

CHEMISTRY AND PHYSICS OF NATURAL BITUMEN AND HEAVY OIL

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Keywords: Bitumen, heavy oil, extra heavy oil, properties, Athabasca deposit, chemistry, recovery, secondary recovery, enhanced oil recovery, mining, upgrading, refining synthetic crude oil, character, elemental, composition, processability, sediment, reservoir, pour point, paraffin, naphthane, aromatic, sulfur compound, emission, petroleum, natural, tar sand, hydrocarbon, organism, rock, trap, feedstock, carbon residue, nitrogen, gravity, viscosity, thermal, carbon, hydrogen, oxygen, metals, refining, porphyrin, fractional, distillate, decomposition, permeability, volatility, process, separation

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Summary

Tar sand (also known as oil sand and bituminous sand) is a sand deposit that is impregnated with dense, viscous petroleum-like material called bitumen. Tar sand deposits are widely distributed throughout the world and the various deposits have been described as belonging to two types: (a) stratigraphic traps and (b) structural traps although gradations between the types of deposit invariably occur.

In order to determine the processability of petroleum a series of consistent and standardised characterisation procedures are required. These procedures can be used with a wide variety of feedstocks to develop a general approach to predict processability. The ability to predict the outcome of feedstock (especially heavy oils and residua) processing offers (1) the choice of processing sequences; (2) the potential for coke lay-down on the catalyst; (3) determining the catalyst tolerance to different feedstocks; (4) predictability of product distribution and quality; and (5) incompatibility during processing; and incompatibility of the products during storage. Thus, efficient refining and understanding behavior requires knowledge of the chemistry and physics of all feedstocks, especially the chemistry and physics of heavy oils and bitumen.

The only commercial operations for the recovery and upgrading of bitumen occur in north-east Alberta, Canada, near to the town of Ft. McMurray where bitumen from the Athabasca deposit is converted to a synthetic crude oil. Therefore most of the data available for inspection of bitumen and determination of behavior originate from studies of these Canadian deposits. The work on bitumen from other sources is fragmented and spasmodic. The exception is the bitumen from deposits in Utah, United States where on-going programs have been in place at the University of Utah for more than three decades.

The API gravity of tar sand bitumen varies from 5° API to approximately 10° API depending upon the deposit, viscosity is very high, and volatility is low. On the other hand, the API gravity of heavy oil is on the order of 10 to 20°. The viscosity of heavy oil is high relative to conventional crude oil but is substantially lower than the viscosity of bitumen. Similarly, a higher proportion of heavy oil is volatile relative to bitumen but the constituents of both heavy oil and bitumen exhibit lower volatility than conventional crude oil.

The lack of mobility of bitumen requires a mining step followed by the hot water process that is, to date, the only successful commercial process to be applied to bitumen recovery from mined tar sand. Many process options have been tested with varying degrees of success and one of these options may even supersede the hot water process at some future date.

In addition, bitumen is relatively hydrogen-deficient when compared to heavy oil and conventional crude oil therefore requires that there be substantial hydrogen addition during refining. Heavy oil and conventional crude oil can be commercially upgraded and refined by a variety of processes. Bitumen is currently commercially upgraded by a combination of carbon rejection (coking) and product hydrotreating. Coking, the process of choice for residua (i.e., the non-volatile portions of conventional crude oil and heavy oil), is also the process of choice for bitumen conversion. Bitumen is currently converted commercially by delayed coking and by fluid coking. In each case the bitumen is converted to distillate oils, coke, and light gases. The coker distillate is a partially upgraded material and is a suitable feed for hydrodesulfurisation to produce a low-sulfur synthetic crude oil.

1. Character

In order to determine the processability of petroleum a series of consistent and standardised characterisation procedures are required. These procedures can be used with a wide variety of feedstocks to develop a general approach to predict processability. The ability to predict the outcome of feedstock (especially heavy oils and residua) processing offers (1) the choice of processing sequences; (2) the potential for coke lay-down on the catalyst; (3) determining the catalyst tolerance to different feedstocks; (4) predictability of product distribution and quality; and (5) incompatibility during processing; and incompatibility of the products during storage. Thus, efficient refining and understanding behavior requires knowledge of the chemistry and physics of all feedstocks, especially the chemistry and physics of heavy oils and bitumen.

Tar sand is defined as sand saturated with a highly viscous crude hydrocarbon material not recoverable in its natural state through a well by ordinary production methods. Chemically, the material should perhaps be called bituminous sand rather than tar sand since the organic matrix is bitumen (i.e., carbon disulfide-soluble material). As defined, bitumen is a hydrocarbonaceous material that consists of carbon and hydrogen with smaller amounts of nitrogen, oxygen, sulfur, and metals (especially nickel and vanadium).

Heavy oil and bitumen are naturally-occurring materials that contain hydrocarbons but hydrocarbons that are synthesised by living organisms usually account for less than 20% by weight of the petroleum and petroleum-like materials. The majority of the hydrocarbons in heavy oil and bitumen are produced by a variety of processes that converts other organic material to hydrocarbons as part of the maturation processes generally referred to as diagenesis, catagenesis, and metagenesis. These three processes are a combination of bacteriological action and low-temperature reactions that convert the source material into petroleum. During these processes, migration of the liquid products from the source sediment to the reservoir rock may also occur.

It is generally proposed that heavy oil and bitumen are formed through the progressive chemical change of materials provided by microscopic aquatic organisms that have been incorporated into marine or near-marine sedimentary rocks at the time of formation of the sediments. However, the details of the mechanisms by which the chemical transformations and the mechanisms by which petroleum-like materials are expelled from the source sediment and accumulate in reservoir rock are still uncertain.

Transformation of some of this sedimentary material to petroleum probably began soon after deposition, with bacteria playing a role in the initial stages and clay particles serving as catalysts. Heat within the strata may have provided energy for the reaction, temperatures increasing more or less directly with depth. Some evidence indicates that most petroleum and petroleum-related materials formed at temperatures not exceeding about 100-120°C (210-250°F), with the generation of petroleum hydrocarbons beginning as low as 65°C (150°F).

Both the nature and the quantity of the organic and inorganic settling matter may vary. As a consequence, it must be expected that the characteristics of the crude oil, heavy oil, and bitumen found in different reservoirs and deposits will vary. The nature of crude oil, heavy oil, and bitumen is related not only to the nature of the source material but also to the relative amounts of the different constituents in the source material. In addition, the temperature, pressure, and any other physical conditions prevailing in the area will also affect the character of the material.

The debris that settles at the bottom of the marine environment is attacked by bottom-dwelling (benthic) organisms that feed both on the sediment and on any water-soluble material. The benthic bacteria are largely responsible for the decomposition of organic compounds and the synthesis of new organic compounds through enzymatic transformations. The remaining material is partly transformed by bacteria and buried under the steadily increasing cover of sediments.

As the pressure in the sediment increases, the water content diminishes from 70-80% by weight to less than 10% by weight, depending on the depth and the type of sediment. At this time, there is also the onset of anaerobic bacterial decomposition, which usually continues for a considerable length of time and during which biochemical transformations occur. It has been estimated that 60 to 70% by weight of the sedimentary organic carbon is typically liberated as carbon dioxide during this process; the majority of the remaining organic carbon is converted into new products, and the end result is a very complex mixture.

The organic compounds that contribute to the formation of petroleum, heavy oil, and bitumen are generated from finely disseminated organic matter in source beds. Processes of primary and especially secondary migration, which finally lead to the formation of petroleum accumulations, must therefore encompass mechanisms that concentrate dispersed petroleum compounds.

In general, the organic detritus of sediments varies with the environment just as the aquatic organisms vary in their chemical makeup. This is very important in understanding the differences between petroleum, heavy oil, and bitumen. Gross differences and structural variations of petroleum constituents are now believed to arise because of required variations in the source materials and also variations in the conditions (geophysical) under which the petroleum, heavy oil, and bitumen was formed.

Accumulations of petroleum, heavy oil, and bitumen are usually found in structural highs where reservoir rocks of suitable porosity and permeability are covered by a dense, relatively impermeable cap rock, such as an evaporite or a shale. A reservoir rock sealed by a cap rock in the position of a geological high, such as an anticline, is known as a structural petroleum trap. Other types of traps, such as sand lenses, reefs, and pinch-outs of more permeable and porous rock units are also known and occur in various fields. In all these situations, the changes in permeability and porosity determine the location of an accumulation.

Any porous and permeable stratum will suffice as the reservoir, and a very common reservoir rock is a porous or fractured limestone (especially of the reef, bioherm type); several such reservoir structures are found throughout the earth. Most reservoir rocks are sedimentary rocks, almost always the coarser grained of the sedimentary rocks: sand, sandstone, limestone, and dolomite. A less common reservoir is a fractured shale or even igneous or metamorphic rock. It is only rarely that shale acts as a reservoir rock, and again fractures and other relatively wide openings are believed to confer the required reservoir properties on an otherwise unsuitable rock. It may be that petroleum found in at least some reef structures is indigenous because of the large concentration of organisms in reefs, and there is often no other obvious source of the oil.

Once the oil has been transferred to the reservoir rock, it is free to move under any force that may be applied. Gravitational forces are presumed to be dominant, thereby causing the oil, gas, and water to segregate according to their relative densities in the upper parts of the porous stratum. Favourable locations where the oil can accumulate may be anywhere along the path of fluid travel, and even though the porous zones adjacent to a

compacting mud are commonly sand (sands form important reservoir rocks), almost any porous and permeable stratum will suffice.

Once the oil has accumulated in the reservoir rock, gravitational forces are presumed to be dominant, thereby causing the oil, gas, and water to segregate according to their relative densities in the upper parts of the reservoir. If the pores in the reservoir rock are of uniform size and evenly distributed, there are transition zones, from the pores occupied entirely by water to pores occupied mainly by oil to those pores occupied mainly by gas. The thickness of the water-oil transition zone depends on the densities and interfacial tension of the oil and water as well as on the size of the pores. Similarly, there is some water in the pores in the upper gas zone (the gas cap), which has at its base a transition zone from pores occupied largely by gas to pores filled mainly by oil.

Petroleum, heavy oil, and bitumen cannot be retained as an accumulation unless there is a trap, and this requires that the boundary between the cap rock or other sealing agent and the reservoir rock generally be convex upward, but the exact form of the boundary varies widely. The simplest forms are the flat-lying convex lens, the anticline, and the dome, each of which has a convex upper surface. Many oil and gas accumulations are trapped in anticlines or domes, structures that are generally more easily detected than some other types of traps. Some traps are formed by the reservoir rock being cut off at its upper end by a fault that places sealing rock against the fractured end. Alternatively, the upper end may have been eroded away during a period of unconformity, resulting in the subsequent covering of the eroded top of the reservoir rock by a sealing rock. There are also examples in which the reservoir rock wedges out at its upper end as an original depositional feature due to lateral variation in deposition or abuts against an old land surface (stratigraphic trap). Traps associated with salt intrusions are of various kinds; limestone reefs can also serve as reservoir rocks and give rise to overlying traps of anticlinal form as a result of differential compaction. Last, examples are also known in which the reservoir rock extends to the surface of the earth but oil and gas are sealed in it by clogging of the pores by bitumen or by natural cements. Many reservoirs display more than one of the factors contributing to the entrapment of hydrocarbons.

The distinction between a structural trap and a stratigraphic trap is often blurred. For example, an anticlinal trap may be related to an underlying buried limestone reef. Beds of sandstone may wedge out against an anticline because of depositional variations or intermittent erosion intervals. Salt domes, formed by flow of salt at substantial depths, also have created numerous traps that are both a structural trap and a stratigraphic trap.

Alteration of heavy oil and bitumen in the reservoir or deposit is an accepted occurrence. Alteration may be related to the relative instability of the material or to the traps may be susceptible to incursion to chemical agents, such as oxygen. Physical effects, such as those caused when the level of burial of the trap changes as a result of further subsidence or erosion, may also play a role. It is difficult to draw a precise distinction between chemical and physical processes since it is often more than likely that the two “processes” are often interrelated and may even occur simultaneously.

There are wide variations both in the bitumen saturation of tar sand (0% by weight to 18% by weight bitumen) even within a particular deposit, and the viscosity is

particularly high. Of particular note is the variation of the density of Athabasca bitumen with temperature and the maximum density difference between bitumen and water occurs at 70°C to 80°C (160°F to 175°F), hence the choice of the operating temperature of the hot-water bitumen-extraction process.

Heavy oils and bitumen can be assessed in terms of sulfur content, carbon residue, nitrogen content, and metals content. Properties such as the API gravity and viscosity also help the refinery operator to gain an understanding of the nature of the material that is to be processed. The products from high-sulfur feedstocks often require extensive treatment to remove (or change) the corrosive sulfur compounds. Nitrogen compounds and the various metals that occur in crude oils will cause serious loss of catalyst life. The carbon residue presents an indication of the amount of thermal coke that may be formed to the detriment of the liquid products. Thus, initial inspection of the feedstock (conventional examination of the physical properties) is necessary. From this, it is possible to make deductions about the most logical means of refining. In fact, evaluation of crude oils from physical property data as to which refining sequences should be employed for any particular crude oil is a predominant part of the initial examination of any material that is destined for use as a refinery feedstock.

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Biographical Sketch

Dr. Speight has thirty years of experience in areas associated with the properties and processing of conventional and synthetic fuels. He has participated in, as well as led, significant research in defining the use of chemistry of heavy oil and coal. He has well over three hundred publications, reports, and presentations detailing these research activities.

Dr. Speight is currently editor of the journal *Petroleum Science and Technology* (formerly *Fuel Science and Technology International*), editor of the journal *Energy Sources*, and co-editor of the journal *Reviews in Process Chemistry and Engineering*. He is recognized as a world leader in the areas of fuels characterization and development. Dr. Speight is also Adjunct Professor of Chemistry and Adjunct Professor of Chemical Engineering at the University of Wyoming as well as Adjunct Professor of Chemical and Fuels Engineering at the University of Utah.

Dr. Speight is the author/editor/compiler of twenty books and bibliographies related to fossil fuel processing and environmental issues. As a result of his work, Dr. Speight was awarded the Diploma of Honor, National Petroleum Engineering Society, For Outstanding Contributions to the Petroleum Industry in 1995 and the Gold Medal of Russian Academy of Sciences (Natural) for Outstanding Work in the Area of Petroleum Science in 1996. He has also received the Specialist Invitation Program Speakers Award from NEDO (New Energy Development Organization, Government of Japan) in 1987 and again in 1996. Dr. Speight also received the degree of Doctor of Sciences from the Scientific Research Geological Exploration Institute (VNIGRI), St. Petersburg, Russia For Exceptional Work in Petroleum Science in 1997.