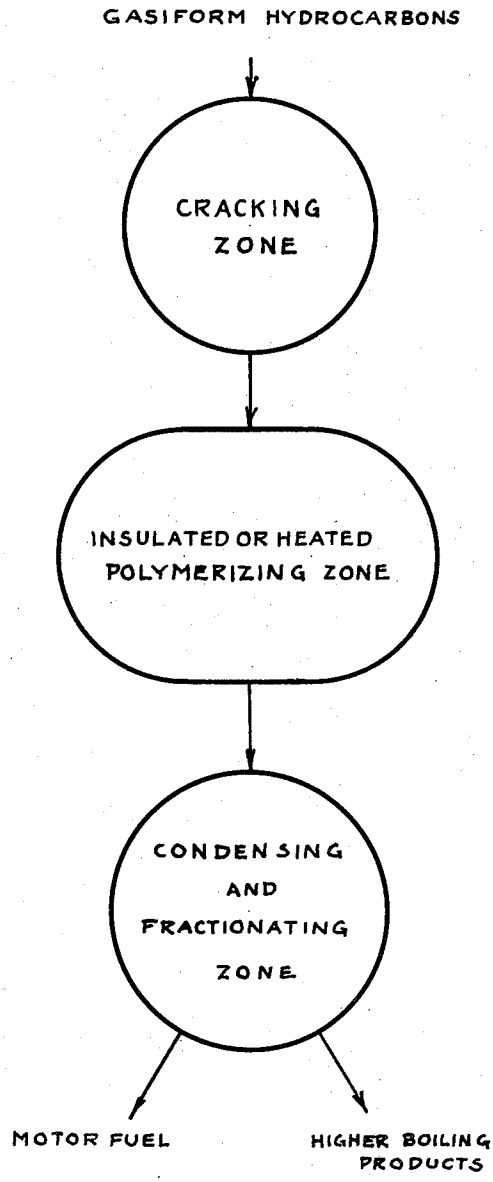
March 10, 1936. R. E. BURK 2,033,878

PROCESS OF ALTERING THE BOILING POINTS OF HYDROCARBONS

Filed Oct. 4, 1930



INVENTOR.

Robert E. Burk

BY

Day, Oberlin & Day

ATTORNEYS.

Patented Mar. 10, 1936

2,033,878

UNITED STATES PATENT OFFICE

2,033,878

PROCESS OF ALTERING THE BOILING POINTS OF HYDROCARBONS

Robert E. Burk, Cleveland, Ohio, assignor to The Standard Oil Company, Cleveland, Ohio, a corporation of Ohio

Application October 4, 1930, Serial No. 486,517

3 Claims. (Cl. 196—10)

If hydrocarbon gases or vapors be heated above the customary cracking temperatures, more or less extensive change in boiling point takes place. Under such conditions cracking or dehydrogenation and polymerization both occur. I have found, though, that these are not consistent in respective optimum conditions, and it is desirable to control each under conditions I find preferable. To the accomplishment of the foregoing and related ends, the invention, then, consists of the features hereinafter fully described and particularly pointed out in the claims, the following description and the annexed drawing setting forth in detail certain embodiments of the invention, these being illustrative, however, of but a few of the various ways in which the principle of the invention may be employed.

In said annexed drawing:

The sole figure is a diagrammatic illustration on the order of a flow-sheet, illustrative of the procedure.

In accordance with my invention, hydrocarbons in gasiform state are subjected to a cracking or dehydrogenation by heating at temperatures above 1500° F., for instance temperatures of 1600°–2100° F. Such heat is desirably applied in a manner to provide efficient heat transfer, and for this, the gas may, for example, be passed through a bank of tubes suitably externally heated. As material for the heating surfaces, it is advisable to avoid predominant iron surfaces. Desirably, alloys may be employed containing chromium, a feasible alloy involving 26–30 per cent. of chromium with the balance iron. Another desirable alloy is made up of 30 per cent. chromium, 9 per cent. nickel, and the balance iron. Surfaces of 70 per cent. or more chromium are likewise desirable where pressure is adequately backed up or is low. Non-metallic surfaces may also be advantageously employed, for instance, sillimanite, alundum, etc.

After this stage of treatment, the products are thence subjected to heat at a lower temperature, for instance 1100°–1750° F. The heat initially attained in the cracking stage may be carried over to a proper extent, if desired, by suitably guarding against serious heat loss, such that the temperature drop occurring will leave the mass within the desired mentioned treating range. The precise temperatures in each of these stages may vary somewhat, depending upon the time factor in treatment; and in general the time of heating may range from 0.05 to one second in the cracking or dehydrogenating stage, and in the second or polymerizing stage the time may be from 0.5 to 15 seconds. In the latter stage it is also desirable that the volume of gas be larger, as compared with the first stage, and larger tubes may be employed. These may, as already indicated, merely be jacketed or lagged against material heat loss; or if desired, they may be separately fired at the indicated temperature range. By operating in continuous flow through a tube-type of apparatus, or at least an apparatus allowing through-flow, more advantageous output may be had, and at the same time a more accurate control is possible.

Either or both of the treating stages may be operated catalytically. For instance, in the cracking or dehydrogenating state it is advantageous to provide contact bodies of catalytic character, for example, ferro-chromium, alumina, etc. These may be provided in granular form, for instance of pea-size, or larger, in any case such as to afford good contact without overblocking of flow. By proper arrangement in the treating passageway or tubes, heating may be attained with a through-put rate which is satisfactory. In the second or polymerization stage, as catalyst, I prefer a hot metallic vapor, as zinc vapor, although alumina may be desirably employed. Zinc vapor I find exercises further a protective action in that the contact time in the polymerization stage may be prolonged without detriment. Zinc vapor also produces a more mobile product.

As a particular illustration of the process: A hydrocarbon gas from a cracking plant, such gas being substantially free of hydrogen, and having about 8 per cent unsaturates, about 50 per cent methane and the balance higher saturates, is passed through a bank of chromium alloy tubes at a temperature of about 1850° F. at a rate to give a contact time of 0.1–0.5 seconds. The gauge pressure may be about fifteen pounds. From the bank of heating tubes, the gaseous material is forwarded to larger tubes guarded against serious heat loss, and functioning as a reaction chamber in which polymerization takes place at a temperature of 1350°–1550° F., with a time of contact of about 1 to 2 seconds. The products are thence forwarded to a collecting and condensing system, preferably with fractionation so as to effect a separation into a cut suitable for motor fuel, and a higher boiling fraction or fractions rich in naphthalene, anthracene, etc.

As another example: Refinery gas is passed through a heating zone at a temperature of about 1625° F., such zone being packed with alumina, and the gas being forwarded at the rate to pro-

vide a contact time of 0.1 to 1 second. The material is then forwarded to a polymerizing zone where it is subjected to a temperature of about 1350°–1550° F., with contact time of one to two seconds, in the presence of zinc vapor. The products thence passed to a condensing system and are fractionated.

Ordinarily, operating pressures may be relatively low, particularly in the first or cracking stage, it being generally unnecessary to exceed fifteen or thirty pounds pressure. Higher pressures, though, may be employed. In the second stage, more pressure is desirable, although it is not essential.

Instead of a hydrocarbon gas, as such, I may also employ vaporized hydro-carbons as raw material. For instance, gas oil or lower boiling fraction may be vaporized, waste oils and residual materials, tars, etc. may particularly well be handled, being vaporized and thus treated, either alone or preferably in association with the gas. And for convenience, any such materials whether gases, vaporized hydrocarbons, or mixtures of gases and such vapors, may be designated as "gasiform". By maintaining an adequate velocity in the treating passages, difficulties from carbon deposit may be avoided. With tubular passages and pressures sufficient to afford active flow, where temperatures are in the neighborhood of 1800° F., it is advisable to maintain a velocity of 500 feet or more per minute. For example, with heating tubes 1½ inches in diameter and gas temperature of about 1850° F., and gauge pressure of 15 pounds, a flow velocity of 540–550 feet per minute is desirable. By an occasional blowout with a mixture of air and steam, the surfaces can in general be kept free from carbon accumulation. By employing a mixture of steam and air, excessive temperature rises by combustion are avoided.

Other modes of applying the principle of the invention may be employed, change being made as regards the details described, provided the features stated in any of the following claims, or the equivalent of such, be employed.

I therefore particularly point out and distinctly claim as my invention:—

1. A process of the character described, which comprises subjecting normally gaseous hydrocarbons to molecular break-down in a temperature zone of 1600–2100° F., then decreasing the temperature of the products but maintaining the temperature above readjustment level of about 1100° F. and transferring the products to another zone, and polymerizing at a temperature of 1350–1750° F.

2. A process of the character described, which comprises subjecting the residual gas from a cracking operation to molecular break-down in a temperature zone of 1600–2100° F., then decreasing the temperature of the products but maintaining the temperature above readjustment level of about 1100° F. and transferring the products to another zone, and polymerizing at a temperature of 1350–1750° F.

3. A process of the character described which comprises subjecting the residual gas from a cracking operation to molecular break-down in a zone at a temperature of 1600–2100° F. while maintaining a flow velocity of about 500–550 feet per minute, then decreasing the temperature of the products but maintaining the temperature above readjustment level of about 1100° F. and transferring the products to another zone, and polymerizing at a temperature of 1350–1750° F.

ROBERT E. BURK.