EXTRACTION NAPHTHAS: AN HISTORICAL OUTLINE

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Abstract

The development of extraction naphthas in the United States is given, showing types of solvent now used and their advantages. Also, extent of the extraction process in the United States is discussed, showing number of plants in operation.

NATURAL gas and petroleum have been known since earliest times; for example, gas and oil have been seeping from springs around Baku, U.S.S.R., for thousands of years. Sometimes this gas became ignited and burned continuously for years, with "Fire Worshipers" frequenting these "Eternal Fires." The earliest reference to petroleum in North America was during 1632, when the letter of a Franciscan missionary mentioned oil springs at what is now Allegany County, New York. The oil that seeped from these springs in Allegany County and Oil Creek was collected and used by the Indians for medicinal purposes, later being sold as "Seneca Oil."

Although oil had been obtained in shallow wells, one of which was dug by a Mr. Williams, during 1857 at Oil Springs near Enniskillen, Ontario, Canada, the development of the petroleum industry really began with the bringing in of the famous Drake well by Edwin L. Drake, drilling for the Pennsylvania Rock-Oil Company, on August 23, 1859, at Oil Creek near Titusville, Pennsylvania. Drake struck oil at about 69 feet but, with this humble beginning only 78 years ago, literally thousands of wells—over 24,000 in the East Texas field alone—are now producing from great depths, as much as 10,000 feet below the surface in some cases, and the petroleum industry has grown into one of the largest industries in the United States. However, the real large scale development of the industry, with the consequent shifting of the center of activities from the Eastern fields to the Mid-Continent fields, began in 1901 with the bringing in of a large gusher by A. F. Lucas at the famous Spindle Top oil field near Beaumont, Texas.

During the early years of the petroleum industry practically all refining effort was devoted to making medicinals, lubricants, and especially, burning oils or kerosene, namely, oil for the lamps of China and all the rest of the civilized world. During that period the more volatile products, such as those which exist in natural gas and modern gasoline or naphthas, were a decided nuisance to the refiner; there was but very little commercial use for these lighter fractions which came as a by-product in the manufacture of burning oils or kerosenes. However, as time went on and the use of the internal combustion engine came into more and more extensive use, the lighter fractions became of ever increasing importance until today the most important products of the industry from a volume and dollars-and-cents standpoint are motor gasolines or the lighter products of the crude oil. And now, natural gas itself is piped over wide areas and used as a fuel for both domestic and industrial heating purposes. Thus, beginning about 1905, we have seen the position of the more volatile petroleum hydrocarbons change from that of an unwanted waste by-product to that of an extremely important and much desired principal product, the largest use of which is as a fuel.

As knowledge in the art and science of petroleum refining increased, it became possible to prepare closer boiling gasoline or naphtha fractions, possessing more definite drying rates and other properties, which found increasing acceptance in the paint, rubber and other industries as "substitutes" for turpentine, benzol and so forth. Thus, from about 1910, there was gradually developed several special naphthas that were used in industrial processes as solvents and thinners. These early naphthas were of three general types; one was a so-called "mineral spirits" that was used as a turpentine substitute, but it was little more than a good grade of light kerosene; another was a so-called "rubber solvent naphtha" that was used in the rubber industry largely as a substitute for benzol or other solvents, but it was little more than high test low end point motor gasoline; still another was a so-called "VM & P naphtha" or "varnish makers' and painters' naphtha," and it was simply intermediate between mineral spirits and rubber solvent naphtha. Fairly large volumes of special naphthas began to be used in industrial processes but the production and use of motor fuels expanded much more rapidly and, since the manufacturing emphasis was placed upon motor fuels, it is almost needless to say that these early naphthas were of very poor and non-uniform quality.

Although petroleum naphthas did have some inherent advantages, their introduction into industrial processes came about largely because of the urge to have a "cheap substitute" for other solvents. The general refining procedure was to make a naphtha of such specification as to fit into the motor fuel operation as smoothly as possible. Then the refiner would sell as much of it as could be forced upon the trade at an attractive price; the user had very little voice in the matter of naphtha quality, and he simply had to take the naphthas as the refiners offered them whether he liked them or not. But even as indefinite and unsatisfactory as the early naphthas were, the materials often did not measure up to the then existing general specifications, and uniform shipments month in and month out were something often wished for but seldom obtained. This situation began to change about fifteen years ago, one of the first really "special" naphthas developed being a lacquer diluent. But even as late as eight years ago there was not much chance of obtaining an entirely satisfactory extraction naphtha.

With this background of cheapness, side line operation, loose specifications, and non-uniformity, it is no wonder that some of those who experimented with extraction operations obtained such unsatisfactory results that even to this day they are prejudiced against extracted oils and meals and the extraction process generally. However, the story is entirely different today! The once indifferent refiners no longer consider industrial naphthas as a nuisance product or as something to be pushed through as a sort of side line to gasoline production—at least, some of them no longer do. On the contrary, some refiners give the production of special industrial naphthas the preferred position from a manufacturing standpoint, so that it is now possible to obtain pure petroleum solvents with a quality hardly imagined possible fifteen years ago. By using these extra quality naphthas in the modern extraction processes that are available today, truly remarkable results are being obtained in the extraction of animal and vegetable oils and fats, this being especially true in the production of edible oils and meals. So, regardless of unsatisfactory results or experiences that may have been encountered in the past, anyone interested in the production of oils and meals owes it to himself to again investigate the possibilities, when using the extra quality extraction naphthas that are now available.

The processing of oil-bearing seeds and animal products by solvent extraction has been such an active subject and has aroused such intense interest during the past four years, that some people, especially non-technical men, in the oil and fat industry, feel that the solvent extraction process is a recent development which is still in the experimental stage. It is true that the large continuous processes are a development of recent years and it is further true that the batch processes have undergone considerable improvement in recent years, but it should be remembered that there have been literally dozens of solvent extraction plants operating in the United States for many years. However, the great majority of these plants have been placed in operation during the past twenty years and, as a matter of fact, all of the large continuous extraction plants, some of which can process one hundred tons or more daily of soybeans or other products, have been installed during the past five years. There are at present about fifty large extraction plants in the United States, the operations of which are extensive enough to permit tankcar purchases of solvent, and there are some fifty to seventy-five smaller extraction plants which obtain solvent on an l.c.l. drum and tank wagon basis. (This does not include the hundreds of solvent plants throughout the country used in the dry cleaning industry for removing grease or soil from clothing.) Although the extraction process finds application in a variety of industries, such as obtaining rosin and turpentine from pine stumps and boards, obtaining pyrethins from pyrethrum flowers, and so forth, the most of these extraction plants are in the oil and fat or their related industries. Some of these plants for one reason or another use ethylene di-chloride, benzol, etc., but by far the greatest number use petroleum naphthas of one type or another.

Most of the older extraction plants had to be content with the poor quality naphthas which the petroleum industry offered in the beginning of its industrial solvents efforts; these naphthas, as previously mentioned, were of the three following types:

1. High test-low end point gasoline type of 100 to 330° F. general boiling range.
2. Low end point light kerosene type of 300 to 440° F. general boiling range.
3. VM & P naphtha type of 190 to 330° F. general boiling range.

Then about fifteen years ago with the development of light lacquer diluents, as a result of more specialization by the refiners in the production of industrial naphthas, the extraction industry had three distinctly better quality solvents as follows from which to choose. At the same time, the older naphthas were improved from an odor and greasy residue standpoint, by eliminating some of the higher boiling compounds with simultaneous shortenening of the general boiling range.

1. Lacquer diluent type of 200 to 270° F. general boiling range.
2. Low end point type of 140 to 220° F. general boiling range.
3. Light lacquer diluent type of 190 to 240° F. general boiling range.

Each of the foregoing naphthas was and still is made by several refiners in processing ordinary crude oil in conjunction with their motor gasoline, and other regular refining activities, more exhaustive chemical treatment and more careful fractionation of course being employed. Thus, it is now possible to obtain extraction naphthas, which are made directly from crude oil, that are capable of giving generally satisfactory results in producing both animal and vegetable oils. However, extraction naphthas made directly from crude oil usually leave much to be desired because, due to the comparatively large amounts of sulphur, nitrogen and high boiling compounds in the crude oil as well as the fact that comparatively high temperatures are employed in the refining processes, they are likely to have fairly large amounts of sulphur compounds, heavy-greasy compounds, and unsaturated compounds which tend to polymerize or gum during use; therefore, they are likely not to be so good from a stability and an odor and taste standpoint, and to require more steam, time and labor for complete removal of solvent from both oils and meals.

With further improvement in the equipment and operating procedure of the batch extraction processes and with the development during recent years of the large volume continuous extraction processes, the advantage and even necessity of still better quality naphthas became apparent. This demand for purer-better extraction solvents was satisfied by the new narrow boiling range naphthas made from natural gas, which became available in large commercial quantities about seven years ago. Prior to about 1930 no large dependable oil company specialized in the production of extraction naphthas; the naphthas which were used by the various extraction plants simply represented business that was obtained by the oil companies as a sort of side-line to their large scale production of cleaners naphthas, rubber solvent naphthas, VM & P naphthas, and so forth—in fact these extraction naphthas were simply the naphthas that were developed for the larger users in the rubber, lacquer and other industries, and the extraction industries received these better naphthas principally as a matter of luck. The reason for this lack of special interest on the part of the average refiner is simply due to the small volume of extraction naphtha business when compared to other naphtha business. However, with the manufacture of naphthas from natural gas, which permitted a flexible and convenient manufacturing operation on comparatively small volumes, there was at last actual specialization by an oil company in the production of extraction naphthas; this was a revolutionary development, and it meant a lot to the extraction industry because it made available solvents with a quality beyond all previous experience in the petroleum industry.

Thus, the industry has three new solvents to choose from; these solvents, almost needless to say, are just about the last word in extraction naphthas. They are quite stable, being fractions of practically pure paraffin type compounds; they are of unusually narrow boiling range, thereby containing a minimum of extremely volatile compounds along with a minimum of heavy-greasy compounds, and they are exceptionally good from an odor and taste standpoint. These new solvents are as follows:

1. Hexane type of 146 to 158° F. general boiling range.
2. Heptane type of 190 to 208° F. general boiling range.
3. Pentane type of 96 to 138° F. general boiling range.

The consumption of extraction naphthas of all kinds in the United States probably amounts to about three hundred sixty-six 8,000-gallon tankcars or about 2,900,000 gallons yearly, divided about as follows according to general boiling range.

1. 117 tankcars yearly of 146 to 158° F. general boiling range.
2. 71 tankcars yearly of 190 to 208° F. general boiling range.
3. 45 tankcars yearly of 110 to 280° F. general boiling range.
4. 31 tankcars yearly of 145 to 210° F. general boiling range.
5. 27 tankcars yearly of 200 to 266° F. general boiling range.
6. 19 tankcars yearly of 205 to 300° F. general boiling range.
7. 12 tankcars yearly of 305 to 395° F. general boiling range.
8. 10 tankcars yearly of 192 to 208° F. general boiling range.
9. 7 tankcars yearly of 96 to 138° F. general boiling range.
10. 27 tankcars yearly of miscellaneous general boiling range.

There seems no reason to doubt that the petroleum industry will be able to supply these extra quality naphthas for many years to come, so anyone contemplating the installation of an extraction plant can proceed without worrying about the solvent problem.

EXTRACTION NAPHTHAS: GENERAL CHEMICAL COMPOSITION

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Abstract

The complexity of extraction naphthas is discussed, showing names and properties of many hydrocarbon, sulphur, and nitrogen compounds that may occur in solvents and giving some points of advantage and disadvantage concerning them. It is shown that "boiling range" can be very misleading in judging an extraction naphtha.

THE manufacture of oils, fats and meals from both vegetable and animal products by means of the solvent extraction process is becoming increasingly important to the industry and, since using the proper solvent is quite essential for obtaining the most advantageous operating results, this being especially true in the production of edible oils and meals, it is felt worth while to outline some of the general chemical and physical characteristics of petroleum naphthas so that the users can more fully understand the complexity of them and better judge the type of naphtha to use for any given operation.

It has been my observation in talking with men in the oil and fat, as well as other industries, that a good many of them refer to "naphtha" and "boiling range" as though these were something definite. So, to begin with, let us consider some of the generalities applicable to extraction naphthas. "Petroleum naphtha" is simply a general term[1] applied to the more volatile petroleum products and liquid products of natural gas; it can have almost any boiling range, gravity and other properties. The nearest thing to an official definition is that of the American Society for Testing Materials which says "petroleum naphtha" is a generic term applied to refined, partly refined or unrefined petroleum products and liquid products of natural gas, not less than 10 per cent of which distills below 347° F. and not less than 95 per cent of which distills below 464° F.

No two oil pools give petroleum that is exactly alike and no two refiners process the crude oil in exactly the same manner so, even though one may obtain naphthas from two different sources which apparently are "duplicates," it should be remembered that, since petroleum is composed of hundreds if not thousands of different compounds, no two extraction naphthas are exactly the same. One may report them the same as a result of distillation, odor, gravity or other routine laboratory tests, but the only reason why they would check the same is that the test methods are too inaccurate to detect the differences. The difference may or may not be of practical significance in any given case, but it should always be kept in mind that there is a difference in all extraction naphthas.

Petroleum and petroleum products are composed principally of paraffin, naphthene, and olefin hydrocarbons in varying proportions depending upon the particular crude oil and manufacturing process in question. Also, many petroleum products contain large amounts of aromatic[2] hydrocarbons. Also, practically all petroleum products contain small amounts of sulphur and nitrogen compounds.

Nitrogen[3] compounds do not occur in crude oils in large quantities, seldom over 2.5 per cent nitrogen ever being reported; Pennsylvania oils contain about .008 per cent, Rumanian oils about .1 per cent, and California oils about .48 per cent. Nitrogen compounds seem to concentrate in the high boiling fractions, many oils actually evolving ammonia when heated to about 450° F., and it has often been observed about stills when reducing to heavy oils and coke.

It is of course common knowledge that practically all crude oil and natural gas has appreciable quantities of sulphur compounds many of which go on into the finished naphtha to greater or lesser extent. There have been cases where men have been killed by hydrogen sulphide coming from the oil; also, there are mercaptans and other sulphur compounds which occur in petroleum. Table I[4] shows the approximate boiling point of some aliphatic mercaptans, while Table II[5] shows the approximate

TABLE I
SULPHUR COMPOUNDS

Name	Boiling Point
methyl mercaptan	43° F.
ethyl mercaptan	94° F.
n-propyl mercaptan	154° F.
iso-propyl mercaptan	126° F.
n-butyl mercaptan	210° F.
sec-butyl mercaptan	184° F.
n-amyl mercaptan	259° F.
sec-amyl mercaptan	235° F.

TABLE II
SULPHUR COMPOUNDS

Name	Boiling Point
methyl thioether	97° F.
methyl ethyl thioether	151° F.
ethyl thioether	197° F.
methylisopropyl thioether	201° F.
ethyl isopropyl thioether	214° F.
ethyl propyl thioether	241° F.
iso-propyl thioether	248° F.
n-propyl thioether	288° F.
methyl disulphide	245° F.
ethyl disulphide	307° F.†
iso-propyl disulphide	346° F.

†(730 mm.)