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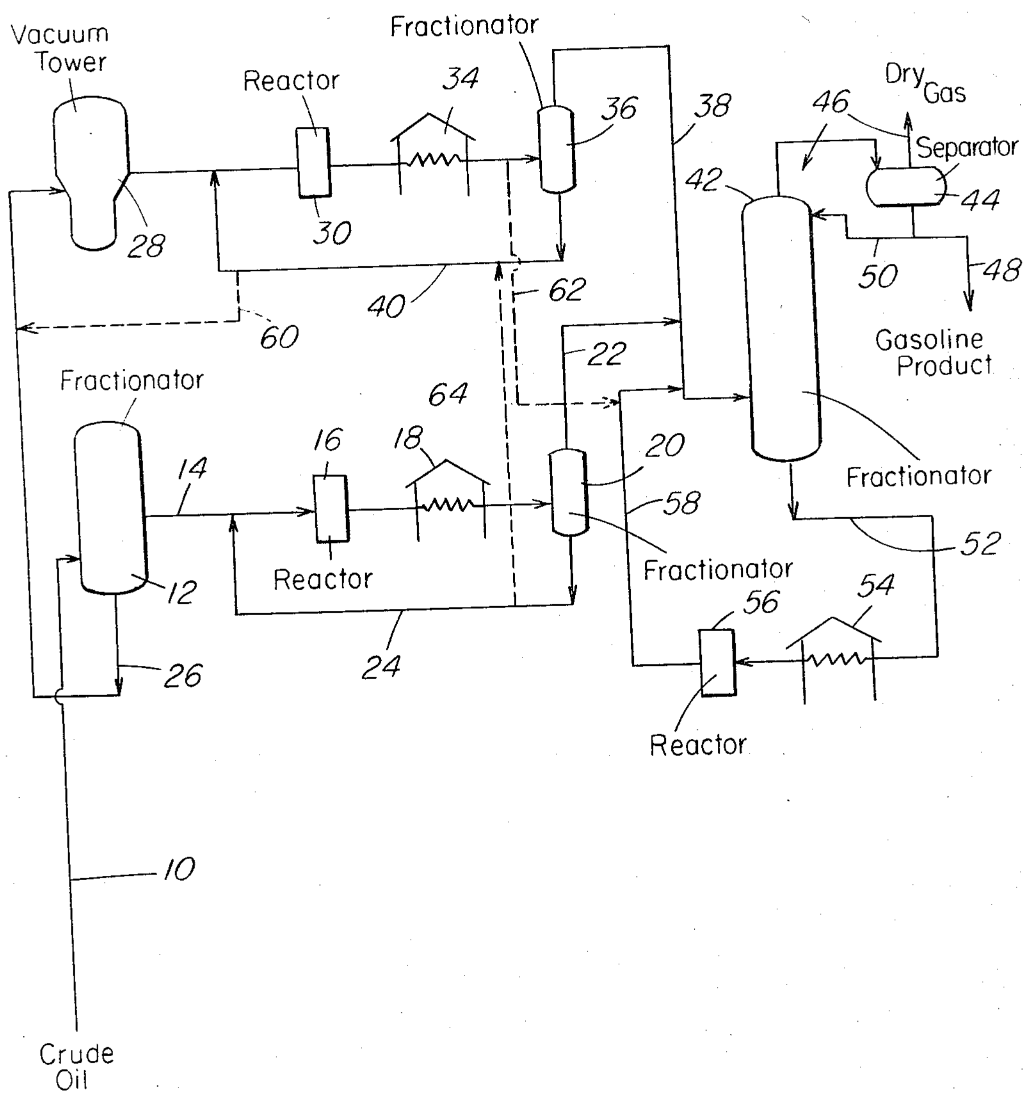

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LIMITED CONVERSION OF HYDROCARBON OVER HIGHLY ACTIVE CATALYST

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This application is a continuation-in-part of application Serial No. 282,670, filed May 23, 1963, now abandoned.

This invention relates to the catalytic cracking of hydrocarbons. More particularly the invention is concerned with a cracking process conducted substantially at feed liquid phase temperature and pressure conditions in the presence of a highly active cracking catalyst.

Since the commercial development of catalytic cracking over 25 years ago, substantially all cracking operations in the industry have been of the type wherein petroleum oils boiling in the range above 400° F. have been fed in vapor form or mixed liquid-vapor form into catalyst-containing reactor at rather high temperatures, generally in excess of 800° F. in order to crack the oils and secure petroleum oil fractions boiling in the motor fuel oil range. In those cases wherein mixed liquid-vapor feed is fed to the reactor, rapid vaporization of the liquid portion of the feed occurs at the catalyst surface or just before reaching the same so that in effect the feed at the moment of cracking is substantially all in vapor form.

The ability for conducting catalytic cracking under relatively mild cracking conditions, i.e., under conditions of pressure and temperature such that the cracking operation is effected at much lower temperatures, which permits maintaining the feed either entirely or predominantly in the liquid phase, has not been completely satisfactory for a number of reasons. Liquid phase cracking at low temperatures has in the past resulted in undesirably low reaction rates and conversion.

The process of this invention relates to conducting catalytic cracking at low temperatures, in a predominantly liquid phase, with a suitable catalyst under conditions to limit the single pass conversion of feed to a low level in the range of 5% to 30% by weight and preferably in the range of 10% to 20% by weight of the feed being converted to material boiling in the gasoline range. The reaction products having the desired boiling range are separated from the heavier material containing unconverted feed hydrocarbon, with the heavy material being returned to the reactor inlet or alternately, to a separate reactor for further conversion at similar low single pass conversion conditions. These steps are repeated until all or virtually all of the feed has been converted into the desired reaction products or until a desired level of conversion has been obtained.

The instant process has a number of advantages. The low temperature and low single pass conversion exposure in the reaction zone permits conversion of the hydrocarbon at conditions that minimize polymer formation on the catalyst. The liquid phase serves to retard formation of heavy polymers on the catalyst. The heat input to the process is minimized because of the lower temperatures utilized and because no heavy oils are vaporized and recondensed unnecessarily. The heat of the reaction is provided for the low conversion by the sensible heat of the total feed liquid, thus permitting operation at a desired catalyst/oil ratio independent of the reactor heat input requirement. The separation of the desirable light reaction products can be easily accomplished by simple flash distillation. The equipment investment and operation costs are much lower because of the inherent simplicity of operation and because catalyst regeneration equipment is minimized or eliminated completely. The operation at con-

trolled low conversion permits the removal of reaction products before their concentration in the reaction zone is high enough to result in appreciable further cracking and degradation to dry gas.

The present process is based on the fact that the low conversion rate per pass of preferably 10–20% does not permit concentrations of converted materials in the reactor to reach the level at which undesirable recontacting and overcracking to coke and/or gas becomes appreciable. Further, any polymers that do form on the catalyst during the reaction can be removed in several ways before condensation thereof to coke-like residues. For example, any polymers formed can be removed from the catalyst by hydrogenating the polymer formed. The polymers formed under the conditions of operation specified herein are far easier to remove from the catalyst than the dense polymers or coke-like polymer product formed under more severe vapor phase conditions at higher temperatures.

According to the present invention, a charge stock is brought into contact with a superactive catalyst, to be described hereafter, at temperatures under 750° F. and preferably in the range of 300–650° F. and pressure sufficiently high so that a liquid phase is maintained in the reaction zone, under conditions of low conversion, preferably in the range of 10–20% per pass with space velocity ranging upward from 5.0 v./v./hr. The gasoline formed in each pass is removed and the unconverted feed and other heavy materials are re-exposed to the low conversion conditions to obtain the desired ultimate conversion of fresh feed.

It is recognized that operation of a catalytic cracking process in the liquid phase and at low temperatures requires a catalyst having very high cracking activity. Suitable catalysts are aluminosilicates of ordered internal structure.

The catalytic materials used in this invention are superactive crystalline aluminosilicates, of either natural or synthetic origin having an ordered internal structure. These materials are possessed of very high surface per gram and are microporous. The ordered structure gives rise to a definite pore size, related to the structural nature of the ordered internal structure. Several forms are commercially available. A 5A material indicates a material of "A" structure and a pore size of about 5 A. diameter. A 13X material is one of "X" faujasite type and 10–13 A. pore diameter and so on. There are also known materials of "Y" faujasite type, and others. Many of these materials may be converted to the "H" or acid form, wherein a hydrogen occupies the cation site. For example, such a conversion may be had by ion-exchange with an ammonium ion, followed by heating to drive off NH_3 or by controlled acid leaching. In general, the "H" form is more stable in materials having higher Si/Al ratios, such as 2.5/1 and above.

One material of high activity is H mordenite. Mordenite is a material occurring naturally as the hydrated sodium salt corresponding to:

$$NA_8(AlO_2)_8(SiO_2)_{40}.24H_2O$$

This mordenite material may be leached with dilute hydrochloric acid to arrive at an H or acid form. In a specific example, the mordenite material may be so treated as to have more than 50 percent in the acid form. A more complete discussion of H mordenite is found in copending application Serial No. 142,778 filed October 4, 1961, now abandoned, in the name of Vincent J. Frilette et al.

Another type of high activity catalyst may be prepared by using Linde 13X molecular sieve, which is described in U.S. Patent 2,882,244. This material may be base exchanged with a solution of rare-earth chlorides (containing 4% of $RECl_3.6H_2O$) at 180–200° F. to remove sodium ions from the aluminosilicate complex and replace at least some of them with the chemical equivalent of rare-earth ions. After washing free of soluble material and drying, there is produced an REX crystalline aluminosilicate containing 1.0–1.5 percent (wt.) of sodium and about 25% (wt.) of rare-earth ions calculated as RE_2O_3.

Similar preparations of high activity may be made by suitable preparation of a variety of crystalline aluminosilicates, such as "Y"-type faujasite, gmelinite, chabazite, and the like. For a fuller discussion of the nature of crystalline aluminosilicates and their method of preparation attention is also directed to U.S. Patent 3,033,778 to Frilette and U.S. Patent 3,013,989 to Freeman.

The crystalline aluminosilicate catalysts may be varied within wide limits as to aluminosilicate employed, cation character and concentration, and added components in the pores thereof incorporated by precipitation, adsorption and the like. Particularly important variables are silica to alumina ratio, pore diameter and spatial arrangement of cations. The cations may be protons (acid) derived by base exchange with solutions of acids or ammonium salts, the ammonium ion decomposing on heating to leave a proton. Polyvalent metals may be supplied as cations, as such or as spacing agents in acid aluminosilicates for stabilization. In addition to the rare-earth metals mentioned above, other suitable cations for exchange in the aluminosilicates include, for example, magnesium, calcium, manganese, cobalt, zinc, silver, and nickel.

The above discussed catalysts possess activities too great to be measured by the "Cat. A" test which is a standard evaluation test, widely established and used for the evaluation of hydrocarbon cracking catalysts, both for preliminary evaluation and for control during commercial use by examination of activity. In this test, a specified Light East Texas gas oil is cracked by passage over the catalyst in a fixed bed, at a liquid hourly space velocity (LHSV) of 1.0, using a catalyst-to-oil ratio (C/O) of 4/1, at an average reactor temperature of 875° F., and atmospheric pressure (LHSV and C/O are expressed in volumes). The volume percentage of gasoline produced is the activity index (AI). The method of this test is described more fully in National Petroleum News, 36, page R–537 (August 2, 1944). The control silica, alumina catalyst employed in the alpha rating test hereinafter more specifically described as an AI value of 46. To measure the activity of the instant superactive catalyst there has been developed a micro test method in which these catalysts are compared for relative cracking activity in the cracking of hexane with a conventional catalyst. This method and a fuller discussion of the development of the activity is fully disclosed in application Serial No. 208,512 filed July 9, 1962. As there explained, alpha is the measure of the comparative conversion ability of a particular superactive catalyst of the type above discussed when compared in the cracking of hexane with a conventional silica-alumina cracking catalyst ($90\% SiO_2$-$10\% AlO_2$) having an activity index as measured by the "Cat. A" test of 46.

Many such superactive catalysts have been found to have an α value of the order of about 10,000 where α is the comparative activity of the catlyst based upon conventional amorphous silica-alumina cracking catalyst as $\alpha=1$.

In order to use such catalyst with conventional equipment and processes now available, particularly in the cracking of hydrocarbons, it is first necessary to modify the activity of such superactive catalysts.

One method for the adjustment of activity may be referred to as steam treating, or more shortly, steaming. It has been found that steaming can effect major decreases in the activity of the superactive catalysts utilized herein, and that controlled steaming can be utilized to acquire any desired degree of activity reduction. For example, a crystalline aluminosilicate of the 13X type which has been base-exchanged with a mixture of rare-

earth chlorides has a relative activity α, when freshly prepared of about 10,000. By controlled steaming in an atmosphere of steam for 5–40 hours, at 1300° F., its relative activity can be reduced to an α of about 10.

Another method of modifying such catalysts to reduce their activity is by dilution in a matrix of controlled activity or of little or no activity. Thus, a catalyst, such as RE 13X of $\alpha \approx 10{,}000$ may be reduced readily to an activity useful in today's technology by incorporating in a matrix of amorphous silica-alumina, for example, of an activity of $\alpha \approx 0.5$–1.0.

Thus, through combinations of the various methods of adjusting activity of the superactive catalytic materials any desired relative activity can be obtained. For example, the freshly prepared RE 13X of relative activity, $\alpha \approx 10{,}000$, which was reduced by steaming to a material of $\alpha \approx 10$, can be further reduced by compounding with an equal amount of catalytically inert material to an activity, $\alpha \approx 5$.

The dispersing of the superactive aluminosilicates in a matrix, e.g., clay or inorganic oxides, may often be carried out as just indicated to dilute the very high activity. Moreover, the formation of pellets or beads is very desirable from the point of view of resistance to attrition in the cracking process. Generally spherical beads may be prepared by dispersing the aluminosilicate in an inorganic oxide sol according to the method described in U.S. Patent 2,900,399 and converted to a gelled bead according to the method described in U.S. Patent 2,384,946.

Under the conditions of the reaction zone the feed stock will be maintained predominantly in the liquid phase. The term "predominantly in the liquid phase" has been used to describe the state of the feed stock since the feeds are generally heterogeneous mixtures which contain components of varying boiling points. Accordingly, it will generally be the case that some low boiling components may remain in the vapor or gaseous phase even at the temperatures and pressures employed.

The liquid phase operation is particularly advantageous since it has been found that the heavy material which forms on the catalyst during the reaction can be carried out of the reactor before it condenses further for removal by hydrogenation.

Thus, when the reaction occurs at low temperatures in such a manner as to get relatively low conversion of the order of 20–30%, a sufficient amount of the unconverted charge material will remain present, as liquid, to handle much of the heavier material resulting from the cracking and carry it out of the reactor. If these heavier products of cracking are not permitted to solidify on the catalyst, but are substantially continuously removed while still in a soft condition, the reactivity life of the catalyst may be greatly prolonged. The catalyst may be treated with a solvent for removal of heavy hydrocarbon constituents. Since these superactive crystalline aluminosilicate catalyst materials are effective hydrogen transfer agents, a hydrogen donor material such as decalin or a hydrogenated recycle oil may be introduced to the liquid phase cracking operation to lessen formation of polymer deposits. Eventually, however, regeneration of the catalyst by combustion or hydrogenation of the deposits can be effected.

A single figure of drawing, attached to and made a part hereof, shows a schematic flow sheet of one typical operation.

In the drawing, a liquid phase multistep catalytic cracking schematic flow sheet is shown which utilizes three reactors. The crude oil feed enters a fractionator **12** through line **10** for separating the feed into two fractions. The lighter fraction leaves the fractionator **12** through line **14** passing into the reactor **16** containing the superactive catalyst. The effluent from the reactor **16** passes through a heater **18** and thence into a fractionator **20** which separates the effluent into a lighter gasoline containing fraction flowing through line **22** and a heavier fraction which is recycled via line **24** to the reactor **16**.

The heavier fraction leaving the fractionator **12** through line **26** flows to a vacuum tower **28** and thence through line **32** to a reactor **30** containing superactive catalyst. The effluent from the reactor **30** passes through a heater **34** and thence into a fractionator **36** (flash drum) which separates the effluent into a lighter gasoline containing fraction flowing through line **38** and a heavier fraction which is recycled via line **40** to the reactor **30**.

The gasoline containing fractions flowing in line **22** and in line **38** are merged and passed into a fractionator **42**. The effluent from the upper portion of the fractionator **42** passes through a separator **44**. Dry gas flows from the separator **44** through line **46** and the gasoline product flows through line **48**. A portion of the gasoline product may be recycled to the fractionator **42** through line **50**. The heavier fraction leaving the fractionator **42** through line **52** passes through heater **54** and thence into reactor **56** containing the superactive catalyst. The effluent is recycled into the fractionator **42** with the gasoline product containing streams through line **58**.

Any polymers which remain in the liquid oil phase leaving the reactors can be reduced or removed by return of a portion or all of the uncracked oil to the feed preparation system, as shown in broken lines **60**, **62** and **64**.

The conditions in the reactors are maintained so that the catalytic reactions occur in liquid phase at relatively low conversion rates per pass, preferably in the range of 10–20%. The velocity should be at least 5.0 v./v./hr. and the pressure can range up to 500 p.s.i.g. and higher, as necessary. The heat absorbed in this system is the sum of the heat required to vaporize the gasoline produced and the heat of reaction to produce the gasoline.

Although the present invention has been described in conjunction with preferred embodiments, it is to be understood that modifications and variations may be resorted to, without departing from the spirit and scope thereof, as those skilled in the art will readily understand. Such variations and modifications are considered to be within the purview and scope of the appended claims.

What is claimed is:

1. A method for converting a hydrocarbon feed to lower boiling products including gasoline boiling range materials which comprises passing the hydrocarbon feed in contact with a superactive crystalline aluminosilicate catalyst at a temperature below about 650° F. and at a pressure sufficient to maintain at least the hydrocarbon feed in a liquid phase condition and at a space velocity of at least about 5 v./v./hr. to obtain less than about 30% conversion of the hydrocarbon charge per pass, whereby the frequency of regeneration of the catalyst required is substantially reduced.

2. The method of claim **1** wherein sufficient pressure is employed to maintain at least gasoline boiling range conversion products in liquid phase condition.

3. The method of claim **1** wherein the conversion rate per pass is maintained in the range of from about 10 to about 20%.

4. The method of claim **1** wherein insufficiently converted material recovered from the conversion step is recycled to the conversion step.

5. A method for converting a relatively high boiling hydrocarbon feed stock which comprises:

(a) passing a hydrocarbon feed stock in contact with a crystalline alumino-silicate cracking catalyst at a pressure sufficient to maintain the hydrocarbon feed substantially in the liquid phase,

(b) limiting conversion of the hydrocarbon feed to gasoline boiling products in the cracking step to below about 30%,

(c) separating gasoline boiling range product from heavier unconverted hydrocarbon by flash distillation,

(d) further converting separated heavier hydrocarbon material by contact with additional crystalline aluminosilicate cracking catalyst in a separate conversion zone under substantially liquid phase conversion conditions maintained at a temperature below about 750° F, and

(e) periodically removing relatively soft polymer condensation products from the catalyst by hydrogenation thereof.

6. A method for converting a hydrocarbon feed to materials boiling in the gasoline range which comprises:

(a) separating the hydrocarbon feed into a low boiling fraction and a high boiling fraction,

(b) separately partially converting said low and high boiling fractions in the presence of a crystalline alumino-silicate conversion catalyst under liquid phase conversion conditions to materials boiling in the gasoline range,

(c) recovering gasoline boiling range material from unconverted low and high boiling hydrocarbon feed by flash distillation,

(d) further converting the uncoverted low and high boiling hydrocarbon feed by further contact under liquid phase conditions with said crystalline alumino-silicate catalyst,

(e) separating the recovered gasoline boiling range material into low boiling gasoline material and a higher boiling material,

(f) and further converting said higher boiling material to said low boiling gasoline material.

7. The method of claim **6** wherein unconverted low and high boiling hydrocarbon separated from gasoline boiling material is separately recycled to the reactor from which obtained.

8. The method of claim **6** wherein unconverted low and high boiling hydrocarbon is treated as a combined stream under conditions to remove undesired high boiling constituents therefrom before passage to the catalyst reactor employed for converting the low boiling portion of the hydrocarbon feed.

9. The method of claim **6** wherein the catalyst employed is periodically regenerated under hydrogenating conditions.

10. The method of claim **6** wherein a hydrogen donor material is introduced with the hydrocarbon feed being converted.

11. A hydrocarbon conversion process which comprises contacting a relatively high boiling hydrocarbon in a liquid phase condition in the presence of a hydrogen donor material with a high activity aluminosilicate cracking catalyst under conditions to maintain conversion of the hydrocarbon feed to gasoline boiling products below about 30%, recovering gasoline boiling hydrocarbons from unconverted hydrocarbons, reheating unconverted hydrocarbons to an elevated temperature and contacting with a separate mass of high activity catalyst under conditions to obtain limited conversion to gasoline boiling hydrocarbons.

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