

NON-CONVENTIONAL HYDROCARBON

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NON-CONVENTIONAL HYDROCARBON

Introduction

At present oil is the most important source of energy and for some applications it is irreplaceable, but till when will it be able to satisfy the growing demand of energy? The day will come when the production of oil shall reach a peak, after which it shall inexorably decrease with a consequent increase in prices. The distribution of the main oil basins around the world is not uniform, however it is not even random. In fact it depends on the geological conditions that are necessary for the formation of large deposits and the difficulty encountered to explore and search for oil in isolated scarcely known areas, as for example areas characterized by environmental conditions that are particularly severe (vast areas in Siberia, the rain forest area in South America and deep offshore areas). The geological history of our country is very complex and has given the peninsula a complicated and not very “tranquil” structural and sedimentary order. This has not favoured the formation of large extensive oil basins but has created local situations that are favourable for the formation of a number of oil provinces that are quite important, even though their extension is not great.

Non-conventional characteristics

The non-conventional hydrocarbon family includes compounds that differ greatly from one another; however, they are all characterized by a high density and viscosity. The “heavy raw materials” are those oils whose density, according to the API (American Petroleum Institute) scale, is less than 25°, while the definition of viscous oils is a viscosity >50 cP (centiPoise; 10 Poise = 1 Pascal/s). Hydrocarbons with viscosity >10,000 cP and density <10° API (and therefore denser than water) are defined “extra heavy”. This latter category also includes tar extracted from sand and clay or oil shale.

Heavy hydrocarbons are also characterized by a significant content of foreign elements, such as sulphur (present in percentages up to 6-8%), nitrogen and heavy metals, in particular nickel and vanadium: all these components can create problems in the refining and manufacturing processes and can cause environmental pollution.

Non-conventional hydrocarbons are generally found at modest depths (<1,000 m), and rarely below 3,000 m, because high temperatures decrease the viscosity; often the reservoirs are found in very porous sandstone. Heavy hydrocarbons are always on the bottom of the reservoirs, and they account for an important part of the reserves, however they can also be found in concentrations when the hydrocarbons migrate from the mother rock where they were produced (in the so called “oil window” at depths from 3,500 to 4,500 m), and undergo degradation and alteration processes (for example due to bacteria) or evaporation and dissolving processes of the lighter more precious fractions. Very often these can be found in large quantities in the basins of rivers that flow on the Earth’s surface (as for example in the Orinoco River basin in Venezuela), and it is in these areas that research is now concentrated.



Bituminous sand

The terms bituminous sand, tar sand and oil sand refer to sand deposits that are not cemented together, and are very porous, and contain non mobile viscous oils. The largest known accumulation is in the region of Alberta (Canada), with an accumulation of oil that is over 60 m thick, at depths ranging from 0 to 600 m, in porous sand. The oil that is produced has a high content of sulphur and a very high viscosity level (2×10^6 cP). The tar sand of the surface deposits at Athabasca (one of the extraction sites in Alberta) have reserves amounting to 75-100 Gbbl. These have been exploited since 1963 with various active mines, and can produce 2.5 Mbbl per day, for 100 years (current production is 600,000 bbl a day). The largest reserves in tar sand are, in fact, in Canada (State of Alberta: Athabasca, Cold Lake, Peace River), in the Orinoco River basin in Venezuela and in Russia (The Siberian platform, Melekes). Other important deposits in tar sand are in China, India, Indonesia, Brazil and Ecuador. It is estimated that tar sand can contain reserves amounting to 5,000 Gbbl (billion barrels). Even if we consider that, at present, only 15-20% of these hydrocarbons can be extracted, these are however considerable amounts; for example, the Middle East has “conventional” reserves that are estimated to be 2,000 Gbbl, of which only 683 are considered extractable with the conventional methods.

Oil shale

Clays that are rich in organic substance are the most common mother rocks and many clays (oil shale) can contain large amounts of organic substance that has still not been completely transformed into hydrocarbons (kerogen), dispersed in small particles or concentrated in thin lenses or laminae: kerogen is typical in mother rocks that were never buried deep enough to generate hydrocarbons. If the kerogen content is greater than 8% of the weight, the rocks may be considered potential future reserves: this content guarantees a production of 40 l of oil per tonne of rock. In the richest oil shale, approximately 12-14% of the weight consists of oil: in the Green River Formation (Colorado, USA), exceptional values of 16% are reached. Kerogen is very abundant, but it is difficult to extract; in fact it is scarcely mobile and it is not easy to separate it from the rock, and furthermore clays have a very low permeability therefore it is improbable that these hydrocarbons can account for more than 10% of the world resources. Tar shale and clay contain reserves amounting to 2,600 Gbbl, of which 2,000 are in the territory of the USA (Green River in Colorado, Uinta Basin in Utah and Washakie Basin in Wyoming), the rest is distributed between Brazil, Australia, China and Estonia.

In an international scenario, use of non-conventional hydrocarbons should not only lead to an increase in the reserves but also to a greater diversification of the extraction sites (that are no longer prevalently concentrated in the Middle East) thus making the price of oil more stable, as it is less sensitive to the geopolitical scenarios and international crises. Serious environmental problems caused by “non-conventional” extraction still have to be solved.



Non-conventional reserves

It is not easy to estimate what lies underground, however it is believed that in the sedimentary rocks worldwide, there are probably 1.8×10^{12} cubic metres (approximately 12×10^{12} barrels) of liquid oil. Liquid hydrocarbons, even though they all belong to the same family, differ from one another. They are made up of compounds with different chemical and physical characteristics: oils, heavy oils, tar and very heavy oils. The oils of the best quality are the less viscous ones, and are called “conventional” oil (or petroleum): in fact these hydrocarbons can be extracted with conventional methods, with technologies that have already been developed, and that are widely utilized since decades all over the world, with relatively low costs, which are therefore very convenient. However, out of all the estimated reserves, conventional oil is only a small part (approximately $0.5 \times 10^{12} \text{ m}^3$): the more consistent part (approximately $1.3 \times 10^{12} \text{ m}^3$) consists of oil with a high viscosity, that is less valuable and more difficult to extract. An analogous quantity of organic material, a potential source of hydrocarbons, is trapped in the form of kerogen (a precursor of petroleum) in particular rocks such as oil shale and tar sand, however this is mostly beyond our range of utilization, at least at present.

Since the reserves of conventional oil are inexorably decreasing, research is pointing towards the exploitation of the more viscous hydrocarbons. These are known as “non-conventional” hydrocarbons because, in order to extract them, special techniques are required, such as extraction by mining, appropriate processing of the rocks that contain these hydrocarbons, or procedures to decrease their viscosity, so that it is easier to extract them. Furthermore, all these “special” hydrocarbons require prior processing before being sent for refining. Therefore, there are potentially enormous reserves, but for the extraction and production of these hydrocarbons, much more complex technologies are required, and these are still in the developmental stage, and due to the additional costs these are not competitive as yet. However, the situation is rapidly changing and the future of oil research is increasingly oriented towards the “non-conventional” hydrocarbons.

Where in the world

Exploiting non-conventional hydrocarbons on a large scale began in the Eighties. These new fossil fuels initially contributed only small percentage amounts, but today they account for approximately 10-12% of the world production. Research began (actually even before the Eighties) in California, Venezuela and Canada, which are considered the pioneer countries for this kind of research. Canada, for example, invested greatly in this type of research starting from the Seventies, and non-conventional hydrocarbons account for 60% of the Canadian production of hydrocarbons. And this is not a small amount if we consider that with a production of 3.4 Mbbl (million barrels), Canada is the sixth producer in the world of hydrocarbons after Russia, Saudi Arabia, USA, Iran and China. Also Venezuela is in the vanguard, with a production that amounts to 40% of the production of fossil fuels in the Country. More recently, other Countries have begun the production of viscous oils, such as Indonesia, the USA, Russia, Kazakhstan, Oman, China and Mexico.



Among the larger deposits and oilfields, the most important is the oilfield of Faja del Orinoco in Venezuela, where there is a production of oils with a viscosity ranging from 500 to 8,000 cP, high density ($<10^\circ$ API) and high sulphur content ($>2\%$), from porous sand at depths between 400 and 900 m. Large quantities can also be found in Kazakhstan, Canada and Russia, however, all the oil reservoirs have rich deposits.

Some history

Asphalts, tar and heavy oils are not a recent discovery, on the contrary, it may be said that these were the first hydrocarbons to be used by man. Since the dawn of human civilization, in fact, these were used for the most varied purposes: as a sealing and waterproofing material for boats and the roofs of houses, as a glue, as fuel for oil lamps and lights, and as a medication for wounds. From the very beginning of industrial exploitation of oil, it was noted that only a very small part of the hydrocarbons present in a reservoir could flow out naturally because of the pressure in the oilfield: which however decreased gradually as the contents of the oilfield were emptied out, and therefore from the very beginning, the need arose to study techniques that could artificially increase the pressure so as to facilitate the oil extraction procedures. The most common technique consists in injecting gas and water in the reservoir, that help to move the oils with a lower viscosity towards the wells.

However, notwithstanding these expedients, the heavier and more viscous oils cannot be moved and at least 50% of the hydrocarbons remains in the reservoir. For this reason, a large number of oil reservoirs have been abandoned, because they were considered unproductive with the “normal” techniques, although these oilfields still contain a very large quantity of viscous hydrocarbons. Now that the conventional oil reserves are becoming depleted, at the end of the 20th century, research has been started to find techniques that enable the extraction and utilization of these “difficult” hydrocarbons.

Heavy hydrocarbons are not economical, but they are abundant and in the 21st century they will be a very important source of fossil fuel. Experimental processes to distil hydrocarbons from rocks such as oil shale or tar sand were studied even far back in the 18th century, to extract asphalts, tar and oils for the lamps. Of course there are a number of historical curiosities: for example, the so-called “sauolo” used to be extracted from a rocky formation known as “scisti bituminosi di Besano” (Besano tar shale), in the province of Varese. This area was well known for the discovery of perfectly preserved fossil remains of fish and large reptiles. The heavy Sauolo oil was thought to be some kind of “dinosaur distillation”, and was considered a very powerful, multipurpose medication! In the second half of the 19th century Sauolo, which is very similar to Ichthyol (that was produced in Tyrol, which is now created artificially), was produced on an industrial scale and marketed by the pharmaceutical companies to cure skin diseases. In particular, it was used to cure cases of dermatitis reported by Italian soldiers who fought in the African campaigns. At the site, already in the 18th century, there was a mining activity to extract oil shale, that was used as fuel for lighting purposes. And starting from 1830, a new project was begun for the extraction of gas for public lighting of the city of Milan.



After this pioneering and experimental phase, researches on non-conventional hydrocarbons started again in the Eighties, with an increasing allocation of funds. New technologies were used for the extraction, production and processing of the viscous oils, with important technological innovations that made exploitation of this resource increasingly profitable in terms of the percentages recovered and costs.

Difficult recovery

The productivity of an oilfield depends on different factors, such as the permeability of the rocks of the reservoir, the pressure inside the oilfield, or the viscosity and density of the hydrocarbons that it contains: because of these limiting factors it is not possible to extract all the hydrocarbons in a reservoir, but only a percentage of the same. The “recovery factor” is an important index that makes it possible to evaluate the percentage of hydrocarbons that can be extracted in an economically profitable manner. Maybe not many people know that with the most well-known and economical technologies that are currently in use, the percentage of recovery is surprisingly low: it rarely exceeds 50%. This means that in the known fields there is more or less the same amount of hydrocarbons as the amount extracted in the history of oil exploitation: an enormous quantity that, if made available in some way, would enable us to shift further the dreaded moment in which the reserves of fossil fuels shall inevitably finish.

Furthermore, till date, hydrocarbons have been available in sufficient amounts to cater to the demand, and only the best quality hydrocarbons, which are lighter and more liquid, have been extracted and utilized: a very large part of the hydrocarbons does not have characteristics that are suited for the refining process, as they are too dense, too heavy, too viscous or rich in unwelcome impurities, such as sulphur or heavy metals. However, our economy and our energy production are necessarily still based on fossil fuels, and the need to dispose of this (for the time being) essential source of energy has intensified research and development programmes, thus leading research institutes and the principal oil companies to pay attention to what some already define (light-heartedly, but not seriously...) the “bottom of the barrel”.

Technologies for extraction

The basic concept for the recovery of non-conventional oils is that the dense not very mobile hydrocarbons must be moved towards the extraction well. This is obtained in different ways: by increasing the permeability of the rock of the reservoir, by artificially creating pressure gradients in the oilfield, or by increasing the mobility of the oils by decreasing their viscosity. Various methods are used, and can be summarized as follows:

- “cold” extraction technologies that use physical and mechanical methods to increase the pressure in the oilfield and the permeability of the rock of the reservoir, while the viscosity of the oils is decreased by injecting chemical solvents;
- “thermal” methods that, instead, utilize heat to increase the mobility of the hydrocarbons in the reservoir.

Some technologies require wells, similar to the extraction wells, while others use mining techniques for the extraction (i.e. the collection) of the rocks (for example in the case of tar sand and shale, these are extracted or dug out and then processed at a later stage). With the use of the more modern technologies the percentage recovered from the reservoirs may increase to 70%. Some methods, such as gravity drainage extraction, and mining and extraction of tar sands, date back to 100 years ago. However, these methods have recently been reviewed and refined, and in the future it is believed that there will be a possibility of also using resources that are unheard of at present, such as methane hydrates or tar clay. These technologies, however, have some disadvantages: great energy consumption, the need to dispose of residues (such as shale and sand contaminated by the hydrocarbons produced in large quantities), a high level of CO₂ emissions and the production of sulphur and mud with a high content of toxic substances.

Other techniques. The first techniques utilized to produce viscous oils on a large-scale date back to 1950 approximately, and this used steam. The countries that first started to study this technology were the USA, Canada, Indonesia, Romania, Russia, China and Kazakhstan, and at present with the thermal steam extraction technique, approximately 4-5 10⁶ bbl/day are produced. Another technique that was initially used more often was in-situ combustion, in which combustion of a part of the hydrocarbons of the oilfield was used to heat and liquefy the remaining hydrocarbons, also the water flooding technique was used, and injection of solvents, polymer displacement and injection of inert gas (such as CH₄ or N₂) and other techniques that use a high pressure gradient to displace the oils and direct them towards the wells. A curiosity: the techniques that utilize repeated pressure impulses in order to make the hydrocarbons move towards the extraction wells were born in California, where it was observed that, after the vibrations of very strong earthquakes, the productivity of some of the oilfields increased spontaneously for some weeks.

In the Eighties new concepts were born that developed highly productive techniques, for example simultaneous use of the Cold Heavy Oil Production with Sand (CHOPS) method, to increase the thrust of the gas that is dissolved in the viscous oils, and Horizontal drilling techniques and gravity drainage extraction, that greatly increase the recovery coefficient.

The more immediate development for the future is the thermal technique, using SAGD (Steam Assisted Gravity Drainage) that combines the steam injection thermal technique with recovery by means of horizontal drilling: a very efficient method that enables a recovery of up to 80% in 5-8 years, however it is still expensive. There are many possible methods, however these are not always suited for all the occasions, therefore it is indispensable to begin accurately planning the interventions, according to the characteristics of the oilfields. Often a number of technologies are used, as a sequence or combined with one another. For example, after having used the CHOPS method that simultaneously extracts sand and hydrocarbons, creating a remarkable increase in the permeability of the reservoir, it is possible to further increase the recovery coefficient by using a thermal method such as VAPEX or SAGD.

The recovery of oils from oil shale or tar sand is more complicated and involves the extraction of the material that cannot be processed in situ by mining. The production methods use heating processes (retorting, in special equipment called "retorts") and destructive distillation, that destroys the rock

leaving the hydrocarbons contained in it as residues. In some cases retorting can be carried out in situ, but prior to this the rock must be broken up by means of explosions. After thermal treatment, the extracted material is “washed” with hot water and emulsifiers in order to separate the hydrocarbons from the rock. The main disadvantage is the production of a large quantity of residual material, that must then be appropriately disposed of.

Treatments for special hydrocarbons

In Estonia, oil shale is burnt directly in thermoelectric power plants, however this is one of the few examples of direct utilization of non-conventional oils. Normally, heavy hydrocarbons cannot be utilized in conventional refinery plants: they are too dense and viscous and contain large quantities of substances such as sulphur or heavy metals. These require a prior treatment, known as upgrading, that transforms them into lighter hydrocarbons, which also purifies them from the more harmful substances. Thus, the large family of so-called “syncrude” oils (or SCO, synthetic crude oil) is born, the raw materials that are produced by synthesis (i.e. by chemical treatment) from other compounds and that, besides the products of the “non-conventional” hydrocarbons, also include the raw materials produced from the liquefaction of coal or liquid hydrocarbons produced from the condensation of natural gas. A family that is rather costly at present, but which will give an ever-increasing contribution to the production of our energy requirements and will be of great help in the difficult and long transition from fossil sources to renewable sources. Since high viscosity oils are rich in carbon, and lack H, the upgrading processes to obtain low viscosity raw material that can be used in the conventional refineries imply three main phases: breaking up of the macromolecules (cracking) and elimination of excess carbon atoms, by means of a process called coking, addition of hydrogen to compensate the excess of carbon (hydrogenation) and removal of the sulphur, nitrogen and heavy metals. In the coking process, the heated viscous oil is vaporized in a low-pressure chamber, and the residues produced are coke, carbon mixed with various minerals (5%) and with sulphur (6-8%). The coke can be utilized as fuel (which is however not advisable as it is one of the “dirtiest” fuels) or in the steel production process. The coking process produces large amounts of CO₂ and therefore there is a trend to decrease its application in favour of hydrogenation. All the more viscous hydrocarbons have a very high content of sulphur (a percentage that varies from 0.1 to 0.2 % up to 4 – 8 %) that is eliminated with the hydrogenation process which, besides producing lighter oils, extracts S, transforming it into H₂S.

This is again transformed later on into elementary S and is then opportunely disposed of or stocked. There are many processes that improve the characteristics of non-conventional oils, transforming them into good quality syncrude, and these are rapidly evolving. In fact, this is one of the research sectors of the oil industry in which investments and efforts are mostly focussed. Even though non-conventional hydrocarbons are not particularly abundant in Italy, it is in the vanguard in research in this field. In fact, ENI and SNAM research laboratories have obtained remarkable results, and have also developed interesting upgrading technologies with which it has become possible to eliminate the intermediate production of heavy fuel oils and coke: this process is known as the ENI Slurry Technology or EST. The upgrading phase does not always take place at the



extraction site, and for this reason the viscous oils must also be treated, by diluting them with lighter oils, so that it is possible to transport them in pipelines: in fact, products that are too viscous cannot be transported in pipelines.

Potential developments

The cost of extracting and treating non-conventional hydrocarbons is about 10-20\$ per barrel more than for conventional hydrocarbons: of these costs, approximately half are for improving the quality of the hydrocarbons (upgrading). Therefore, this is not an economically profitable source, and its utilization will not make the price of oil drop. However, there are abundant reserves that will guarantee a constant production of hydrocarbons in the near future, together with other sources that are also not very “conventional”, such as the production of liquid hydrocarbons from coal liquefaction, from conversion of gas into liquid fuels (Gas To Liquid or GTL technology) and from the biomass, besides the possible exploitation of methane hydrates in the sediments of the ocean floors. While it is believed that the production of conventional hydrocarbons will reach its peak in the next 10 years, and will then inexorably decrease, it is estimated that the production of non-conventional hydrocarbons should continue to increase for the next 50 years and will reach 10% approximately of our energy requirements. Naturally the possibility of disposing of new unexpected reserves of fossil fuels, for a few more decades, must not lead us to forget that however it is necessary to reconvert our energy consumption and our production of energy, diversifying the sources, and favouring technologies that allow a production of energy that is as clean as possible and that respects the environment. For this reason, non-conventional hydrocarbons must not be considered a remedy for the oil crisis but a valid aid, and in the near future, these will become an increasingly important part of the so-called “Energy Mix” (together with clean coal, conventional oil, gas, nuclear power and alternative renewable sources): no more contrasts between the different sources of energy, but “team work” to develop technologies that are increasingly eco-compatible and sustainable.

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