

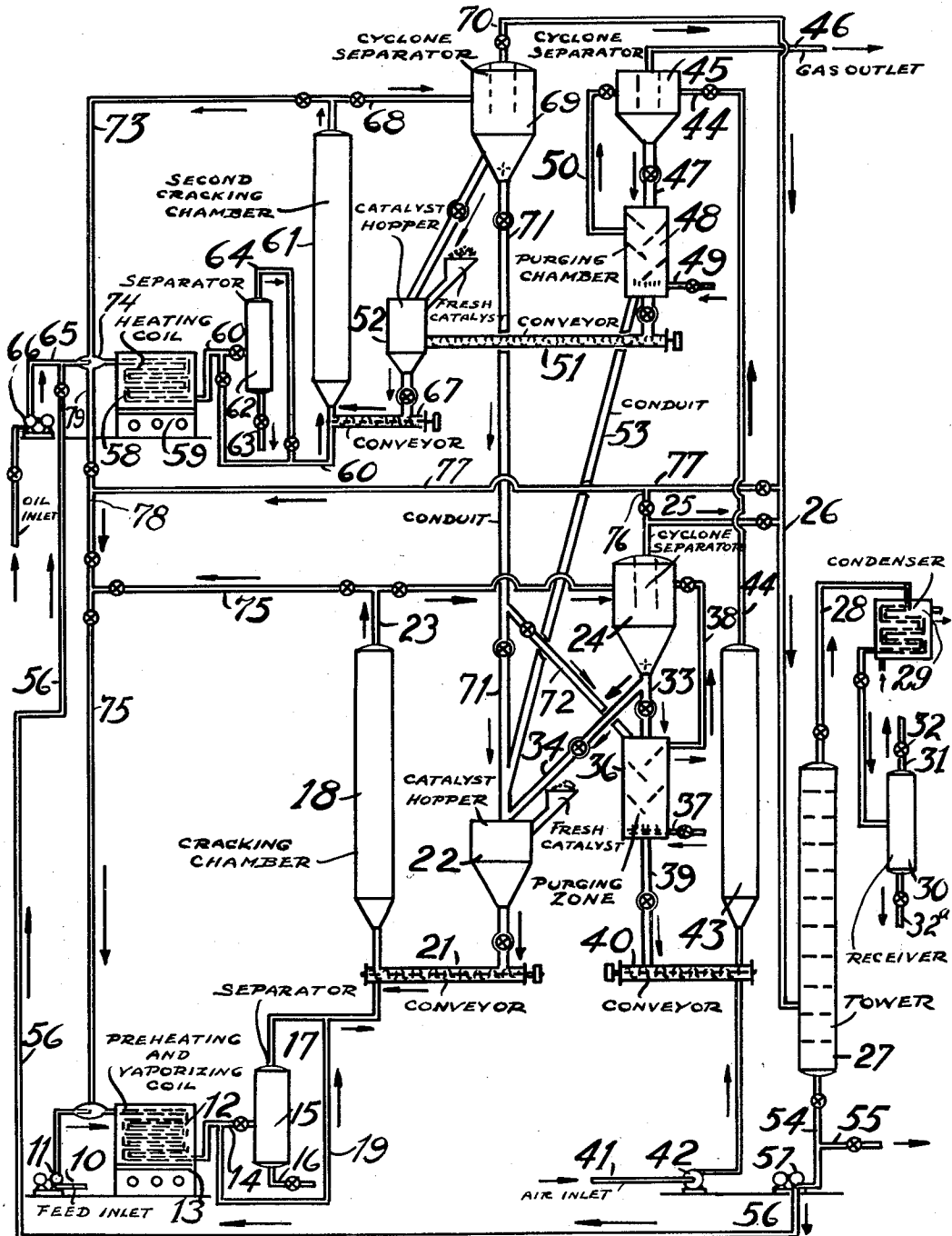
Sept. 22, 1942.

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2,296,722

CRACKING OF HYDROCARBON OILS

Filed Aug. 26, 1939



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UNITED STATES PATENT OFFICE

2,296,722

CRACKING OF HYDROCARBON OILS

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Application August 26, 1939, Serial No. 292,002

4 Claims. (Cl. 196—52)

This invention relates to the cracking of hydrocarbon oils to form lower boiling motor fuel, and pertains more particularly to the cracking of such oils wherein a powdered catalyst is suspended in the oil to be cracked and the suspension passed through the cracking zone.

It has heretofore been proposed to crack higher boiling oils into lower boiling products suitable for motor fuel in the presence of adsorptive cracking catalysts such as activated clays, synthetic gels having similar chemical components and the like.

According to one mode of operation, the oil to be cracked, preferably in vapor form, is passed through a cracking zone containing a bed, or a plurality of beds, of catalytic material. During the cracking operation the catalyst mass rapidly becomes fouled with carbonaceous deposits which reduces the activity of the catalyst and necessitates frequent regenerations to restore the catalyst activity. In such operations, it is necessary to interrupt the cracking operation in order to attain the regeneration. This involves stopping the cracking operation, purging the reaction chamber of volatile hydrocarbons, regenerating the resulting catalyst mass, purging the reaction chamber of regenerating gases and the return to the cracking cycle.

It has been observed that when operating such a process, an excessive amount of low-grade products such as coke and gas is formed at the very beginning of the cracking cycle such as at the first minute or two of operation. In other words, during the early part of the cracking cycle a large portion of the oil treated is degraded to coke and gas with little, if any, formation of gasoline. While the explanation for this is not fully established, there is reason to believe that it is due to the fact that the initial oil vapors contact an excessive amount of catalyst and consequently become over-cracked to gas and coke. As the cracking operation continues the deposition of coke tempers the activity of the catalyst so that the tendency of the oil to overcrack diminishes as the cracking operation continues. For example, assume that the operation is carried out with a feed rate in proportion to the amount of catalyst contained in the reaction chamber of 1.2 volumes of liquid oil per volume of catalyst per hour. During the first minute and for each minute thereafter .02 volume of oil is treated by the total volume of catalyst. This small volume of oil treated in proportion to the amount of catalyst contained in the reaction chamber may explain why excessive overcracking occurs during

the initial part of the cycle when the catalyst is most active.

It has also been proposed to suspend the catalyst in the oil vapors to be cracked and to pass the suspension through a cracking zone. When operating in this manner the resident time of both the catalyst and the oil vapors within the cracking zone is substantially the same and any given quantity of oil vapors can be treated with a definite, fixed quantity of catalyst. In this case the tendency of the oil to overcrack can be controlled by regulating the amount of catalyst added to the oil stream and the resident time of the suspension within the cracking zone.

While this method of operating makes it possible to more effectively control the tendency of the oil to overcrack with resulting excessive degradation of feed stock which is inherent in processes wherein the oil vapors pass through a stationary mass of catalyst, such mode of operation, when carried out according to previous practices, is subject to other disadvantages.

For example, when operating in such manner it has been the practice to pass the suspension of powdered catalyst and cracked products issuing from the cracking zone through separators to remove the catalyst particles. According to previous practices, the powdered catalyst so removed was regenerated, and returned to the cracking zone. If the catalyst is regenerated each time it passes through the cracking zone a large amount of regenerating equipment is necessary for a cracking unit of commercial capacity due to the large number of regenerations to which the catalyst is subjected in a given time. Furthermore, there is a tendency for the catalyst to lose its activity at a faster rate as the number of regenerations to which it is subjected in a given time is increased.

One of the principal objects of the present invention is to provide a process of the type last mentioned which will not be subject to the disadvantages just mentioned.

A further object of the invention is to provide a method of cracking oil with powdered catalyst wherein the number of regenerations of the catalyst can be reduced and controlled as desired.

Another main object of the invention is to provide a process for cracking hydrocarbon oil wherein the inherent activity of the catalyst can be utilized to better advantage. Other objects and advantages of the invention will be apparent from the more detailed description hereinafter in which reference will be made to the accom-

panying drawing which is a partly schematic and partly diagrammatic illustration of an apparatus capable of carrying the invention into effect.

Referring to the drawing, the reference character 10 designates a feed line having a pump 11 through which the oil to be cracked is introduced into the system. The oil treated may be a clean, condensate stock such as virgin gas oil, or a residual stock such as topped or reduced crude. The oil introduced through the feed line 10 is forced by means of pump 11 through a preheating and vaporizing coil 12 located in furnace 13. The oil during its passage through heating coil 12 is preferably heated to a temperature sufficient to vaporize a large percentage of such oil. The outlet temperature of the heating coil may, for example, be in the neighborhood of from 700° F. to 950° F., depending upon the characteristics of the feed stock.

The oil, after passing through the preheating coil 12 is transferred through transfer line 14 to a separator 15 wherein vapors separate from unvaporized residue. If desired, steam or other stripping gas may be introduced with the oil or into the separator 15 for assisting in the vaporization of the oil. Unvaporized residue separated in the separator 15 may be withdrawn therefrom through line 16 and rejected from the system. Vapor liberated in the separator 15 is removed therefrom through line 17 and passed to a cracking chamber 18. In cases where clean condensate stock is employed, the separator 15 may be omitted or the product may be by-passed around the separator through line 19.

In accordance with the present invention there is introduced into the vapor stream passing to the reaction chamber 18 a powdered cracking catalyst. According to one of the more specific phases of the invention the powdered catalyst so introduced is an unregenerated catalyst which has previously passed one or more times through the same or different cracking unit. In the preferred embodiment of the invention, such unregenerated catalyst is that which has previously been employed for treating a more refractory oil or an oil which is more difficult to crack than the fresh feed charged to the unit through line 10. Such refractory oil may, for example, comprise a cycle stock from the same or different cracking unit.

The catalyst may comprise, for example, natural or activated clays, synthetic compounds having similar chemical components and the like.

Referring to the drawing, the powdered catalyst is injected into the oil vapor passing to the reaction chamber 18 by means of a suitable feeding mechanism such as through screw conveyor 21 into which catalyst is fed from the hopper 22.

The relative amounts of powdered catalyst and oil vapor passing to the reaction chamber 18 may vary over a substantial range depending upon the activity of the catalyst, the characteristics of the feed stock, the time of contact of the suspension within the reaction zone and other factors. In general, the ratio of catalyst to oil should be in the order of from 0.3 to 20 parts of catalyst per part of oil by weight, preferably between 0.5 and 3 parts of catalyst per part of oil.

The oil vapor catalyst suspension is passed through the cracking chamber 18 at a rate sufficient to maintain the catalyst in suspension. For illustrative purposes, the cracking chamber 18 is shown in the form of a vertical tower hav-

ing a conical bottom although it may take any other desired form such as, for example, an elongated coil, horizontal chamber or the like. The reaction chamber may be heated if desired to offset radiation losses or to introduce heat into the suspension.

The suspension of cracked products and catalyst after passing through the reaction chamber 18 is passed through line 23 to a suitable solid gas separator such as a cyclone separator 24 in which the powdered material is separated from the cracked vapor. It is preferred to operate the separator at a temperature sufficient to avoid any substantial condensation of the cracked products therein so that the powdered catalyst so separated can be removed therefrom in a relatively dry form. While a single cyclone separator has been shown in the drawing for purposes of simplicity, it will be understood that additional ones may be provided for effecting substantially complete removal of the powdered material from the cracked vapors. The cracked products, after separation of the solid catalyst therefrom, are passed overhead from the cyclone separator 24 through lines 25 and 26 to a fractionating tower 27 in which the vapors are subjected to fractionation to condense constituents boiling above the desired motor fuel. Vapors remaining uncondensed in the fractionating tower 27 are removed therefrom through line 28 and may be passed to a condenser 29 in which the desired liquid distillate is condensed. Products from the condenser 29 may be then passed to a receiver 30 wherein normally gaseous products formed in the cracking operation may be segregated from liquid distillate. The gases so separated may be released from the system through line 31 having a valve 32 for imposing the desired back pressure on the system. Liquid distillate collected in the receiver 30 may be withdrawn therefrom through line 32a as a final product of the process.

Returning to the cyclone separator 24, the solid catalyst separated from the cracked product therein is withdrawn from the cyclone separator through conduit 33. If desired, a portion of the catalyst so withdrawn may be returned directly to the catalyst hopper 22 for return to the cracking zone through conduit 34, or a part or all of the catalyst from the cyclone separator 24 may be passed through the line 35 to a purging zone 36 in which volatile hydrocarbons are removed from the catalyst in any suitable manner such as by steam stripping or by evacuation of the purging chamber. For example, steam may be introduced into the purging chamber 36 through line 37 for steam stripping the catalyst contained therein. The stripping gases may be released from the purging chamber 36 through line 38 and introduced into the cyclone separator 24. The catalyst, substantially free of volatile hydrocarbons, is then removed from stripping chamber 36 through conduit 39 leading to a suitable transfer mechanism such as screw conveyor 40 which feeds the catalyst into a stream of regenerating gas containing oxygen introduced into the system through line 41 and blower 42. The suspension of catalyst and regenerating gas is then passed through a regenerating chamber 43 maintained at a temperature sufficient to ignite the carbonaceous deposits on the catalyst formed during the cracking operation. It is ordinarily desirable to control the temperature during regeneration in order to avoid reducing the activity of the catalyst. For example, in

connection with naturally active or activated clays, the temperature of the regenerating zone should be maintained below 1200° F. and preferably below 1000° F. Generally the temperature within the regenerating zone can be readily controlled due to the relatively low concentration of carbonaceous deposits on the catalyst. In some cases, however, it may be desirable to regulate the oxygen concentration of the regenerating gas or to provide suitable cooling means, such as heat exchangers, within the regenerating chamber to control the temperature.

The catalyst is maintained in suspension in the regenerating gas within the regenerating chamber 43 for a period to remove the carbonaceous deposit formed on the catalyst from the cracking operation.

The suspension of regenerating gas and catalyst passes from the regenerating chamber 43 through line 44 to a suitable solid-gas separator such as cyclone separator 45 in which the regenerated catalysts are separated from the regenerating gases. The regenerating gas, after separation of the powdered catalyst therefrom, may be rejected from the system through line 46.

The regenerated catalyst may be removed from the separator 45 through a conduit 47 leading to a purging chamber 48 in which the regenerated catalyst is stripped of oxygen. To this end steam may be introduced into the purging chamber 48 through line 49 and the purge gases vented to the cyclone separator 45 through line 50.

According to one phase of the invention, the regenerated catalyst is utilized for cracking an oil which is more refractory and more difficult to crack than the oil charged to the heating coil 12. Such oil may comprise, for example, cycle stock segregated in the fractionating tower 27 as hereinafter described. When operating in this manner, the regenerated catalyst is fed by means of a screw conveyor 51 to a catalyst hopper 52 serving a separate cracking unit processing cycle stock as later described.

If desired, however, a part or all of the regenerated catalyst may be returned to the hopper 22 through valved conduit 53. It will be understood that it is also within the purview of the present invention to operate with a single cracking circuit in which a part of the catalyst is recycled to the same circuit. For example, if the recycle circuit is out of operation or not employed, all the regenerated catalyst can be passed to hopper 22 for return to the fresh oil circuit.

Returning to the fractionating tower 27 in which the cracked products are fractionated, the condensate formed in the fractionating tower 27 is withdrawn therefrom through line 54 and may be rejected from the system through line 55. According to one of the specific phases of the present invention, however, a part or all of the condensate formed in the fractionating tower 27 is passed through lines 54, 56, and pump 57 to the inlet side of heating coil 58 located in furnace 59. The oil passing through the heating coil 58 is heated to a temperature sufficient to vaporize the oil. Vapors from the heating coil 58 may be then passed through transfer line 60 to a second cracking chamber 61. In case the oil passing to the heating coil 58 contains unvaporizable constituents, the products from the heating coil 58 may be passed to separator 62 wherein unvaporized residue may be dropped

out of the oil stream and removed from the separator through line 63. In such case, the vapors liberated in the separator 62 pass overhead through line 64 which merges with line 60 leading to the cracking chamber 61.

If desired, fresh oil from an extraneous source may be fed to the heating coil 58 through line 65 and pump 66.

Before passing to the cracking chamber 61 there is injected into the oil vapors to be cracked fresh or regenerated catalyst from hopper 52. Such catalyst may be introduced into the oil vapor through a suitable feeding mechanism such as a screw conveyor 67. The suspension of oil vapors and catalyst is passed through the cracking zone 61 at a velocity sufficient to maintain the catalyst in suspension within the vapors. The length of the cracking chamber and the velocity of the suspension should be controlled to give the required contact time to obtain the desired cracking of the oil into gasoline. The time required for the passage of the suspension through the cracking chamber 61 may range from one second up to a minute or two depending upon the desired conversion, the characteristics of the feed stock, the temperature and other factors. The cracking zone should be maintained above active cracking temperature such as from 750° F. to 1000° F.

The suspension of the cracked product and catalyst after passing through the cracking chamber 61 is transferred through line 68 to a suitable solid-gas separator such as cyclone separator 69 wherein the powdered catalyst is removed from the oil vapors. The separator 69 is also preferably maintained under a temperature which will avoid any substantial condensation of cracked products. The cracked products after passing through the cyclone separator 69 are passed through line 70 which merges with line 26 leading to the fractionating tower 27.

While there is shown a common fractionating tower 27 for fractionation of cracked products from both cracking chambers 18 and 61, it will be understood that the products from the two cracking zones may be subjected to independent fractionation if so desired. In such case, the products from the two cracking operations may be kept separate from each other.

Returning to the cyclone separator 69, the catalyst separated therein is removed from the bottom thereof through conduit 71. In accordance with the preferred embodiment of the invention, the catalyst so separated is passed directly through conduit 71 to a catalyst hopper 22 and again used for cracking the fresh feed introduced through line 10 without any intervening regeneration. If desired, however, a part or all of the catalyst separated in the cyclone separator 69 may be recycled to the catalyst hopper 52 feeding catalyst to the cracking chamber 61, or a part or all of the catalyst removed from the cyclone separator 69 may be passed to the regenerating circuit through conduit 72.

With respect to the above, it is desired to emphasize that in accordance with the present invention it is not essential to regenerate the catalyst after each cracking operation but the catalyst after passing through a cracking chamber may be recycled to the same or different cracking units for a predetermined period before subjecting the same to a regenerating treatment. As a result, the number of regenerations to which the catalyst is subjected may be reduced with

resultant reduction in capacity of the regenerating and purging equipment. Furthermore, in practical operations it is not possible to obtain 100% recovery of catalyst from the regenerating gas since some extremely fine particles normally remain in the regenerating gas. By reducing the number of regenerations to which the catalyst is subjected, loss of catalyst during regeneration can be reduced.

According to the preferred embodiment of the invention, fresh or freshly regenerated catalyst is first utilized for cracking a relatively refractory stock such as a cycle gas oil from the cracking operation and the catalyst after passing through this process is utilized directly without regeneration as catalyst for cracking a less refractory stock such as virgin oil introduced into the system through line 10.

While there have been illustrated two separate cracking units operating more or less in successive stages, it will be understood that additional stages may be added to the system as desired. For example, catalyst separated from the cracked products separated in the separator 24 or 69 may be passed to a third cracking circuit without regeneration, or a part may be recycled to the same circuit.

The invention also comprehends the further cracking treatment of cracked vapors before or after dry separation of powdered material therefrom and without any intermediate condensation. For example, a part of the suspension of cracked vapors and catalyst removed from the recycle cracking chamber 61 may be returned through line 73 and injected into the stream of oil passing to the heating coil 58. For illustrative purposes there has been shown an injector 74 for introducing the suspension into the oil stream although a fan or other suitable means may be substituted therefor. When operating in this way it is desirable to omit use of separator 62.

Likewise a part of the cracked vapors and catalyst suspension from the reaction chamber 18 operating on fresh feed may be returned through line 75 and injected into the fresh oil feed line 10 passing to the heating coil 12.

As a further alternative a part of the vapors from either the fresh oil or recycle circuit or both may be passed to either one of the two circuits for further cracking without intermediate condensation. For example, a part of the vapors from the vapor line 25 leading from the cyclone separator 24 to the fractionating tower 27 may be passed through lines 76 and 77 and transferred either through lines 78 and 75 to the inlet of heating coil 12 or a part or all may continue through line 79, to the inlet of heating coil 58 for further cracking.

Both methods of operating as just described have advantages.

By recycling a part of the suspension of cracked vapors and catalyst, the cracking time for a cracking unit of given size can be controlled and additional heat supplied to the recycled suspension to assist in maintaining temperature.

By first separating the bulk of the catalyst in dry state and then independently recycling a portion of catalyst and vapors to the same or separate circuit, the relative proportions of catalyst and vapors can be controlled as desired. This is not possible when a portion of the suspension of cracked vapors and catalyst is recycled.

Having described the preferred embodiment of the invention, it will be understood that it embraces such other variations and modifications as come within the spirit and scope thereof.

What is desired to be protected by Letters Patent is:

1. A method of catalytically cracking hydrocarbon oils to form lower boiling motor fuel products which comprises suspending a cracking catalyst substantially free of carbonaceous deposit in a stream of oil to be cracked, passing the resulting suspension through a cracking zone maintained at cracking temperature, keeping said suspension within the zone for a period sufficient to effect the desired cracking thereof, thereafter separating the catalyst from cracked products, suspending catalyst so separated in a stream of oil which is more amenable to cracking treatment than said first named stream, passing said last named suspension through a cracking zone separate and independent from said first named cracking zone, keeping said suspension within said last named cracking zone for a period sufficient to effect the desired cracking thereof and fractionating cracked products to separate a motor fuel fraction therefrom.

2. The invention defined in claim 1 wherein cracked products from one of said cracking operations are fractionated to segregate insufficiently cracked constituents above the motor fuel boiling range and the fraction so segregated is employed as feed stock in said first named cracking step.

3. The invention defined in claim 1 wherein virgin oil is employed as charging stock for said second named cracking step and cracked oil is employed in said first named cracking step.

4. The invention defined in claim 1 wherein catalyst separated from the second named cracked product is regenerated to remove carbonaceous deposit formed thereon and the regenerated catalyst employed in said first named cracking step.

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