

UNITED STATES PATENT OFFICE

2,021,923

PROCESS OF CRACKING
HYDROCARBON OILSArthur E. Pew, Jr., Bryn Mawr, Pa., assignor to
Sun Oil Company, Philadelphia, Pa., a corpo-
ration of New JerseyNo Drawing. Application July 26, 1932,
Serial No. 624,906

4 Claims. (Cl. 196—50)

It is known to crack heavy naphtha, either straight run or cracked, in order to increase its anti-knock or anti-detonating value. By "heavy naphtha" I mean to include the heavy end of gasoline (which may comprise more or less than half of a complete gasoline cut) and also a cut comprising the heavy end of gasoline and a fraction heavier than the heavy end of gasoline, say a cut having an end point of 460–500° F.

Except for the process set forth in my application filed January 19, 1932, Serial No. 587,480, the cracking of heavy naphtha has been effected only in vapor phase, for two reasons. First, it is generally assumed that gasoline produced by vapor phase cracking of any petroleum fraction heavier than light gasoline yields a synthetic gasoline having a higher anti-knock value than synthetic gasoline produced by liquid phase cracking. Second: since a light petroleum fraction of a given stock has a lower critical temperature than a heavy petroleum fraction of the same stock, and since the lighter the fraction the higher the temperature required to crack it, it is generally assumed that it is impossible to effectively crack heavy naphtha except mainly or wholly in vapor phase.

On the other hand, it is well known that the gas losses incident to vapor phase cracking far exceed the gas losses in a well designed and operated liquid phase cracking process and that gasoline produced by vapor phase cracking requires special subsequent treatment for degumming, which reduces its anti-knock value.

Since the issue of my Patent No. 1,825,977, dated October 6, 1931, it is known that, contrary to pre-existing beliefs or assumptions, the critical temperature of petroleum hydrocarbons, and specifically gas oil, undergoing cracking, rises during the cracking operation, whereby it is found possible to heat the oil to just below its critical temperature and as the critical temperature of the oil rises, raise the temperature of the oil to maintain it just below the changing critical temperature, whereby the maximum heat consistent with liquid phase cracking may be applied to the gas oil and a synthetic product produced from which may be fractionated gasoline of high anti-knock value.

In the cracking of heavy naphtha the same phenomenon occurs as in the cracking of gas oil, namely, the critical temperature rises as the cracking proceeds. However, the critical temperature of heavy naphtha, especially straight run heavy naphtha, is so much lower than that of gas oil from the same crude, while the tem-

perature required to effectively crack it is so much higher than that required to crack the gas oil, that it would seem impracticable to crack it substantially in liquid phase.

I have discovered, however, that if the heavy naphtha, while flowing continuously through a pipe coil, be subjected to a pressure much higher than has hitherto been used in commercial plants and is therein subjected to a temperature high enough to effectively crack it, the cracking will proceed at such an increased rate that the critical temperature of the stock will rise more rapidly and to within a higher temperature range than if the pressure be maintained within the lower pressure range within which liquid phase cracking is usually conducted.

I have also discovered that the critical pressure of straight run heavy naphtha is substantially below the critical pressure of the synthetic crude produced by the cracking of such heavy naphtha, and that the critical pressure of any heavy naphtha that may be fractionated from such synthetic crude is substantially below the critical pressure of the synthetic product produced by the cracking of the last named naphtha.

I have also discovered that if the pressure imposed upon the heavy naphtha within the cracking coil is maintained higher than its highest vapor pressure, the critical temperature will rise more rapidly than with a lower pressure and that with a sufficiently high pressure the critical temperature may quickly exceed a highly effective cracking temperature so that cracking may be conducted mainly or wholly below the critical temperature. The most effective pressure is not less than the critical pressure of the synthetic crude produced. At the pressure specified the conversion into vapor (so-called incondensable gas) will be substantially less than ten per cent.

In order that the meaning of the terms herein used may not be misapprehended, it is to be understood that the critical temperature is that temperature above which, irrespective of the pressure applied, a substance which is capable of being converted into a gas cannot be liquefied; and that the critical pressure of such substance is that pressure which will just liquefy the gas of such substance at its critical temperature.

As an example of a heavy naphtha to which the process is applicable I may specify a straight run heavy naphtha derived from East Texas crude having a gravity of 45.5 A. P. I., an initial boiling point of 238° F., an end point of 485° F., and containing about 80% of heavy gasoline having an end point of 437° F., the heavy naphtha having

a critical temperature of 892.4° F. (478° C.) and a critical pressure of about 1375 pounds per square inch. If the same be cracked in a bomb at 900° F. for six minutes at a maximum pressure of 1495 pounds per square inch, the synthetic cracked product has a gravity of 47.1 A. P. I., an initial boiling point of 84° F., an end point of 625° F., and contains about 75% of light and heavy gasoline having an end point of 437° F., the synthetic product having a critical temperature of 923° F. (495° C.) and a critical pressure of about 1800 pounds per square inch.

By running the straight run heavy naphtha through a coil in which the pressure is maintained higher than the highest vapor pressure of the oil, the temperature to which the oil is heated may range upward from 890° F. and gradually increase as the oil progresses through the coil and may much exceed 900° F. and still be maintained below its critical temperature. Indeed the temperature of the oil may be raised to any point within the heat resisting capacity of the metal of which the tubes are composed without exceeding the critical temperature provided the pressure is maintained above the highest vapor pressure of the oil. In order that this pressure may with certainty be maintained, the pressure at the outlet end of the coil should be so regulated that it will not be below the critical pressure of the synthetic cracked product. This critical pressure will vary with different crudes and is never less than about 1250 pounds per square inch, and is usually considerably higher. There is no upper limit to workable pressures except that imposed by engineering limitations and there is no discoverable upper limit to the possible temperature to which the oil under extremely high pressure may be raised without exceeding the critical temperature. It may be said, however, that it is entirely practicable to maintain a pressure so high that the permissible temperature will be within the range common in vapor phase cracking; that is, from 900 to 1000° F.

The critical temperature of the charging stock in case of straight run heavy naphtha, will usually, if not always, be below 900° F. and usually very much below 900° F. My process contemplates the heating of the oil through the necessary temperature range required to heat it to over 900° F. It will be understood, therefore, that in claiming the heating of the oil to a temperature exceeding 900° F. I do not mean to exclude the preliminary heating of the oil through a lower temperature range.

The great advantage of the process is that, as compared with vapor phase cracking, it gives a higher yield of synthetic gasoline with a much smaller production of fixed gases, these being held substantially below 8 or 10% and being often

much lower; the gum content is low if the gasoline be filtered in the vapor phase; there is no necessity for chemical treatment; and the octane number is high and if the distillate be not chemically treated, is not reduced by storage.

The gasoline may be separated from the synthetic cracked product in any known way, one example of which is disclosed in the Pew Patent No. 1,825,977.

Having now fully described my invention, what I claim and desire to protect by Letters Patent is:

1. In the process of producing gasoline by cracking heavy naphtha having a critical temperature within its cracking range but below the temperature at which it can be effectively cracked, which comprises heating a continuously flowing stream of such heavy naphtha to a temperature within its cracking range and so close to but below its critical temperature as to effect a rise in its critical temperature and increasing the temperature of the oil in the flowing stream while still maintaining it under its rising critical temperature, and maintaining the pressure during the cracking procedure not below the highest vapor pressure of the oil so that the critical temperature of the oil will be raised to an efficient cracking temperature and be still maintained below its increased critical temperature.

2. In the process of producing gasoline by cracking heavy naphtha having a critical temperature within its cracking range but below the temperature at which it can be effectively cracked, which comprises heating a continuously flowing stream of such heavy naphtha to a temperature within its cracking range and so close to but below its critical temperature as to effect a rise in its critical temperature and increasing the temperature of the oil in the flowing stream while still maintaining it under its rising critical temperature, and maintaining the pressure during the cracking procedure not substantially below the critical pressure of the synthetic crude produced by the cracking procedure, whereby the critical temperature of the oil will be raised to an efficient cracking temperature and be still maintained below its critical temperature.

3. The process set forth in claim 1 wherein the critical temperature of the heavy naphtha charging stock is below but so close to 900° F. that the critical temperature of the oil under the specified pressure may be raised so far above 900° F. as to be efficiently cracked.

4. The process set forth in claim 2 wherein the critical temperature of the heavy naphtha charging stock is below but so close to 900° F. that the critical temperature of the oil under the specified pressure may be raised so far above 900° F. as to be efficiently cracked.

ARTHUR E. PEW, JR.