OIL INDUSTRY I. PETROLEUM AND ITS PRODUCTS
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OIL INDUSTRY

i. PETROLEUM AND ITS PRODUCTS

Petroleum has been known throughout historical time. It was used in mortar, for coating walls and boat hulls, and as a fire weapon in defensive warfare. By the middle of the 19th century, the Industrial Revolution had brought about a search for new fuels in order to power the wheels of industry. Moreover, due to the social changes, people in the industrial countries wished to be able to work and read after dark and, therefore, needed cheap oil for lamps to replace the expensive whale oil or the malodorous tallow candles. Some believed that rock oil from surface seepages would be a suitable raw material for good quality illuminating oil.

In 1854, Benjamin Silliman, Jr., the son of the great American chemist and himself a distinguished professor of chemistry at Yale University, took an outside research project given by a group of promoters headed by George Bissel, a New York lawyer and James Townsend, president of a Bank in New Haven, Connecticut, to analyze the properties of the rock oil and to see if it could be used as an illuminant (Yergin, p. 20). In his research report to the group, Silliman wrote that the petroleum sample (collected by skimming the seepages on streams) could be brought to various levels of boiling and thus distilled into several fractions, all composed of carbon and hydrogen. One of the fractions was a very high quality illuminating oil. Although others in Britain and Canada had already produced clean burning lamp fuel from rock oil, it was the publication of Silliman's report that provided the impetus to the search for crude oil in the deeper strata of the earth's surface.

The modern petroleum industry began in 1859, when "Colonel" Edwin L. Drake, hired by the same group of promoters, set up operations about two miles down Oil Creek from Titusville in Pennsylvania on a farm that contained an oil spring. Drake and his team built a derrick and assembled the necessary equipment to drill a well that, towards the end of August 1859, struck oil at the depth of 69 feet. Many wells were then drilled in the region, and kerosene, the chief product, soon replaced whale oil lamps and tallow candles. Little use other than lamp fuel was made of petroleum until the development of internal combustion engines (automobiles and airplanes). To day, the world is highly dependent on petroleum for motive power, lubrication, fuel, synthetics, dyes, solvents, and pharmaceuticals (Yergin, p. 26).

Origin of petroleum. There are two theories for the origin of petroleum: Inorganic and Organic. The Inorganic theory, which has some supporters (amongst chemists and astronomers rather than geologist), believes in magmatic origin of petroleum. Mendele'ev (Mendeléeff, I, p. 552) suggested that the mantle contained iron carbide. This iron carbide could react with percolating water and form methane and other hydrocarbons that is analogous to production of acetylene from reaction of calcium carbide and water.

The Organic theory, which has far more supporters, states that the amount of carbon in the earth crust has been estimated to weigh 2.6 times 10 to the power of 28 grams (Hunt, 1977, pp. 100-16). Some 82% of this carbon is located as CO3 in limestone and dolomite (Ca CO3 and Mg CO3). About 18% occurs as organic carbon in coal, oil and gas (M. Schedlowski, R. Eichmann, and C. E. Junge, "Evolution des irdischen Sauerstof Budgets und Entwicklung de Erdatmosphare," *Umschau.*, 22, 1974, pp. 703-707). The key reaction is the conversion of inorganic carbon into hydrocarbon by photosynthesis. This process happens within plants or within animals, which eat the plants. Plants and animals die and their organic matters are oxidized into carbon and water. In certain exceptional circumstances, the organic matter may be buried in sediment and preserved, albeit in a modified site, in coal, oil and gas, by a complex process of chemistry. Occurrence of petroleum reserves in sedimentary rocks is a strong proof of this theory.

Geological requisites for an oil and gas field. The first requisite for an oil or a gas field is a reservoir: a rock formation porous enough to contain oil or gas and permeable enough to allow their movement through it. Oil and gas occur in sedimentary rock formation laid down in ancient riverbeds or beaches, and also occasionally in dune sands or deep-sea sands. Where the limestone is porous and permeable they also form reservoirs, as in reefs built up by corals, and in places where waves and tidal currents exist. In carbonate formation, limestone (Ca CO3) and dolomite (Mg CO3), which are more brittle and soluble than sandstones, secondary porosity is found in fractures, solution channels and vugs. The more prolific Iranian Petroleum Reservoirs are made of fractured carbonates.

The second requisite is a source of hydrocarbons. Most source rocks are fine-grained shales deposited in quiet water and containing appreciable (more than 0.5%) of mostly insoluble organic matter called kerogen. Kerogen is an intermediate organic compound formed by the body of animals and plants buried under sediments by the passage of time, action of bacteria, and overburden pressure of sediments, preserved by lack of oxygen under water or sediment thus not oxidized. Kerogen, depending on the depth of burial and its corresponding temperature at its nature, changes to gas, mainly methane or heavier hydrocarbons (oil), specifically if it contains more fatty materials. As the shale (source rock) becomes compact, pressure squeezes out water and hydrocarbons, thus migrating until the fluids find a porous medium.

The third requisite is the trap to hold the oil and/or gas. Because oil and gas are lighter than the water saturating the earth crust, they would rise to the surface and escape unless stopped by an impermeable layer (cap rock) or surrounding. Traps are divided into three categories, structural, stratigraphic and combination. The structural traps are formed by the deformation of the earth crust, commonly anticlines.

Stratigraphic, traps are barriers to fluid flow formed by the termination of the permeable reservoir rock (Figure 1; Figure 2; Link, 1983, pp 193-94).

One half of the petroleum in the world is obtained from Cenozoic era (present to 63 million years ago). The Paleozoic era (255-580 million years ago) ranks next in production, followed by Mesozoic era (63-255 million years ago). Most of the oil in Iran is obtained from rocks of tertiary and cretaceous systems

(27-145 million years ago); For geological time scale see Table 1; Link, 1983, p. 7). For location and true scale cross-sections of the anticline traps of some of the Iranian reservoirs, see Figure 3 and Figure 4; Selley, p. 283). *Geophysical exploration*. Traps are sought by geophysical methods, of which the seismograph is the most useful. Sound waves are produced at the earth's surface by explosions or by a heavy, vibrating weight and by air guns at sea beds (offshore). Part of the wave energy is then reflected back to the surface, where it can be detected by sensitive receivers and recorded. The recorded data then are processed mathematically and portrayed graphically as a sort of geological section. Seismographs, while giving subsurface geological cross sections will not determine whether oil is present in the structure.

Two other cheaper geophysical techniques are gravity and magnetic methods, but they are seldom able to locate individual traps. Rather, they are used regionally to ascertain the shape of sedimentary basins. Surface geology and geo-chemical studies of shallow cores, also help to show the possibility of the presence of hydrocarbon traps.

Exploratory drilling. The presence of oil and gas is confirmed only by drilling into the prospective rock formation. The first well drilled in a new area is called an exploratory, or wildcat well, because the chance of finding oil or gas is speculative. Step-up wells are drilled to extend the boundary of a known producing area in an attempt to discover new pools or define the limits of known reservoirs. Development wells are drilled to produce oil or gas from a reservoir that has been located by exploratory wells.

Before drilling can begin, it is usually necessary in the United States to obtain the right to drill by securing a lease from the landowner. Outside of the United States, the subsurface usually belongs not to the landowner but to the government, as is the case in Iran.

DRILLING FOR PETROLEUM

Cable tool drilling **.**For many years in the early days, oil and gas wells were drilled by cable tools, but that has been replaced practically everywhere by rotary drilling.

Rotary drilling. The rotary drilling method consists of revolving a steel bit at the end of a string of pipes called the drill pipe. The most common types consist of three cones with teeth made of hard metals with embedded industrial diamond bits or carburandum. The rotation of the bit grinds the rock to fingernail-size cuttings. Drill pipes and the bit are rotated by the rotary table on the surface of the well. Liquid drilling fluid (mud) is pumped, down the hollow drill pipes, and out of the jet orifices onto the bit. Mud then returns to the surface through the space between the drill pipe and the wall of the well with cuttings that are removed at the surface, once the mixture is passed through surface screens. The drilling mud's functions are to remove cuttings and to cool and lubricate the bit. Mud also exerts pressure at the bottom of the hole so that water, oil, or gas in porous rocks cannot enter the hole (Figure 5; Figure 6; Selley, pp. 38-41).

When a good sample of the formation is desired, a special hollow bit is used and a short section of the formation (core) can be retrieved. Cores are necessary to determine the kind of rock and to measure its porosity and permeability, and fluid saturation.

Directional drilling. In directional drilling, an oil well is drilled at an angle rather than straight down. Crews use such tools as whip-stocks and turbo-drills to guide the bit along a slanted path. This method is often used in offshore operations because many wells can be drilled directionally from one platform. By means of remote control, drillers could rotate to expose a new drilling surface. Such a bit would coordinate the need to pull the drill pipe out of the hole at the time the bit is changed.

Horizontal drilling. When the angle of directional drilling can be adjusted to 90 degrees, horizontal wells are drilled. This is a technique that is successfully applied in certain reservoirs. Horizontal drillings are most effective in oil production when the thickness of producing formation is not large and has good vertical permeability. This type of drilling is being used in some of fractured carbonate reservoirs of Iran in recent years (A. R. Zahedani, "Optimization of Horizontal Drilling in Iranian Oilfields," M.Sc. thesis, Sharif University of Technology, 2003, Iran; Jamshid-Nezhad, pp. 43-46)

Experimental methods of drilling include the use of electricity, intense cold, and high frequency sound waves. Each of these methods is designed to shatter the rocks at the bottom of the hole. Petroleum engineers are also testing a drill that has a bit with a rotating surface.

Logging. Graphical records called logs show the position and character of geological formation encountered as the well is drilled. One type of log is made by examining samples of the cuttings, taken every 3-9 meters. However, rotary drilling mixes the cuttings considerably, and the heavy mud conceals shows of oil or gas. Consequently, the geologist must depend on logs taken by geophysical methods. The most useful logs determine the formation's natural radioactivity, resistivity, and acoustic velocity. Other physical properties may also be measured.

Offshore drilling. Drilling offshore has become increasingly important, as large petroleum reserves have been discovered in the ocean. Modern offshore drilling began in the Gulf of Mexico, where some producing fields are 100 miles (160 km) from the coast. Offshore fields are found in many parts of the world including the Persian Gulf, the Atlantic and the Pacific coasts, the Caspian Sea and the North Sea. Depending on water depth, offshore drilling rigs may be mounted on bottom-supported vessels such as jack-ups or submersibles, or on floating vessels such as ships or semi-submersibles. Jack-ups typically have three long legs that are lowered to the bottom when the rig is in place and the rig is lifted out of the water. Drilling ships and semi-submersibles are held over the well location with anchor chains and anchors. If an oil or gas field is discovered, the mobile drill vessel is moved away, and a fixed, permanent platform is installed with a drill mounted on it. As many as 30 wells can be drilled from a platform, deviated from the vertical in different directions so as to penetrate the producing formation in a desired pattern. The platforms are large structures with living quarters for the personnel, who are served by special ships and helicopters.

Completing the well. The usual method of completing a well is to drill through the producing formation. The drill pipe is withdrawn and a larger diameter pipe called casing is run into the hole, section by section, to the bottom. A measured amount of cement is pumped down the inside of the casing, followed by mud. The cement rises to fill the annular space between the casing and the hole. The mud is replaced by water or a non-damaging fluid to the producing zone, prior to perforation of the producing formation. Perforation usually takes place by creating holes by jet or gun perforators. After perforating the formation the fluid in the borehole is removed, and the oil or gas from the formation is free to enter the well. If the formation is damaged by prior operations or the permeability of the producing rock is too low, the well has to be stimulated. There are two general techniques of well stimulations, acidizing and fracturing.

PRODUCTION OF PETROLEUM

Petroleum is recovered in the same way as underground water is obtained. Like water, if the pressure at the bottom of the well is high enough the oil will flow to the surface. Otherwise pumps or other artificial means have to be used. Once the oil reaches the surface through wellhead equipments, it passes through separators in which oil is separated from gas and water. If natural pressure provides the required energy for free flow of the oil to the surface, production of petroleum is called primary recovery **.**If artificial techniques are used, the process is called enhanced recovery.

Primary recovery: The natural energy used in recovering petroleum comes chiefly from gas or water in reservoir rocks. The gas may be dissolved in the oil or separated at the top in the form of gas cap. Water that is heavier than oil collects below the petroleum.

Depending on the source, the energy in the reservoir is called: (i)solution -gas drive, or (ii) gas-cap drive or (iii) water drive (Allen and Roberts, p. 20).

Solution-gas drive. The oil in nearly all reservoirs contains dissolved gas. The impact of production on this gas is similar to what happens when a can of soda is opened. The gas expands and moves towards the opening, carrying liquid with it. Solution-gas drive brings only small amounts of oil to the surface.

Gas-Cap Drive. In many reservoirs, gas is trapped in a cap above the oil as well as dissolved in it. As oil is produced from the reservoir, the gas expands and drives the oil toward the well.

Water-drive. Like gas, water in the reservoir is in place mainly by underground pressure. If the volume of the water is sufficiently large, the reduction of pressure that occurs during production of oil will cause the water to expand. The water then displaces the petroleum, making it flow to the well.

Enhanced recovery. This includes a variety of means designed to increase the amount of oil that flows into the producing well. Depending on the stage of production in which they are used, these methods are generally classified as secondaryrecovery or tertiary level recovery.

Secondary and tertiary recovery **.**Many oilfields that were produced by the solution-gas drive mechanism until they became uneconomical have been revived by water flooding. Water is injected into specially drilled wells, forcing the oil to the producing wells. After water flooding about 50% of the original oil still remains in place. This would constitute an enormous reserve, if recovery were possible. Many methods of tertiary enhanced recovery have been researched and field-tested. Certain fluids will recover most of the residual oil when injected into the rock. These include such solvents as propane and butane, and such gases as carbon dioxide and methane, all of which will dissolve in the oil and form a bank of lighter liquid, which picks up the oil droplets left behind in the rock and drives them to the producing wells.

Moreover, surfactants (detergents) in water reduce the interfacial forces between oil and water and make the oil easier to move. Thickening agents may be added to the injected water, and viscous emulsions of oil and water have been used. Some of these methods seem promising in laboratory and pilot tests, but they have been generally uneconomical in the field.

In Venezuela, and in Alberta in Canada, where primary methods only recover about 15% of the heavy oil existing initially in the reservoir, the only commercially successful enhanced recovery method to date has been steam injection. Another thermal recovery method that shows promise but has not generally been successful is *in situ* combustion (Moore, Gordon, Department of Chemical and Petroleum Engineering, University of Calgary, Canada, Authority on *in situ combustion,* Personal Communication, 2004). Large amounts of air are injected into the reservoir, and the oil is ignited. The hot products of combustion vaporize the oil and water ahead of the burning zone and drive them toward the producing wells. In Iran at present, the technique of secondary recovery for carbonate reservoirs is confined to gas injection for reservoir pressurization, and to a limited extent, water flooding in one of the offshore fields in the Persian Gulf (A. Badakhshan et al., 1993; P. A. Bakes and A. Badakhshan, 1988).

PETROLEUM COMPOSITION AND CLASSIFICATION

Petroleum exploration is largely concerned with the search of oil and gas, two of the chemically and physically diverse, group of compounds called hydrocarbons. Physically, hydrocarbons grade from: gases, liquids (crude oil) and plastic substances (bitumen) to solids (tar sand, oil shale and hydrates).

Gas. Petroleum gas or natural gas is defined as a mixture of hydrocarbons and varying amount of non-hydrocarbons that exist either in gaseous phase or in solution with crude oil in underground reservoirs. Natural gas is classified into dissolved, associated, and non-associated gas. Dissolved gas is in solution in crude oil in the reservoir. Associated gas, commonly known as gas-cap gas, overlies and is in contact with crude oil in the reservoir. Non-associated gas is in reservoirs that do not contain significant amount of crude oil. Apart from hydrocarbon gases, *non-hydrocarbon* gases also exist in the reservoirs in varying amounts. The non-hydrocarbon gases are nitrogen, hydrogen, carbon dioxide, hydrogen sulfide, and rare gases such as helium.

In general, hydrocarbon reservoirs, dependent on their phase status under the ground are classified as: under- saturated, saturated, retrograde condensate, dry gas and wet gas Reservoirs(Allen and Roberts, pp.43-46).

Crude oil. Crude oil is defined as a mixture of hydrocarbons that exists in liquid phase in natural state under ground and remains liquid at normal conditions after passing through surface separators. In appearance crude oils vary from straw yellow, green, brown to dark brown or black in color, and with varying viscosities. The density of crude oil or its API (American Petroleum Institute) gravity is a good indicator of its quality, and is the major basis for its pricing.

Chemistry. Crude oil consists largely of carbon and hydrogen (hydrocarbons with three sub-groups) and the hetero-compounds that contain with minor amounts of oxygen, nitrogen and sulfur together with trace amounts of metals such as vanadium, nickel etc. These compounds which exist in various amounts in different crude oils have adverse effects on quality of crude oil, its price, and cause difficulty in crude oil refining and, if not removed from petroleum products, would cause environmental pollutions upon utilization.

Hydrocarbons subgroups are: paraffins, naphthenes and aromatics. Paraffins are saturated hydrocarbons, either as straight or branched chain (iso-paraffins). The paraffins in crude oil start from pentane to very high molecular weight compounds. Paraffins are the major compounds of crude oils- about 50%. Naphthenes are the second major group of hydrocarbons. Examples are cycloheptane and cyclohexane. They make up to 40 % of crude oils. Aromatics or unsaturated cyclo-hydrocarbons start with the smallest molecule of benzene. The aromatic hydrocarbons are liquid at normal conditions. They are present in relatively minor amount- about 10%- in light crude oils, but increase with density of crude oils.

CRUDE OIL CLASSIFICATION

Broadly speaking the classifications fall into two categories:

(i) Those proposed by chemical engineers interested in refining of the crude oil and

(ii) Those devised by geologists, and geochemists, as an aid to understanding, the source, maturation, history, etc., of crude oil occurrence.

(i) Is concerned with the quantities of various hydrocarbons present in the crude oil and their physical properties.

(ii) Is concerned with the molecules structure of the crude oil. One of the first schemes was developed by the U. S. Bureau of Mines. In this case the crude oils are classified into; paraffinic, napthtenic, aromatic intermediate, aromatic asphaltic and aromatic naphthenic types according to their distillate fraction at different temperatures and pressure. Tissot and Welte have given another classification (Selley, pp. 30-33) that has the advantage of demonstrating the maturation paths of oil in the subsurface (Table 2).

The quality and quantity of products produced by crude oil depend on its initial type. For example, a paraffinic type is better for producing kerosene and diesel oil, but not so suitable for producing gasoline. Aromatic types are good for producing gasoline and naphthenic oils give better lubricating oils.

Tar sands and oil shales (plastic and solid hydrocarbon). Besides crude oil and gas, vast reserves of energy are also locked in the tar sands and oil shales. Terminology and classification of plastic and solid hydrocarbons are shown on Figure 7 (Abraham, p. 432).

The solid and heavy viscous hydrocarbons occur as lakes or pools on the earth's surface and are disseminated in the veins and pores in the surface. Notable examples of such kinds of hydrocarbons (inspissated deposits) as seeps are known all over the world particularly in Oklahoma, Venezuela, Trinidad, Burma, Iran, and Iraq and in other localities in the Middle East.

Tar sands. Heavy viscous oil deposits occur at or near the earth surface in many parts of the world Table 3 shows the vast reserves of tar sand deposits, worldwide (Hills, 1974, p. 263).

Two basic approaches for extraction of oil from tar sands are in practice: surface mining and subsurface extraction. In the first case the technology of strip mining, and separation of oil from the quarried tar sand is done either by hot water or by steam. Where overburden is too thick, two types of extraction methods, namely the injection of solvent (vapex) (R. M. Butler, Chemical and Petroleum Engineering Department, University of Calgary, authority on vapex, personal) to dissolve the oil and the use of heat in the form of steam (steam stimulation, or steam flooding) and *in-situ* combustion to extract and reduce the viscosity of the oil is used (G. Moore, Department of chemical and Petroleum Engineering, University of Calgary, authority on *in situ* combustion, personal communication, 2004). In these operations the oil flows to the well bore where it is pumped to the surface.

Oil shale. Oil shale is a fine grain sedimentary rock that yields oil on heating. It differs from tar sands in that in tar sands oil is free and occurs in the pores, but in oil shale the oil is contained within the complex structure of kerogen, from which it may be distilled. The reserves of oil shale are widely distributed in the world. Its reserves are estimated at 30 trillion barrels of oil. Only about 2% is accessible using present-day technology (Yen and Chillingarian, p. 292; Dinneern, pp. 181-98).

As in the case of tar sands, there are two basic methods of winning oil from shale: (i) by retorting shale quarried at the surface or (ii) by underground *in-situ* extraction. The cost of extraction of oil from oil shale is very high at present (Hunt, 1979, p. 617).

Figure 8. Map of oil resources of the Persian Gulf region.

Figure 9. Map of oil resources of the Caspian Sea region.

Gas hydrate. Gas hydrates are compounds of frozen water that contain gas molecules. The ice molecules themselves are referred to as clathrates. Physically, hydrates look similar to white, powdery snow. Gas hydrates occur only in very specific pressure-temperature conditions. They are stable at high pressures and low temperatures. Gas hydrates occur in shallow arctic sediments and in deep oceanic deposits. Gas hydrates in arctic permafrost have been described from Alaska and Siberia (Holder et al., 1976, pp. 981-88) and (Makegon et al.; “Detection of A Pool of Natural Gas in Solid State,” *Dokl., Akads., Nauk*, SSR 196, 1971, pp. 197-200).

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