integrated control of the processes (Direct Digital Control/DDC from 1963) transformed the control rooms, necessitating highly specialized personnel, although in smaller numbers than previously.

The evolution of the refining processes and, consequently, of the plants, became more and more regulated by political decisions as of the 1970s, which had in turn been provoked by public demands, aimed at obtaining ever 'cleaner' fuels which were also more efficient. The legislation of many countries on energy saving, on environment protection, and on hygiene and safety of places of work more and more conditioned, with the composition of the products, the choice of the processes and construction of the plants. In particular, in the United States, air pollution by motorized traffic was combated first by modifying vehicle engines and then, from 1975 onwards, with the catalytic cleaning of exhaust gases and the elimination of lead from gasoline, having recourse also to tax facilities. The refineries collaborated by rapidly making available lead-free gasoline in the quantities needed and of the required quality. Nevertheless, the results obtained were not considered sufficient. Again in the United States, from 1990 the composition of gasoline was ordered to be modified, limiting the concentration of benzene and of aromatic hydrocarbons and adding components and additives not produced in the refinery.

These regulations, in the course of the years, acted as a stimulus for the formulation of commercial gasoline by adding to the traditional hydrocarbon components oxygenated compounds such as the methyl esters MTBE and TAME (*tert*-amyl-methyl-ether) and their ethylic homologues, obtained by the reactions between olefins and alcohols discovered in 1907 by the Belgian Albert Joseph Marie Reychler (Owen, 1989; Ogden, 1991; Borza, 1993).

Various companies (Snamprogetti/ANIC, BP, Elf, Chemische Werke Huels, ARCO, DSM, Shell and others) have patented proprietary processes for the synthesis of these compounds, with great success at world scale. Added to commercial gasoline without altering its conformity to laws, standards and specifications, oxygenates improve combustion, causing a diminished concentration in exhaust gases of the pollutants regulated: carbon oxide, unburned hydrocarbons and VOC (Volatile Organic Compounds).

Reformulation with oxygenates has an indirect influence on the yield in commercial gasoline from a given crude, and on the availability of hydrogen from the processes producing it (catalytic reforming and cracking). In Europe, Directive 67/548/CEE and its updates have classified as toxic or noxious various aromatic hydrocarbons. Directive 85/210/CEE requires member states to reduce the lead content in gasoline and Directive 2003/30/CE established that the use of bio-fuels should be increased to at least 2% of the energy content of gasoline and diesel fuel by the end of 2005, and 5.75% by the end of 2010.

Regarding diesel gas oil, traditionally used in the United States only for heavy-duty road vehicles and railway locomotives, by 1982 the Clean Air Act fixed limits for its emissions as from 1988.

The final activity of the refineries has always consisted of appropriately mixing fractions from the various productive plants so as to obtain the end products to be placed on the market, taking legal prescriptions into account. Thus, the present refineries have to make provision to supply gas oil (for diesel engines and for heating) in conformity with specifications which are partly different, to the extent that it may even be coloured or denatured (in the case of fishery and agriculture) so that unauthorized and fiscally unregulated uses can be identified.

The amount of polluting emissions by heavy-duty vehicles derives in part also from the composition of the lubricants. For some time now, the refineries have upgraded their processes for producing base oils, limiting the addition of additives containing metals or adding dispersive additives to the lubricant and supplying partly synthetic lubricants.

In the European Union, legislation on eliminating lead from gasoline, after a certain amount of protests, did not cause any important consequences. The legislation was backed up by self-regulation by the companies. Quite apart from the legislation, in the industrialized countries, standards have been drawn up for the analysis and quality of the products, issued by organizations on a voluntary basis – the action of ASTM (American Society for Testing and Materials) in the United States is typical – and after that by associations in which companies and institutions participate. Currently a large part of the standards is on an international and European basis with such institutions as ISO (International Standards Organization) and CEN (Comité Européen de Normalisation).

Another theme of growing interest is connected with the assessment of the time of exhaustion of oil reserves. By the end of the 1940s, the future of oil as one of the primary sources of energy and chemical products was reckoned to be less than 50 years. Moreover, it is evident that the recent impetuous entry of countries such as China and India on the markets as large-scale consumers of raw materials, and not just oil but of all or nearly all the resources which have come to be traditional for the industrialized countries, will lead to a serious social and economic crisis. Associated with the foreseeable shortage of raw materials there will be the need to protect even more health and environment in the emergent countries themselves, hitherto defaulters to some extent regarding the provisions that have for some time been in force in the industrialized countries. Therefore, as a priority, interest must be immediately turned to looking for alternative energy sources to traditional ones, as well as appropriate processing methods. Fuels that have for long been available and which have been successfully exploited are oil shales in the United States and in the Baltic States formerly part of the USSR, the bituminous sands of Canada, and certain grades of coal. The technologies for exploiting them are already available. One difficulty in applying these fuels is their composition, as they mainly consist of aromatic hydrocarbons and have a high sulphur content which, apart from making it necessary to carry out costly desulphurization, has the drawback already examined of the accumulation of sulphur produced. The cost-effectiveness of exploiting these resources, initially and for the most part linked to the price of crude, still needs to be assessed from instance to instance.

The use of coal as a raw material for fuels and lubricants, substituting downstream oil products, gained ground in Germany as from the 1920s, with the aforementioned Fischer-Tropsch synthesis. For decades, this process was studied, modified and adapted to obtain different end-products: from the polymerization of olefins to lubricants down to solid paraffin and oxygenated compounds (alcohols, fatty acids, etc.).

In fact, Fischer and Tropsch devised a catalytic process to obtain a great variety of products, including the common derivatives of petroleum refining. The catalyst for the F-T synthesis used for producing hydrocarbons and alcohols was at first the same one used for the synthesis of ammonia, namely Fe(II) and Fe(III) oxides. Subsequently, cobalt/thorium oxide/manganese oxide catalysts were developed on *kieselguhr*, and others. The industrial applicability of their process (originally at a temperature between 150 and 250°C, at a pressure of up to 10 bar, with an H_2/CO ratio between 0.5/1.0 and 2.0/1.0) depends very largely on the availability and the price of crude oil.

Developments have been made to the initial process from the 1930s until now, in numerous research centres which in many countries were dedicated to studying and applying the F-T synthesis: apart from in Germany, also in the United States, in Great Britain, in France, in the USSR and in the South African Republic. Over time, this synthesis has been studied, developed and modified, up to the creation of a number of derived processes, using different catalysts and under different conditions of temperature, pressure, H_2/CO ratios in the synthesis gas, fixed-bed technologies, under typical conditions of mobile or fluidized catalytic cracking, or in the liquid phase, i.e. with the catalyst in suspension (slurry).

Recently the F-T synthesis has received a fresh boost from the increased price of crude and from the increasing ratio between the reserves of coal and natural gas, on the one hand, and the reserves of crude oil, on the other. In 2006, SASOL of South Africa announced the construction of a semi-industrial plant using the new slurry technology. The great flexibility of the ensemble of the processes downstream of the synthesis gas puts the F-T modified process among the leading candidates of the technologies to substitute the traditional downstream oil technology.

A number of treatments of petroleum residues, such as hydrovisbreaking, the process with a hydrogen donor and the processes with a fine catalyst in suspension, have already been studied, but only at a pilot scale. However, it is not to be excluded that even in the near future they could be studied at an industrial scale (Le Page *et al.*, 1992).

The recurrent oil crises since the Seventies have each time suggested turning our attention to alternative fuels and to the formulation of commercial products, traditionally oil-based, also with substances extraneous to oil and downstream technology as already defined a number of times. In particular, they have stimulated the repetition of research projects on the use of fatty substances – as they are or modified – as substitutes or as components of diesel gas oil. In the early 1980s, almost simultaneously in a number of big consumer countries, mixtures of gas oil with these products were prepared and tried out: in France, IFP with the Institut pour les Huiles et Oleagineaux, in Italy, CNR with Agip and with two experimental stations for the industry, prepared and successfully tested on the road 1:1 mixes of gas oil and esters of fatty acids. The cracking of fatty oils was also tried out, between 400 and 500°C in the presence of catalysts, obtaining aromatic hydrocarbons, olefins and saturated hydrocarbons (normal and branched). Furthermore, ever since the beginning of the Twentieth century no few inventors, including Rudolf Diesel himself, had considered fuels for their engines different from those derived from petroleum: alcohols, ethers, esters (including glycerol triesters with fatty acids), as well as natural gas or gas obtained artificially, the latter possibly to be produced aboard the motor vehicles, with wood or charcoal slack burning gas generators.

At the moment, the economic aspects of the problem seem to condition the effective application of these products. Moreover, geopolitical problems have suggested the use of vegetable oils in developing countries: for example, for some countries, especially in Africa, importing petroleum or its products entails unsustainable expenditure of hard currency, even though their consumption is very limited (in 1983, according to IFP, 1 billion inhabitants consumed less than 1% of the oil produced in the world, and 2 billion inhabitants less than 4%). To assess the convenience of *non food* crops of oleaginous plants intended for the production of diesel oil, it is also necessary to consider the possible co-production of food proteins, of essences and of intermediates for medicines. The interest in alternative fuels is also linked to their lesser environmental impact. Hence, it must be considered that the production of biodiesel with methanol or ethanol esters produced by the interesterification of fatty substances, involves a sequence of operations and processes, at the end of which the overall energy balance is at the very least uncertain; furthermore, the economic balance, adding the costs of the agroindustrial part to the chemical costs, does not seem to hold, without external incentives. Among other things, the chain that stretches from growing of the biomass to interesterification and to the purification of the final product means a significant side-production of polluting liquid wastes. Again, the production of energy from biomass seems likewise problematic; thus the burning of natural fuels, such as firewood and other biomasses, pollutes the external air more than burning oil-based hydrocarbon fuels, duly refined.

Such is the situation at the beginning of the Twenty-first century. Obviously, current research may be liable to give rise to strongly innovative future processes. Among the feasible, what must also be considered is the aforementioned catalytic cracking, hydrocracking and visbreaking, applied to non-hydrocarbon feedstocks, to obtain alternative gas oils suitable for combustion in diesel engines (as the processes under study by UOP and by Neste Oy). At the basis of possible comparisons, apart from the laws of the market – in short, the real price of crude oil – those of thermodynamics must be considered.

In the past, and for a very long time, the refining industry had to produce enough gasoline and then gasoline and diesel fuel to satisfy the growing qualitative and quantitative demands of the automobile industry. At present (and even more in the future) it must be observed that that there will not be an increase in the consumption of products for motor vehicles in the more industrialized countries, where the motor vehicle market is saturated. However, if it is true that other large states are appearing as consumers of downstream products, it is easy to foresee that they will only slowly liberalize their internal markets and will want to exercise the tax lever on items of consumption deemed non-essential. The automobile industry, in the United States and in Europe, which in the past conditioned – not always favourably – the refining industry, will have to target their ‘residual’ production on engines with high performance but lower consumption.

Separate mention should be made of what is termed the ‘hydrogen economy’, envisaged as coming into effect in the future as from the year 2020, and for which it is necessary to possess first and foremost low-cost primary energy from non-fossil sources (to limit the emissions of carbon dioxide). Electrolysis and thermal decomposition of water (Lurgi, Bamag, Norsk Hydro, General Electric and others), nuclear energy, solar furnaces, thermochemical cycles (CCR Ispra, Italy; Livermore Laboratory, United States) and other non-conventional hypotheses such as the biophotolysis of water, have been proposed – or re-proposed – as of the 1970s. The availability of hydrogen at a reasonable cost evidently conditions its use in refinery processes and in syntheses such as F-T (Eni, 1962-71). Hydrogen, as a direct source of energy aboard motor vehicles, however it might be produced and contained, requires reliable, cheap fuel cells. Such devices have existed since the pioneering invention by William Grove (1839) of an electro-chemical generator which he himself baptized ‘voltaic gas battery’, but so far they have not been developed to the point of being practically applicable, except in rather particular cases (for example, since 1968 United States astronautical technology has availed itself of fuel cells aboard space vehicles).

Many automobile companies have experimented with hydrogen and fuel cells aboard buses or cars, but to date only as prototypes. Thus electrochemistry, apparently a long way removed from the petroleum downstream sector, is approaching it through hydrogen and fuel cells. However, it is as well to remember that, together with the high energy costs of its productive technology, some characteristics of hydrogen – flash point –253°C; limits of inflammability in air (% vol) L_i 4.0, L_s 75.0; flame temperature $>$2000°C; ignition velocity $>$280 cm/s – call for particular solutions for safety purposes.

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