

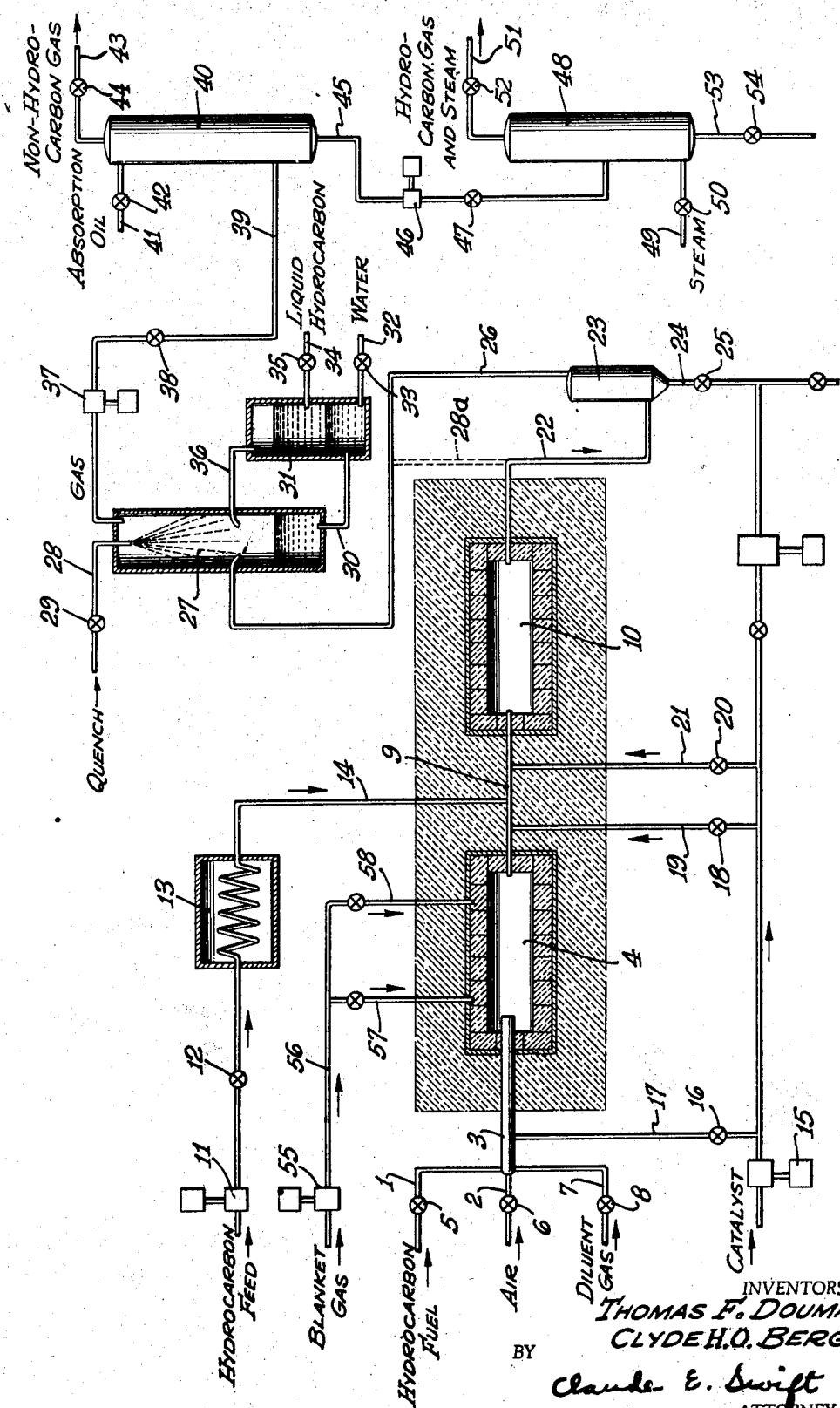
Feb. 12, 1946.

T. F. DOUMANI ET AL

2,394,849

PROCESS FOR TREATING HYDROCARBONS

Filed Aug. 11, 1942



UNITED STATES PATENT OFFICE

2,394,849

PROCESS FOR TREATING HYDROCARBONS

Thomas F. Doumani and Clyde H. O. Berg, Long Beach, Calif., assignors to Union Oil Company of California, Los Angeles, Calif., a corporation of California

Application August 11, 1942, Serial No. 454,384

8 Claims. (Cl. 196—67)

This invention relates to a process for the thermal treatment of hydrocarbons. More specifically the invention relates to the thermal treatment of hydrocarbons in the presence of hot spent combustion gases.

It is the object of our invention to provide improvements in the process of thermal treatment of hydrocarbons in the presence of hot spent combustion gases, whereby we are able to produce unusually high yields of products, such as mono-olefins, di-olefins (such as for example butadiene), aromatics and many other valuable hydrocarbons from charging stock which is largely paraffinic or naphthenic in character and may be normally gaseous or liquid.

The process of our invention comprises burning hydrocarbon fuel to obtain spent fuel gas having a temperature above about 2000° F.; mixing this hot spent fuel gas with the hydrocarbons to be treated and with fluid catalysts, if desired; passing this mixture to a reaction zone; suddenly lowering the temperature of the mixture to a point where no further reaction or conversion of the hydrocarbons being treated takes place; and separating the desired fraction from the product.

The invention resides in the use of relatively high temperatures, short contact times, low partial pressures of hydrocarbon, and rapid quenching of hot products; the use of a "blanket" gas to protect the refractory linings of the hot zones; the use of fluid catalysts and their regeneration in the combustion zone; the elimination of nitrogen in the combustion gas; the use of an excess of oxygen in the combustion mixture; the use of extremely high gas velocities to prevent excessive carbon deposition; and the pre-heating of the hydrocarbon feed to an incipient cracking temperature, with or without the presence of diluents or recycled materials.

Referring to the figure, hydrocarbon fuel and air are admitted through lines 1 and 2 to burner 3 which leads into combustion zone 4. The proportions of hydrocarbon fuel and air may be adjusted by means of valves 5 and 6 so that when the fuel is burned the resulting combustion gases contain a minimum amount of free oxygen. A diluent such as water, steam or spent combustion gases may be introduced as through line 7 controlled by valve 8, in order to maintain the temperature in combustion zone 4 at the desired value.

The combustion gases leaving zone 4 pass through line 9 into reactor zone 10. During their passage through line 9 they are mixed with hy-

drocarbon feed which is introduced through pump 11, valve 12, preheater 13, and line 14.

When a fluid catalyst is used, it is introduced through pump 15 either into burner 3 (as through valve 16 and line 17) or into line 9. In the latter instance, it may be introduced either before junction with line 14 (through valve 18 and line 19) or after junction with line 14 (through valve 20 and line 21) as desired. The gases leaving reactor 10 are then passed through line 22 to separator 23 in which the solid catalyst is separated and drawn off through line 24 and valve 25 for reactivation and reuse. The gas passing through separator 23 is then passed through line 26 to quenching zone 27. When no catalyst is used in the process the gases from reactor 10 are passed through line 28a directly to line 26 and quenching zone 27.

A spray of a quenching medium is introduced into zone 27 through line 28 controlled by valve 29. This quench may be water, gasoline, or any other hydrocarbon fraction. The liquid product gathers in the bottom of zone 27 and is passed through line 30 into settling zone 31. If water is used as a quenching means it will stratify with the water condensed from the combustion gases as a lower liquid layer in zone 31 and may be drawn off through line 32 and valve 33. The liquid hydrocarbon product may then be drawn off through line 34 and valve 35. The pressure on settling zone 31 is equalized with that in zone 27 by means of vapor line 36.

The gas fraction leaving the top of zone 27 passes through pump 37 (which may act as a compressor), valve 38 and line 39 to absorber 40. In the absorber, it contacts an absorption oil introduced through line 41 and valve 42 and is separated into two fractions, one a non-hydrocarbon gas fraction which may also include hydrogen and methane if desired, and which is taken off through line 43 and valve 44, and the other a hydrocarbon fraction which passes with the absorption oil through line 45, pump 46 and valve 47 to stripping column 48. Steam may be introduced into stripping column 48 through line 49 and valve 50 and the mixture of hydrocarbon gas and steam may be taken overhead through line 51 and valve 52, thereafter to be separated into the desired fractions by conventional methods. The absorption oil is drawn off the bottom of stripper 48 through line 53 and valve 54 and may be recycled to the absorber.

In order to protect the refractory with which combustion zone 4 is lined, by preventing outward diffusion of combustion gases, it has been found

desirable to introduce a blanket gas through pump 55 and line 56 into the steel shell of combustion zone 4 behind the refractory lining. This gas may be introduced at multiple points as illustrated by lines 57 and 58. The pressure on this gas is 5 desirably slightly in excess of the combustion zone pressure, causing a slow flow of gas through the refractory.

In a specific example of our non-catalytic process, a hydrocarbon fuel gas having a heating value of about 950 B. t. u. per S. C. F. (standard cubic foot) was introduced into burner 3 at a rate of about 90 S. C. F. (about 4 lbs.) per hour, together with about ten times this volume of air, and about 6 lbs. (120 S. C. F.) per hour of steam. 10 The combustion of this gas maintained a temperature estimated as about 3500° F. in zone 4. A hydrocarbon feed comprising a 170° F. to 380° F. boiling range gasoline fraction from Los Angeles Basin crude, and having a gravity of about 20 52° A. P. I. and a sulfur content of about 0.05% by weight, was preheated to about 1100° F. and introduced through line 14 at a rate of about 3.4 gallons (22 lbs.) per hour. The hydrocarbon feed and combustion gases were mixed in line 9 25 and passed to reactor 10 where they remained at a temperature of about 1500° F. and a pressure of about 12 lbs. per square inch gage for a period of about 0.2 second. The exit gases were immediately quenched with a water spray in zone 21 to a temperature of about 115° F. The hydrocarbon liquid product withdrawn from settling zone 31 through line 34 was emulsified and the 30 yield of this product was estimated at about 7% of the weight of the hydrocarbon feed. About 35 93% of the feed stock was converted to gases which were taken off at the top of quenching zone 27, mixed with the combustion gases. The C₄ fraction (containing only those hydrocarbons having 4 carbon atoms) recovered from this mixture by absorption and distillation consisted of approximately 66% butadiene, 32% butenes and 2% butanes, and totaled about 8% by weight of the feed. Ethylene and propylene were obtained also, in yields of about 14% and 8% of the feed, respectively. Hydrocarbons having more than 4 carbon atoms were recovered from the gas fraction in a yield of about 18% of the feed, making the total yield of product having over 4 carbon atoms about 25% of the feed. This product contained appreciable amounts of isoprene and other diolefins, and consisted principally of olefinic and aromatic type hydrocarbons.

In a second example employing the same apparatus, about 80 S. C. F. of the same fuel gas was burned per hour with the theoretical quantity of air, adding only about .8 lb. of steam per hour. The same hydrocarbon feed stock was preheated to a temperature of about 920° F., and introduced into the hot combustion gas stream at a rate of about 7.7 gallons per hour. The reactor temperature was maintained at a temperature of about 1250° F. and a pressure of about 13 lbs. per square inch gage, the contact time again being about 0.2 second. The exit gases were again quenched with water to a temperature of about 115° F.

The yield of butadiene in this instance was about 1.5% of the hydrocarbon feed (45% by weight of the C₄ hydrocarbon product) with yields of ethylene, propylene and butylene of about 2, 3, and 2% by weight of the feed, respectively. The total of hydrocarbons having more than 4 carbon atoms recovered from both gas and liquid products amounted to about 80% of the weight of the

feed stock. This product contained appreciable amounts of diolefins, and large amounts of olefin and aromatic-type hydrocarbons.

The operating conditions are critical in many respects as indicated by the following description of the apparatus and the limiting operating variables.

The combustion chamber may be operated at temperatures between about 2000° and 5000° F. using a liquid or gaseous fuel. In order to achieve the higher temperatures, preheaters on the hydrocarbon fuel and air lines 1 and 2 may be required. For the lower temperatures, diluent gases such as steam or spent combustion gases are introduced in the required quantity through line 7.

The combustion chamber is designed as a steel shell with a high temperature lining such as fire brick and carborundum. This lining may be protected by the use of a blanket gas as described earlier. In the apparatus employed in the above examples, the burner was a surface combustion type burner described in Bulletin PR-38 of the Surface Combustion Corporation of Toledo, Ohio, page NL-5. It was Tunnel Burner No. 1302. This burner was inserted for a distance of about 9 inches into the combustion chamber, which had a length of about 9 inches (beyond the burner tip), and a volume of about 28 cubic inches. In the later work, smaller combustion zones have been employed, one for example, having a length of only about 3 inches, and a volume of about 9 cubic inches. In the latter apparatus, the hydrocarbon feed entering through line 14 is injected practically into the burner "flame" or combustion zone.

The design of the mixer or that portion of line 9 adjacent to its intersection with line 14 is rather critical. In the apparatus used in the examples cited, line 9 was a tube made of carborundum and was of approximately 1/2 in. inside diameter. At the point of junction with line 9, line 14 which was a stainless steel line, had an internal diameter of approximately 1/8 in. Under the conditions existing in the first example above, the mass velocities of the gases in the constricted portions of lines 14 and 9, before intersection with line 14, respectively, were approximately 250,000 and 75,000 pounds of gas per square foot of cross section per hour, respectively. In an earlier operation in which lower mass velocities were used, (about 20,000 pounds per square foot per hour in each of the above lines) there was appreciable carbon deposition in the equipment and even in the product. It is desirable in larger plants to employ correspondingly larger equipment, but to maintain a gas mass velocity in the constricted portion of line 9 between 25,000 and 500,000 pounds per square foot per hour with a corresponding mass velocity in the constricted portion of line 14 at least double that in line 9. These high mass velocities are effective in preventing excessive carbon deposition and in providing good mixing. The constricted portion of line 9 between line 14 and reactor 10 need only be long enough to ensure thorough mixing (about 6 to 20 diameters) and may be considered as part of the reactor.

The reactor 10 is built in approximately the same manner as combustion zone 4, its size being sufficient to allow contact times of 0.005 to 5.0 seconds, preferably below 1.0 second when no catalyst is employed. The temperature and pressure to be used in the reactor will depend on the type of product desired. In general, tempera-

tures between 1000° F. and 2000° F. are suitable although temperatures of 1300° F. to 1600° F. are preferred, with pressures ranging from atmospheric to approximately 100 lbs. per square inch. The lower temperatures are used where high yields of liquid product are desired, this being essentially a thermal or catalytic reforming operation, and the higher temperatures are more suitable for production of highly unsaturated materials, low boiling materials, and aromatic type hydrocarbons. The latter processes may be called deep cracking, dehydrogenation or aromatization processes. The contact time is desirably shorter at the higher temperatures and at higher partial pressures of hydrocarbon in the reaction mixture. The pressures indicated above are total pressures, the partial pressure of the hydrocarbon gas (calculated as moles of hydrocarbon feed divided by the total moles of hydrocarbon feed plus the combustion gas and diluent gas, times the total pressure) being generally much lower, preferably below atmospheric. The partial pressure of the hydrocarbon may be controlled independently of the reactor temperature by regulating (1) the amount of diluent gas introduced through line 7 (2) the amount of nitrogen introduced with the air or oxygen entering through line 2, or (3) the degree of preheating of the hydrocarbon feed.

Preheater 18 may be replaced or augmented by a feed preheater system located in or around the combustion or reaction zones to utilize the heat liberated in these zones.

In quenching zone 27 either water or a hydrocarbon oil may be used. In the mode of operation indicated in the example, water was used in a sufficient amount to reduce the temperature of the effluent gas well below 200° F. in order to condense substantially all of the water. It may be advantageous in some instances, however, to quench the exit gases from reactor 16 only to a temperature of about 600° F., or a temperature sufficiently low to prevent further reaction, cooling the product mixture thereafter by heat interchange to the temperature desired for the separation of the gases, hydrocarbon liquids and aqueous liquid phase as above. A portion of the liquid hydrocarbon product may be used as a quench. This has beneficial effects on the octane number or gum stability of the liquid product in many instances.

The separation and purification of the desired products need not be carried out as indicated in the figure. As indicated above, where one of the desired products is butadiene, this material may be recovered either from the liquid hydrocarbon phase or from the gaseous hydrocarbon phase or both. The process of recovery of this or other desired products may be one of the simple distillation or extraction or absorption processes or combinations of these processes which are known by those skilled in the art.

If desired, oxygen may be used rather than air in the burner. This has the advantage that no nitrogen would be included in the combustion gases and these gases would then consist almost exclusively of carbon dioxide and water. These may be separated from the product hydrocarbons by a system of condensation and extraction, rather than the absorption system indicated in the figure.

The liquid hydrocarbon product may be treated to remove aromatic type hydrocarbons or other desired fractions as by fractionation, extraction or azeotropic distillation and the residue recircu-

lated with the hydrocarbon feed. Part or all of the liquid hydrocarbon product may also be recirculated with the hydrocarbon feed, without preliminary removal of the aromatics. This increases yields of desirable products.

Recycling of part of the gaseous product such as ethylene, for example, is beneficial in increasing the yield of butadiene, butenes and aromatic hydrocarbons. Other hydrocarbon gases have a similar effect. They may be returned to the reactor together with the feed, or introduced into the combustion zone. It is similarly desirable, particularly when a gaseous fuel is used, to introduce an excess of fuel over that required for combustion.

It has been found desirable in some instances to use as much as 50% excess of air or oxygen in the combustion mixture over that theoretically required for complete combustion. The excess air acts as a diluent to control the temperature of the combustion zone, and the excess oxygen reacts with a portion of the hydrocarbon feed and appears to initiate desirable reactions or accelerate reaction rates.

Normally the hydrocarbon feed is preheated to a temperature between 500° F. and 1500° F. Somewhat improved conversions are obtained in some instances by preheating to a cracking temperature which may vary from about 800° F. to about 1500° F., being higher for the lower boiling hydrocarbons, in general.

The hydrocarbon feed stock may be liquid or gaseous, as stated earlier, and may contain considerable amounts of olefinic and aromatic type hydrocarbons. Higher boiling aromatic hydrocarbons may be stripped of side chains, for example, and converted to lower boiling aromatic hydrocarbons, in our process.

The catalysts which may be used in this process are those which retain an active, generally non-crystalline form, at the temperatures employed. Magnesia and vanadium trioxide, for example, are suitable for use throughout the above specified reactor temperature ranges. Certain silicates and metallic oxides are suitable in the lower part of this temperature range. These catalysts may be introduced in suspension in the hydrocarbon fuel when a liquid fuel is used. They may also be injected as dry powders into the hydrocarbon feed line 14 or into any of the lines 17, 19 or 21 as indicated in the figure. Lower reaction temperatures and longer contact times are generally used when catalysts are present. Introduction of the catalysts into the hot combustion gases, as through line 17, has the advantage that regeneration of spent catalysts may be accomplished in this combustion zone in some instances.

The catalyst separator 23 may be an electric Cottrell type precipitator or may be one of the "Cyclone" or mechanical types. This separator may be placed after the quenching zone if a high temperature such as 300° to 600° F. is maintained in this zone and no condensation of liquid is realized.

Other minor modifications of the above described process, which are apparent to those skilled in the art may be made, without exceeding the scope of the invention as claimed. For example, interchangers may be employed to achieve heat economies, a flash drum may be used in the feed line following the preheater, steam or gas may be added to the feed, the combustion

and reaction zones may be encased in a single shell, etc.

We claim:

1. A process for hydrocarbon conversion, comprising burning a mixture of spent finely divided solid catalyst and hydrocarbon fuel to obtain a mixture of regenerated catalyst and spent combustion gas containing substantially no excess oxygen; mixing this combustion gas mixture having a temperature of 2000° to 5000° F. with a hydrocarbon feed stock preheated to a temperature of 500° to 1500° F.; maintaining this mixture at a temperature of 1000° to 1800° F. and a pressure of 0 to 100 lbs. per square inch gage for a period of 0.1 to 5.0 seconds; suddenly quenching the reaction products to a temperature below 600° F.; separating the spent catalyst and desired conversion products; and recycling the spent catalyst to the combustion zone.

2. A process according to claim 1 in which additional catalyst is injected into a portion of the reaction zone.

3. A process according to claim 1, in which additional catalyst is introduced into the hydrocarbon feed line.

4. A process according to claim 1, in which the catalyst is introduced by suspension in a liquid fuel.

5. A process according to claim 1, in which the reaction products are quenched to a temperature below 600° F. without condensation, before separation of the solid catalyst.

6. A process according to claim 1 in which the catalyst is a metal oxide.

7. A process for hydrocarbon conversion, which comprises burning a mixture of spent finely divided solid catalyst and hydrocarbon fuel in a combustion zone to obtain a suspension of regenerated catalyst in spent combustion gas; mixing the said suspension with a preheated hydrocarbon feed stock and thereby heating the feed stock to a reaction temperature between about 1000° F. and 1800° F. for a reaction period less than about five seconds; quenching the reaction products to a temperature sufficiently low to prevent further reaction; separating spent catalyst and desired conversion products; and recycling spent catalyst to the combustion zone.

8. A process according to claim 7 in which a gasoline feed stock is employed and butadiene is produced.

THOMAS F. DOUMANI.
CLYDE H. O. BERG.