

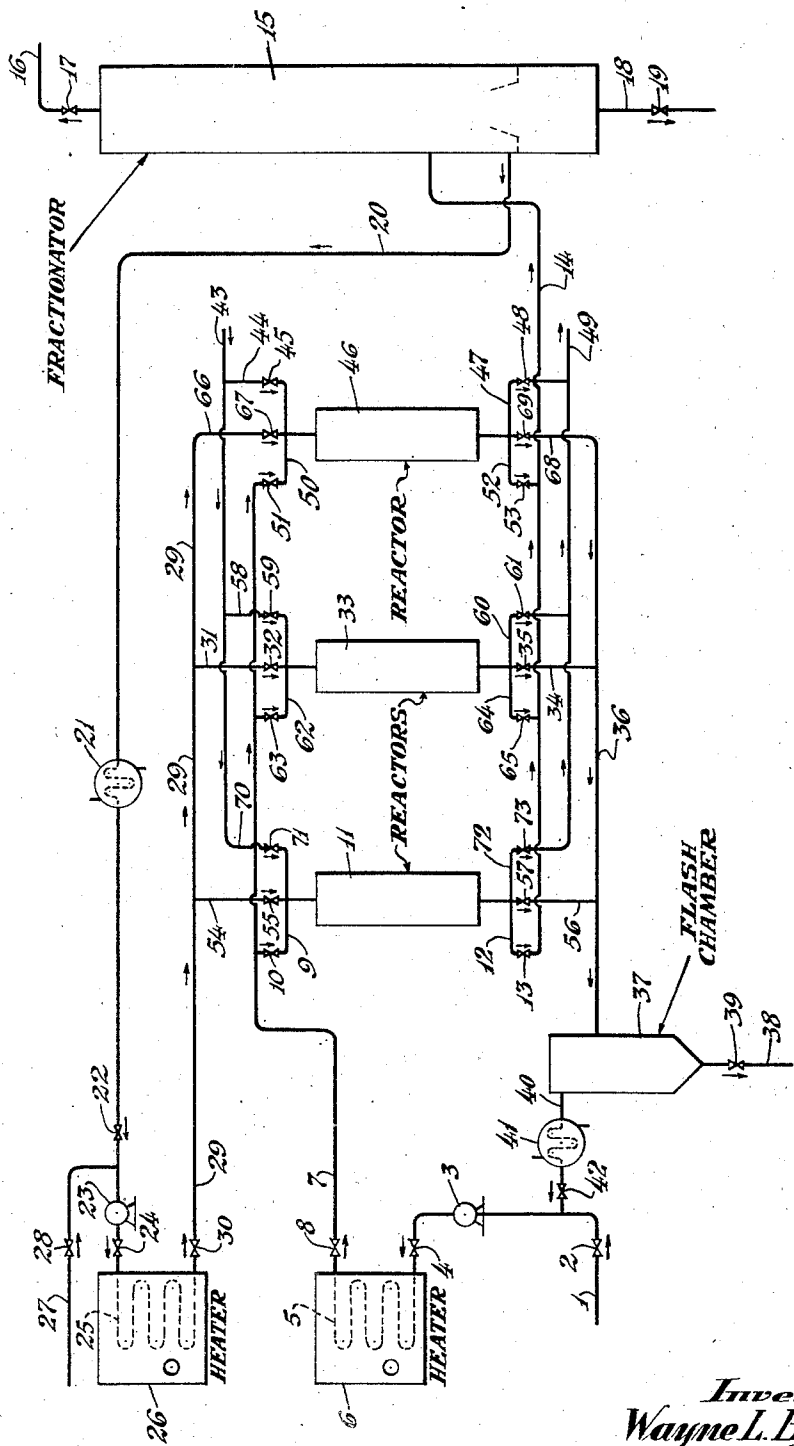
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CATALYTIC CRACKING OF HYDROCARBONS

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CATALYTIC CRACKING OF HYDROCARBONS

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This invention relates to a process for converting hydrocarbon oil into substantial yields of desirable products including gasoline of high antiknock value. Although the charging stock is usually of petroleum origin, similar stocks from other sources may also be converted. Normally, distillates which can be distilled at ordinary pressures without substantial decomposition are used, and these include naphtha, kerosene, gas oil and the like.

The use of thermal non-catalytic processes for converting high boiling hydrocarbons into increased yields of gasoline and gas has been practiced and the reactions involved are fairly well understood. When employing catalysts to assist in such conversions, however, knowledge is much less complete and as a consequence, a discussion of such reactions is best kept to a factual basis.

Various catalytic agents have been proposed for catalytic cracking reactions, among which are the reduced metal catalysts, including iron, nickel, cobalt, etc. These catalysts are subject to poisoning by sulfur compounds contained in the oils undergoing conversion, and moreover, tend to promote gas and carbon-forming reactions. Another type of catalytic agent which has found application is the naturally-occurring clay type which has been activated by treatment with acids or other chemicals.

Still another type of catalyst, which is the preferred catalyst of the present invention, is the so-called silica-alumina, silica-zirconia, and silica-alumina-zirconia type catalyst. These are synthetic composites prepared by the separate or simultaneous precipitation of the component materials, followed by washing, drying and calcining steps to produce a finished catalytic agent of a high degree of activity.

The conditions under which the catalysts are employed for catalytic cracking range from approximately 500–1200° F. and pressures of substantially atmospheric to 1000 pounds per square inch. The temperature is of considerable importance in determining not only the amount but also the type of reaction which takes place, since gasolines of entirely different character may be obtained by varying the operating conditions even though the amount of conversion per pass on a percentage basis may remain substantially the same. For example, when operating in the range of 500–900° F. and 50–1000 pounds per square inch pressure, a substantially olefin-free gasoline suitable in all respects for use in aviation motor fuel is obtainable. At temperatures above 900° F. and at pressures of the order of

atmospheric to 100–150 pounds per square inch, gasolines containing substantial amounts of olefin hydrocarbons are obtained.

The lower temperature cracking operation is subject to certain disadvantages from an operating standpoint, and these are largely connected with the difference in temperature level necessary for processing and for carrying out the reactivation step. Since the catalytic agents become carbonized at intervals, it is necessary to reactivate them periodically by treatment with an oxygen-containing gas at a temperature in excess of 900° F. The temperature of reactivation is usually of the order of 1200–1400° F. but it is necessary that the mass of the catalyst be increased to a temperature of approximately 900° F. or higher before burning begins. Moreover, under the lower temperature conditions a certain amount of hydrocarbon oil is adsorbed in the catalytic mass, and, being insufficiently removed, is destroyed in the subsequent reactivation step with resultant relatively high volumetric losses. The present invention is a method of overcoming the difficulties of low temperature cracking, reducing the losses, and increasing the efficiency of the operating cycle.

In one specific embodiment the present invention comprises a process for converting hydrocarbon oil into substantial yields of gasoline suitable for use in aviation fuel which comprises contacting said hydrocarbon oil with a cracking catalyst in a plurality of cracking zones serially arranged wherein the following repeated sequence of steps is carried out at each of said cracking zones comprising a primary step of cracking said hydrocarbon oil at a temperature of 500–900° F. and a pressure of approximately 50–1000 pounds per square inch to produce a substantially olefin-free gasoline, a secondary step of heating the insufficiently converted portion of reaction products from said primary step to a temperature within the range of approximately 950–1200° F. and contacting it with partially spent cracking catalyst previously used in said primary step to increase the temperature of said cracking catalyst to approximately 900° F., and a tertiary step of reactivating the cracking catalyst used in said primary and secondary steps by treating it with an oxygen-containing gas at a temperature within the range of 900–1500° F., fractionating the reaction products from said primary step into gas, gasoline and insufficiently converted oil, heating and supplying the insufficiently converted oil to said secondary step, and supplying the reaction products

from said secondary step to said primary step.

In addition to the three steps described, a fourth step in which the catalyst is cooled from the reactivation temperature to the operating temperature may be included. This step is not illustrated in the accompanying drawing, but is considered within the scope of the invention.

The invention is further illustrated by reference to the attached drawing which is diagrammatic, and should not be interpreted as limiting the process to any particular type of apparatus. No attempt has been made to proportionate the equipment or to draw it to an exact scale.

Referring to the drawing, hydrocarbon oil is charged through line 1, valve 2, pump 3, valve 4 to coil 5 which is disposed in heater 6. After being heated to a temperature within the range of 500-900° F., it is passed through line 7, valve 8, line 9 and valve 10 to catalytic reactor 11 which may be any suitable type of reactor such as manifolded tubes or a chamber or tower containing catalyst particles therein. The reaction products pass through line 12, valve 13 to line 14 and thence to fractionator 15. Gasoline and gas are removed through line 16 and valve 17. A residual oil may be withdrawn through line 18 and valve 19, although it is within the scope of the invention that all of the insufficiently converted oil should be returned through line 20, heat exchanger 21, valve 22, pump 23, valve 24 to coil 25 which is disposed in heater 26. If desired, additional oil may be introduced into line 20 through line 27 and valve 28, although this is not usually done. The oil is heated to a temperature within the range of 900-1200° F. and preferably of the order of 1000° F., and passed through line 29 and valve 30 to line 31 and valve 32 to reactor 33. This reactor has previously been used for converting hydrocarbons in the lower temperature range. The pressure is reduced to substantially atmospheric or slightly superatmospheric, and the oil which is at the higher temperature increases the temperature of the catalyst to a point substantially in excess of 900° F. The reaction products pass through line 34 and valve 35 to line 36 and thence to flash chamber 37. Residual oil may be withdrawn through line 38 and valve 39. The vaporous reaction products pass through line 40, heat exchanger 41 and valve 42 to line 1, and are thus returned to the primary reaction step being carried out in reactor 11. At the same time, reactivation gases containing oxygen are passed through line 43, line 44 and valve 45 to reactor 46 which is substantially identical with reactors 11 and 33, and which has previously passed through both the primary and the secondary steps of the cycle. The reactivation gases pass through line 47 and valve 48 to line 49, and are either vented to the atmosphere or recirculated in part by means not shown. After a suitable interval of time determined by the activity of the catalytic agent in the primary reaction step, the valve settings are changed and the next phase of the cycle begins. The heated hydrocarbon oil from line 7 is introduced into reactor 46 through line 50 and valve 51 and are removed to fractionator 15 through line 52, valve 53 and line 14. The insufficiently converted oil from line 29 is introduced into reactor 11 through line 54 and valve 55, passing thence through line 56 and valve 57 to line 36, flash chamber 37 and by previously described routes to line 1. Reactivation gases from line 43 pass through line 58 and valve 59 to reactor 33 and are removed through line 60,

valve 61 and line 49. The next regular step consists in processing in reactor 33, increasing reactor 46 to the high temperature range, and reactivating reactor 11. This is accomplished by introducing hydrocarbon oil through line 62 and valve 63 to reactor 33, removing the reaction products through line 64, valve 65 and line 14 to the fractionator. The heated recycle oil is introduced from line 29 through line 66 and valve 67 to reactor 46 and the cracked products removed through line 68 and valve 69 to line 36 and thus recirculated. Reactivation gases are passed through line 43, line 70 and valve 71 to reactor 11, being removed through line 72, valve 73 and line 49. The cycle is completed and the next cycle is begun by returning the valves to the original settings so that reactor 11 is processing at low temperature, reactor 33 is being increased to the high temperature range, and reactor 46 is being reactivated.

The drawing has been simplified by omission of various auxiliary equipment such as stabilizers, heat exchangers, condensers, etc.

In addition to the advantages mentioned in the foregoing specifications, the process has the advantage that during the secondary step while the temperature of the catalyst is being increased from that in the processing region to the reactivation range, a considerable portion of the recycle oil is converted to gasoline and gas incidental to the operation. The gasoline produced is relatively olefinic, but upon being passed through the primary stage this is converted to substantially olefin-free motor fuel.

The following example illustrates the usefulness and practicability of the process but should not be construed as limiting it to the exact conditions employed therein.

A Mid-Continent gas oil may be converted according to the method described in the foregoing specification, the insufficiently converted oil being recycled by way of the high temperature step. The main processing step may suitably be carried out at a temperature of 800° F. The catalyst in the secondary step is heated to a temperature of approximately 900° F. by heating the recycle oil to 950° F. and passing it over the catalyst. Reactivation is begun at 900° F. and reached a maximum temperature of about 1300° F. A fourth reaction zone may be provided to allow cooling of the catalyst from the temperature of reactivation to approximately 800° F. before resuming processing. A total yield of 65% of substantially saturated cracked gasoline may be obtained in this manner, the remainder being gas, and oil suitable for furnace distillate. There is an average of 4%-5% of unaccounted for loss. When operating in the usual manner without the step of passing heated and cracked recycle over the catalyst bed in the primary cracking step, the loss amounted to approximately 12% of the oil charged.

I claim as my invention:

1. A process for converting hydrocarbon oil into substantial yields of valuable products including gasoline which comprises maintaining cracking catalyst in a plurality of catalytic reaction zones simultaneously operated in a plurality of concomitant steps comprising a primary step of contacting said hydrocarbon oil with a cracking catalyst under conditions of temperature and pressure adequate to effect substantial conversion thereof to relatively olefin-free gasoline, a secondary step of heating insufficiently converted oil from the primary step to a temperature within

the range of approximately 950–1200° F. and contacting it with cracking catalyst previously used in said primary step to increase the temperature thereof to a point above approximately 900° F. and to form olefinic gasoline, a tertiary step of reactivating said cracking catalyst previously used in said primary and secondary steps by treating it with an oxygen-containing gas at a temperature of approximately 900–1500° F. before cooling thereof to below approximately 900° F. and a quaternary step of returning the temperature of said reactivated catalyst to the operating temperature of said primary step, fractionating the reaction products from said primary step into gas, gasoline and insufficiently converted oil, recycling at least a portion of said insufficiently converted oil to said secondary step, and supplying olefinic gasoline from said secondary step to said primary step.

2. A process for converting hydrocarbon oil into substantial yields of valuable products including gasoline, suitable for use in aviation motor fuel which comprises maintaining cracking catalyst in a plurality of catalytic reaction zones simultaneously operated in a plurality of concomitant steps comprising a primary step of contacting said hydrocarbon oil with a cracking catalyst at a temperature of 500–900° F. and a pressure of approximately 50–1000 pounds per square inch to produce a substantially olefin-free gasoline, a secondary step of heating insufficiently converted oil produced in said primary step to a temperature within the range of approximately 950–1200° F. and contacting it with the cracking catalyst previously used in said primary step to heat said catalyst to a temperature in excess of 900° F. and to form olefinic gasoline, a tertiary step of reactivating the cracking catalyst which has previously passed through said primary and secondary steps by treating it with an oxygen-containing gas at a temperature of approximately 900–1500° F. before cooling thereof to below approximately 900° F. and a quaternary step of returning the temperature of said reactivated cracking catalyst to a temperature within the range of said primary step, fractionating the reaction products from said primary step into gas, gasoline and insufficiently converted oil, heating and supplying at least a portion of the insufficiently converted oil to said secondary step, and passing olefinic gasoline from said secondary step to said primary step.

3. The process of claim 1 wherein the cracking catalyst is selected from the group consisting of silica-alumina, silica-zirconia, and silica-alumina-zirconia.

4. A process for converting hydrocarbon oil into substantial yields of valuable products including a relatively olefin-free motor fuel which comprises converting said oil in a plurality of catalytic reaction zones simultaneously operated in a repeated sequence of steps comprising contacting said hydrocarbon oil with a cracking catalyst at a temperature and pressure adequate to effect substantial conversion thereof into relatively olefin-free gasoline in a primary reaction zone, fractionating the reaction products into gas, gasoline and insufficiently converted oil, heating at least a portion of said insufficiently converted oil to a temperature of approximately 950–1200° F. and contacting it in a secondary reaction zone with cracking catalyst previously used in the production of relatively olefin-free gasoline from said hydrocarbon oil, supplying olefinic gasoline formed in said secondary zone

to said primary reaction zone, reactivating the cracking catalyst in a tertiary reaction zone by contacting it with an oxygen-containing gas at a temperature of 900–1500° F., periodically diverting the flow of said hydrocarbon oil to said tertiary reaction zone to produce substantially olefin-free gasoline, simultaneously diverting the flow of said insufficiently converted oil to said primary reaction zone at a temperature of 900–1200° F., supplying olefinic gasoline now formed in said primary zone to said tertiary reaction zone while reactivating the catalyst in said secondary reaction zone by treating it with an oxygen-containing gas, periodically diverting the flow of said hydrocarbon oil to said secondary reaction zone and the flow of said insufficiently converted oil to said tertiary reaction zone, reactivating the catalyst in said primary reaction zone by contact with an oxygen-containing gas and finally completing the cycle by directing the flow of said hydrocarbon oil to said primary reaction zone, directing the flow of said insufficiently converted oil to said secondary reaction zone and the flow of said reactivation gases to said tertiary reaction zone.

5. A process for converting hydrocarbon oil into substantial yields of valuable products including high antiknock motor fuel which comprises maintaining cracking catalyst in a plurality of catalytic reaction zones simultaneously operated in a plurality of concomitant steps, comprising a primary step of contacting said hydrocarbon oil with a cracking catalyst at a temperature and pressure adequate to effect substantial conversion thereof to relatively olefin-free gasoline, a secondary step of heating insufficiently converted oil produced in said primary step to a temperature within the range of approximately 950–1200° F. and contacting it with the cracking catalyst previously used in said primary step to heat said catalyst to a temperature in excess of 900° F., a tertiary step of reactivating said catalyst which has been previously used in said primary and secondary steps by treating it with an oxygen-containing gas at a temperature of approximately 900–1500° F. before cooling thereof to below approximately 900° F., fractionating the reaction products from said primary step into gas, gasoline and insufficiently converted oil, heating and supplying a portion of said insufficiently converted oil to said secondary step, passing the reaction products from said secondary step to a flashing zone, separating and passing the vaporous portion of said reaction products to said primary step and removing the residual portion of said reaction products from said flashing zone.

6. A process for converting hydrocarbon oil into substantial yields of valuable products including high antiknock gasoline which comprises maintaining cracking catalyst in a plurality of catalytic reaction zones simultaneously operated in a plurality of concomitant steps comprising a primary step of contacting said hydrocarbon oil with a cracking catalyst at a temperature and pressure adequate to effect substantial conversion thereof into relatively olefin-free gasoline, a secondary step of heating insufficiently converted oil produced in said primary step to a temperature within the range of approximately 950–1200° F. and contacting it with the cracking catalyst previously used in said primary step to heat said catalyst to a temperature in excess of 900° F., a tertiary step of reactivating the cracking catalyst previously used in said primary and

secondary steps by treating it with an oxygen-containing gas at a temperature of approximately 900–1200° F. before cooling thereof to below approximately 900° F., fractionating the reaction products from said primary step into gas, gasoline and insufficiently converted oil, heating and supplying at least a portion of said insufficiently converted oil to said secondary step at a temperature of approximately 900–1200° F., supplying a vaporous portion of the reaction products from said secondary step to said primary step, and withdrawing a residual portion of the reaction products from said secondary step.

7. A catalytic conversion process which comprises contacting hydrocarbon oil with a body of cracking catalyst at a temperature in the ap-

proximate range of 500–900° F. to produce gasoline of relatively low olefin content, then contacting said body of catalyst with hydrocarbon oil heated to a temperature of about 950–1200° F. to produce gasoline of higher olefin content than the first-named gasoline and to raise the temperature of the catalyst body to that at which combustion of carbonaceous matter, deposited on the catalyst during the aforesaid conversion steps, will be initiated in the presence of oxygen, and then contacting said body of catalyst with oxygen-containing gas to burn carbonaceous matter from the catalyst and thereby reactivate the latter.

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