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HIGH TEMPERATURE CATALYTIC CRACKING OF GAS OILS

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U.S. Cl. 208—113 9 Claims

ABSTRACT OF THE DISCLOSURE

This invention is concerned with a process for carrying out the catalytic cracking of hydrocarbons, e.g., gas oils, into products of lower molecular weight wherein the heat necessary for carrying out the cracking reaction is provided at least in part by a simultaneous shape selective combustion of lower molecular weight hydrocarbons. Both the cracking reaction and the selective combustion reaction take place in the same reactor and are carried out at specific temperatures, space velocities and catalyst-to-oil (cat-oil) ratios.

BACKGROUND OF THE INVENTION

This invention relates to the catalytic conversion of hydrocarbon oils into lower normally liquid and normally gaseous products. More particularly, the present invention is directed towards a process wherein a high boiling hydrocarbon or hydrocarbon mixture, for example, a petroleum fraction, is subjected to cracking under very unusual conditions including elevated temperatures which would normally be considered to be in the thermal cracking range and wherein heat necessary to effect the cracking reaction is supplied at least in part by the selective combustion of a portion of the feed and/or reaction products wherein both the cracking and the selective combustion reaction take place in the same reactor.

The concept of carrying out a selective combustion reaction in order to supply at least a portion of the heat necessary for carrying out cracking reaction is not new and is, in fact, taught in the prior art including U.S. 3,136,713. It is to be noted, however, that the heretofore practiced processes were carried out within the range of conventional operating conditions in regard to temperature, space velocity, cat-oil ratios, etc. so that although this combination of processes was indeed novel, the operating conditions employed were not that drastic a departure from conventional technology with regard to either the cracking or combustion reaction.

In copending application Ser. No. 582,584, filed Sept. 28, 1966, now Pat. No. 3,420,770, a novel process is disclosed and claimed involving the catalytic cracking of a gas oil to produce gasoline under very specific and unusual conditions. In said application, the catalytic cracking is carried out by contacting a feed material with a cracking catalyst at an average range temperature from a minimum of 1100° F. up to a practical maximum of about 1350° F. and that a minimum space velocity (LHSV) of 32 at 1100° F. to about 1200 at 1300° F. and the maximum cat-oil ratio of about 0.1 and, more preferably, 0.01.

As can be readily appreciated, the above-described conditions are a drastic departure from conventionally practiced cracking processes. As can be seen from the minimum temperature of 1100° F., it can generally be stated that thermal cracking conditions are being employed. It should also be obvious that if, in fact, thermal cracking conditions were being employed then, irrespective of what catalyst was being used, no useful result would be obtained, i.e., if conditions were used which would in and

of themselves produce an inordinate amount of gas without any catalyst then the inclusion of a catalyst at those conditions could not significantly improve the product pattern.

Accordingly, the particular space velocities employed are such that the degree of thermal cracking which can take place does not exceed 10%. In this regard, reference is made to FIG. 1, which is a graph representing a plot of the temperature versus the minimum space velocity necessary to insure no more than 10% thermal conversion. As can be seen, there is a definite cracking space velocity for each individual temperature within the specified range in order to insure a minimum of thermal conversion.

It should be readily apparent that just as the above set-forth conditions are a drastic departure from conventional cracking conditions the same comment can be made with respect to the combustion conditions. Thus, it is not sufficient merely to employ a catalyst which will be shape selective at conventional conditions, but rather, it is mandatory to employ a catalyst which is shape selective at the drastic operating conditions of this invention.

In addition to the above, when it was attempted to carry out the shape selective combustion process simultaneously with the cracking process, unexpected results were obtained due to the particular operating parameters of this invention. As has been described in the prior art, a shape selective combustion process is carried out by providing oxidation surfaces within the internal pore structure of a crystalline aluminosilicate having a pore size such that only a portion of a hydrocarbon stream can enter within the internal pore structure thereof and be combusted. Thus, selective combustion of a combustible mixture of molecules of differing molecular shapes is obtained by passing the same together with an oxidant at reaction conditions over a crystalline aluminosilicate having rigid three-dimensional networks and crystalline cavities accessible through ports of dimension of about 5 A., said cavities having included therein a material having catalytic activity for oxidation whereby at least one species of molecules is selectively admitted because of its molecular shape and acted upon.

As has heretofore been stated, when this process was attempted at the conditions of this invention, very unexpected results were observed.

The first surprising result stemmed from the fact that it was immediately observed that there was a critical correlation between the activity of the cracking catalyst and the ability to carry out the process. Contrary to what had heretofore been the case in those high temperature cracking processes carried out without the introduction of an oxidant, the operable activity range was found to be considerably narrow. In this connection, it was found that the cracking catalyst should have an alpha value no less than about 0.5 or more than about four and, more preferably, an alpha value of about 2.

The alpha value describes the relative activity of a catalyst with respect to a high activity conventional silica alumina cracking catalyst. Thus, an alpha value of 2 indicates an activity which is two times greater than the conventional reference catalyst.

To determine the alpha value conversion of n-hexane is determined and converted to a rate constant per unit volume of catalyst and compared with that of a silica-alumina catalyst normalized to specific conditions. This method of determining alpha values is more fully described in the Journal of Catalysis, vol. IV, No. 4, August 1965, pp. 527–529.

Thus, the first criticality in the novel process of this invention is the use of a cracking catalyst having an alpha value of from about 0.5 to 4. If materials are employed having an alpha value less than the designated limit, in-

sufficient activity will exist to carry out the cracking process in a desirable manner. Conversely, if cracking catalysts having alpha values greater than four are employed, the presence of oxygen for reasons not completely understood cause a drastic drop in the conversion ability of said catalyst so that it is rendered useless for its intended purpose.

The second criticality of the cracking catalyst employed in this invention is that it not have oxidation activity. This requirement is not too surprising since the purpose of this invention is to limit the oxidation activity to within the pore size of the shape selective combustion catalyst. However, it was immediately discovered that under the operating conditions of this invention certain catalysts were found to have oxidation activity which did not possess said activity at conventional cracking conditions. Thus, by way of specific example, a preferred cracking catalyst in the majority of conventional catalytic operations are rare earth aluminosilicates. Such materials cannot be used in the instant process since rare earth aluminosilicates have oxidation activity under the conditions of this invention.

Representative cracking catalysts which can be used in the instant process include certain types of silica-alumina, silica-magnesia, silica-zirconia, zirconia-alumina and, more preferably, crystalline aluminosilicates.

Aluminosilicates which are operable as cracking catalysts in the novel process of this invention include a wide variety of compounds, both natural and synthetic. Aluminosilicates can be described as a three-dimensional framework of SiO_4 and AlO_4 tetrahedra in which the tetrahedra are cross-linked by the sharing of oxygen atoms whereby the ratio of total aluminum and silicon atoms to oxygen atoms is 1:2. The hydrated form aluminosilicates may be represented by the formula:

$$\frac{M_{2}}{n}:OAl_2O_3:wSiO_2:yH_2O$$

wherein M represents at least one cation which balances the electrovalence of the tetrahedra, n represents the valence of the cation, w the moles of SiO_2 and y the moles of H_2O. The cation can be any or more of a number of metal ions depending whether the aluminosilicate is synthesized or occurs naturally. All or a portion of the cations originally associated with the aluminosilicate can be replaced with other cations providing they have no oxidation activity such as hydrogen ions, ammonium ions or other metal cations such as, for example, calcium, magnesium, etc. or mixtures thereof. It is to be noted that the replacing cations or mixtures of cations need only be present in an amount sufficient to give the aluminosilicate composition an alpha value of from 0.5 to 4.0 and, more preferably, about 2.0.

Aluminosilicates falling within the above formula are well known and include synthetized aluminosilicates, natural aluminosilicates, and certain caustic treated clays.

Among the preferred aluminosilicates one can include zeolites Y, L, X, beta, ZSM–4 and natural materials such as faujasite and mordenite.

If it is desirous to selectively crack straight-chain hydrocarbons from a mixture of the same with other components, zeolites having pore sizes of about 5 A. can be employed. These materials would include zeolites A, D, R, S, T, Z, E, F, Q, B, ZK–4, ZK–5, alpha, ZSM–5, erionite, chabazite, gmelinite, and dachiarite.

The particularly preferred aluminosilicates, however, are those having pore diameters of at least about 6 A.

It should also be stated that since the alpha value of a particular aluminosilicate increases with decreasing alkali metal ion content this invention specifically includes those aluminosilicates which have alpha values greater than four as a result of replacement of a substantial portion of the alkali metal cations with protons, other metal cations or mixtures thereof provided they are pretreated in order to reduce the alpha to the desired alpha range of 0.5 to 4.

The alpha value of an aluminosilicate can be reduced by many techniques including heat treatment, steaming as well as a combination of both these techniques. Reduction by alpha by heat treatment can be accomplished by heating the aluminosilicate at temperatures of at least about 1500° F. for 1 to 48 hours or longer. Steaming to reduce alpha values can be carried out at elevated temperatures of 800° F. to 1500° F. and preferably at temperatures of about 1000° F. to 1400° F. The treatment may be accomplished in an atmosphere of 100% steam or in an atmosphere consisting of steam and gas which is substantially inert to the aluminosilicate. A similar treatment can be accomplished at lower temperatures in elevated pressures, e.g., 350° F. to 700° F. at 10 to about 200 atmospheres.

It should also be noted that one aspect of this invention resides in the development of a process which does not require regeneration of a catalyst and therefore other types of aluminosilicates can be used which have heretofore been thought to be impractical. Thus, for example, aside from the question of activity, a catalyst in a regenerative process must also be stable to steam since, in fact, steam is generated in the regenerative operations. In view of this, high sodium content aluminosilicates, i.e., the sodium faujasites of the X and Y type were generally thought to be unsuitable for cracking processes due to their lack of steam stability. In view of the fact that regeneration is not absolutely necessary in the instant invention, steam stability is also not necessary and high sodium content aluminosilicates can be employed.

As has heretofore been stated, the novel process of this invention is carried out at temperatures ranging from 1100 to 1350° F. at certain critical minimum space velocity. It is to be understood that all figures given for space velocity refer to a charge that is 100% hydrocarbon, i.e., no diluent gas is added.

It is specifically pointed out that this invention also includes mixing a hydrocarbon charge with a diluent and passing said mixture over the catalyst. In situations where a feed is employed which is not 100% hydrocarbon then the space velocities must be chosen so as to insure that the previously set forth minimums will be applicable to the hydrocarbon portion of the feed. Thus, for example, it has been stated that for conversion at 1100° F. a minimum space velocity of 32 (LHSV) must be employed in order to insure that no more than 10% thermal cracking will be obtained. If, however, the hydrocarbon feed employed for conversion at 1100° F. is not all hydrocarbon, but rather, a mixture of a hydrocarbon with a gas such as steam, flue gas or helium then the minimum space velocity which is employed is merely the space velocity previously set forth multiplied by the fraction of the hydrocarbon vapor in the feed so as to give the same vapor contact time. By way of specific illustration at 1100° F. a minimum space velocity of 32 is necessary for a feed which is 100% hydrocarbon. If, however, a feed which is employed which is 50 volume percent hydrocarbon and 50 volume percent helium, steam, flue gas, etc. then the minimum space velocity employed would merely be ½ of 32 or 16. It should be immediately apparent that a 16 space velocity based on a 50–50 mixture of hydrocarbon and diluent is, in fact, equivalent to a 32 space velocity based on 100% pure hydrocarbon.

The shape selective combustion catalysts which are operable in the novel process of this invention are crystalline aluminosilicates having a pore size of about 5 A. and containing within the intercrystalline spaces thereof an oxidation catalyst.

Examples of suitable crystalline aluminosilicates are to be found among a number of aluminosilicate materials, and among synthetically prepared crystalline aluminosilicate materials, and among synthetically prepared crystalline aluminosilicates which have structure alalogous to and sometimes differing from the materials known to occur naturally. Specific aluminosilicates include charbazite, gmelinite, stilbite, erionite (offretite), zeolites S, T,

A, ZK–4, ZK–5 and others. It is to be noted that the term erionite and offretite will be considered to be identical in meaning as regards reference to the same or closely equivalent structural mineral form in accordance with the findings reported in Mineralogical Magazine, vol. 33, pp. 66–67, 1962, by H. M. Hey et al. entitled "The Identity of Erionite and Offretite."

It is preferred, however, to employ aluminosilicates having silicon to aluminum atomic ratios of at least 1.8 and in this connection aluminosilicates such as erionite (offretite), gmelinite, chabazite, etc. are particularly preferred.

Suitable catalytic oxidation surfaces are achieved by deposition within the pores of the crystalline aluminosilicate structure of a transition metal or compounds thereof capable of catalytically promoting oxidation. Such metals are well known to those in the art and include metals of atomic numbers 22 to 29, 42 to 47 and 74 to 78 inclusive. Rare earth elements and compounds thereof may also, in some instances, be found useful. Deposition of the metal within the crystalline aluminosilicate may be accomplished by growth of the aluminosilicate crystals in a solution containing an ion of such metal. Thus, suitable crystalline inorganic aluminosilicates containing a transition metal distributed within the pores thereof may be produced by effecting the growth of crystals of the aluminosilicate from an aqueous mixture containing a water-soluble ionizable transition metal compound, dehydrating the resulting transition metal containing crystalline product and subjecting the same to a thermal treatment at an elevated temperaure. The resuling product comprises a transition metal dispersed within the pores of the crystalline aluminosilicate structure characterized by rigid three-dimensional networks and an effective pore diameter within the approximate range of about 5 angstroms. An effective crystalline aluminosilicate having a platinum metal distributed within its uniform structure may be prepared, as described in U.S. 3,373,109 by introducing into an aqueous reaction solution having a composition, expressed as mixtures of oxides, within the following ranges SiO_2/Al_2O_3 of 0.5 to 2.5, Na_2O/SiO_2 of 0.8 to 3.0 and H_2O/Na_2O of 35 to 200, a minor proportion of a water-soluble ionizable platinum metal compound, inducing crystallization of the resulting reaction mixture by subjecting the same to hydrothermal treatment, replacing sodium ions of the resulting crystalline product with calcium, dehydrating the material so obtained and thermally treating at a temperature in the approximate range of 250° F. to 1100° F. to effect at least partial conversion of the platinum metal-containing ion to a catalytically active state, thereby yielding a resulting composition having platinum metal dispersed with the pores of a crystalline aluminosilicate characterized by rigid three-dimensional networks and uniform pores approximately 5 angstroms in diameter.

Aside from introducing the transition metal into the aluminosilicate structure during the process of crystal growth, such metal may be deposited within the interior of the crystalline aluminosilicate by base-exchange of an initially formed alkali metal or alkaline earth metal aluminosilicate with a solution containing an ion of the desired metal. Utilizing this manner of operation, it is generally desirable to remove active catalytic oxidation surfaces attributable to deposition of the metal ion on the outer surface of the crystalline aluminosilicate lattice by either of two methods. One method utilizes the effect of additional base-exchange treatment with a solution containing an ion of size too large to enter the cavities, but effective in exchanging catalytically active to catalytically inactive ions in all external locations. Another method relies on contacting the base-exchanged material with a substance capable of poisoning the oxidation active ions externally but incapable of reaching and thus effecting the active sites located within the cavities. By whatever method may be employed, the catalytic oxidation surface is caused to be contained only within the crystalline pore structure and to thereby afford a resulting product capable of effecting desired selective catalytic combustion.

As has heretofore been pointed out, the novel process of this invention is carried out by introducing a mixture of hydrocarbons such as a petroleum fraction together with an oxidant into a reactor containing a shape selective combustion catalyst and a cracking catalyst and carrying out the reactions under certain critical conditions. The selective combustion catalyst acts upon a portion of the feed and/or reaction products from the cracking reaction in order to provide at least a portion of the necessary heat for the cracking reaction. The ratio of combustion catalyst to cracking catalyst is not narrowly critical and weight ratios from about 0.01 to 0.5 are operable with from 0.05 to 0.2 being particularly preferred.

A wide variety of oxidant materials may be employed including oxygen, ozone, sulfur dioxides, sulfur, chlorine, nitrogen, nitrogen oxides, and the like as well as mixtures thereof including air. For all practical purposes, it is preferred to use air or oxygen.

It has also been found that the amount of oxidant employed has a definite bearing on the ability to carry out selective combustion reaction. Too much oxidant causes oxidation of desirable portions of the feed whereas too little does not accomplish the desired purpose. The exact amount of oxidant employed will obviously vary depending upon the specific oxidant used. However, sufficient oxidant should be used such that 100 to 600 and preferably 300–400, B.t.u./lb. of charge stock are generated. This is accomplished by burning 0.5 to 3, and preferably 1.5–2 weight percent of the charge.

If oxygen is employed as the oxidant, the amount required would be 0.017 to 0.115 pounds per pound of charge. Preferably, the amount of oxygen used ranges from 0.05 to 0.07 pounds per pound of charge. The amount of oxygen needed can also be expressed in cubic feet instead of pounds. Thus, the necessary oxygen ranges from 0.22 to 1.8, and preferably from 0.67 to 0.90 cubic feet per pound of charge.

If air is used as the oxidant, it should be present in amounts ranging from approximately 1–10 and preferably 3–5 cubic feet per pound of charge.

Another, though less preferred, embodiment of this invention resides in the incorporation of the crystalline aluminosilicate cracking catalyst in a matrix. Typical matrices and techniques for incorporation are disclosed in U.S. 3,140,253.

The novel process of this invention is applicable to a wide variety of feed materials including, but not limited to, those feed stocks typically used in commercial refineries. However, maximum benefit is obtained from the instant process if a feed stock is chosen such that the proper carbon-hydrogen balance is obtained. By way of considerable oversimplification, it should be realized that a cracking process involves the redistribution and rearrangement of carbon and hydrogen, and in order to produce desired products, there must be a sufficient amount of carbon and hydrogen originally present in the feed. If a feed stock is chosen which is "hydrogen deficient" the maximum yield to useful products is governed by stoichiometric considerations. Thus, particularly preferred feed stocks are those which have hydrogen contents of at least 12.3 weight percent and even more desirably at least 12.8 weight percent. However, it is to be understood that feed materials outside the range of desired hydrogen content can be hydrotreated or hydrogenated prior to being cracked in accordance with the instant invention.

The following examples will illustrate the novel process of this invention.

EXAMPLES 1–3

A mixture of helium and a Light East Texas Gas Oil (LETGO) having a hydrogen content of 13.05 percent by weight was preheated to 900° F. and thereafter charged

into a reactor filled with quartz chips and maintained at elevated temperatures in order to effect conversion of the gas oil. After five minutes, a material balance of the product stream was made, and the results of the analysis as well as the specific experimental conditions are shown in the following table.

TABLE

	Example		
	I	II	III
Catalyst	None	None	None
Charge rates per minute:			
gas oil, g	0.423	0.423	0.423
He, cc	420	420	420
Average temperature, °F	1,062	1,255	1,150
Vapor contact time, sec	0.008	0.008	0.023
Conversion, wt. percent	2.1	2.9	2.3

From the above three examples, it can be seen that even at high reaction temperatures little conversion was obtained at the high space velocities employed. In these experiments the effect of thermal cracking has been minimized due to the novel combination of high temperature and high space velocities.

In all the examples which follow, unless otherwise indicated, prior to each individual catalyst being evaluated for cracking, it was calcined at the reaction temperature for 30 minutes with a 50/10 cc. per minute flow rate of a helium/oxygen mixture after which the reaction was purged with helium at a flow rate of 50 cc. per minute for 20 minutes.

EXAMPLE 4

This example will illustrate that a rare earth aluminosilicate cannot be used as the cracking catalyst in the instant process, although said materials are excellent cracking catalysts at these conditions in the absence of an oxidant.

A catalyst mixture consisting of seven parts by volume of a steamed rare earth aluminosilicate having an alpha value of 2.8 and 3 parts by volume of a shape selective combustion catalyst comprising platinum containing zeolite T was tested for the cracking of a hydrotreated Beaumont charge stock according to the following procedure:

A hydrogen deficient Beaumont charge stock having the following composition:

13.6 weight percent Light Mid-Continent Gas Oil;
9.7 weight precent Light Coker Gas Oil;
37.2 Heavy Virgin Mid-Continent Gas Oil;
11.5 weight percent Heavy Coker Gas Oil;
28 weight percent of an overhead of a 1:1 ratio of T.C.C.;
Heavy cycle stock and furfural extract.

was contacted with hydrogen under hydrogenation conditions until the total weight percent of hydrogen in the treated material was 12.27.

This material was then passed over the catalyst mixture above-described at a temperature of 1150° F., a helium to hydrocarbon ratio of 3.0 and an LHSV of 300. After 2.5 hours a material balance of the product stream was made. After 4½ hours, oxygen was introduced at a flow rate of 10 cc./minute and another material balance was made.

The results are as follows:

	With oxygen	Without oxygen
Time, hours	4.6	2.5
Conversion, wt. percent	3.4	42.0
Product, selectivity, we. percent:		
C^1–C^3	14.7	13.8
C^5 plus gasoline	50.0	73.9
CO_2	29.4	0

As can be seen, the presence of oxygen drastically reduced the effectiveness of the rare earth aluminosilicate both in conversion and in product selectivity for gasoline.

Examples 5–8 illustrate the effect of the oxygen to hydrocarbon ratio on the oxidation activity of the shape selective catalysts at the reaction conditions of this invention. The mixture used in the examples contains helium and hydrocarbons in the following proportions:

	Percent
Propylene	0.24
Isobutane	0.24
Isohexane	0.06

EXAMPLE 5

A calcium aluminosilicate identified as zeolite 5A containing 0.4 weight percent platinum was contacted with the mixture of helium and hydrocarbons at an apparent contact time of 0.0001 second and at a temperature of 1300° F. The following table illustrates the results of this experiment at two different concentrations of oxygen. The expression "O_2HC of .8" signifies 80% of the theoretical amount of oxygen necessary to convert all the carbon atoms to CO_2 and all the hydrogen atoms to water. A O_2/HC of 0.4 signifies 40% of the theoretical amount of oxygen necessary to convert all the carbon atoms to CO_2 and all the hydrogen atoms to water.

TABLE

O_2/HC of 0.8:	Wt. percent
Propylene	83
Isobutane	19
Isohexane	19
O_2/HC of 0.4:	
Propylene	43
Isobutane	About 1
Isohexane	1

EXAMPLE 6

The above example was repeated with the exception that the contact time was 0.00017 second.

TABLE

O_2/HC of 0.8:	Wt. percent
Propylene	100
Isobutane	37
Isohexane	61
O_2/HC of 0.4:	
Propylene	95
Isobutane	5
Isohexane	14

EXAMPLE 7

A synthetic crystalline aluminosilicate identified as zeolite T containing 0.2 weight percent platinum was tested in the identical manner as Example 5 at an apparent contact time of 0.0021 second with the following result.

TABLE

O_2/HC of 0.8:	Wt. percent
Propylene	100
Isobutane	67
Isohexane	88
O_2/HC of 0.4:	
Propylene	98
Isobutane	7
Isohexane	21

EXAMPLE 8

An ammonium exchange zeolite identified as erionite and containing 3.5 weight percent nickel was tested in the same manner as Example 5 at an apparent contact time of 0.00048 second. The results at two different levels of oxidant concentration are as follows:

TABLE

O_2/HC of 0.8:	Wt. percent
Propylene	68
Isobutane	26
Isohexane	39

O_2/HC of 0.4:

Propylene	50
Isobutane	9
Isohexane	7

Examples 5 to 8 illustrate that excellent results are obtained at lower concentration of oxidant whereas at the higher concentration of oxidant unselective oxidation of the feed takes place.

EXAMPLE 9

A catalyst mixture was prepared by mixing together

(1) Seven volumes of a synthetic crystalline aluminosilicate cracking catalyst having an alpha rating of about 1.3 and prepared by treating synthetic faujasite of the Y type as follows:

164 grams of zeolite Y was oven-dried at 230° F. and thereafter steamed at 1000° F. for 90 minutes with 4400 cubic centimeters of steam per minute. The steamed material was then base exchanged with a 1 normal solution of ammonium chloride overnight at room temperature. The aluminosilicate was then filtered, washed and dried overnight at 230° F. and refluxed for 90 minutes at 216° F. with 2070 cubic centimeters of a 0.25 normal solution of ethylenediaminetetracetic acid which had its pH adjusted to about .1 with sodium hydroxide. The aluminosilicate was then filtered and washed with 2070 cubic centimeters of water and dried at 230° F. overnight.

5 grams of the above aluminosilicate were mixed with 50 cc. of a 0.5 normal solution of sodium acetate for 1½ hours at room temperature. This procedure was repeated for a total of three times. The mixture was then filtered and washed three times with 50 cc. of distilled water. The catalyst was then dried for 64 hours at 100° C. to yield a catalyst having a sodium content of 2.96 weight percent; and

(2) Three volumes of a shape selective combustion catalyst prepared in the following manner:

7.87 grams of sodium aluminate, 17.6 grams of sodium hydroxide, 9.8 grams of potassium hydroxide in 122 ml. of water and 178 grams of colloidal silica were mixed together for 10 minutes to form a thick gel. To this mixture was added 25 cc. of platinum amine chloride solution with stirring for five minutes. The mixture was then placed in a steam bath and heated at 190° F. overnight without steaming. This preparation yielded a catalyst identified as zeolite T containing 0.5 weight percent platinum within its internal pores.

The above catalyst mixture was placed in a reactor and charged with a 3 to 1 mol ratio mixture of helium and the hydrotreated Beaumont charge stock of Example 4 at a temperature of from about 1150° to 1200° F., an LHSV of 420 based on the cracking catalyst. Oxygen was also charged in an amount of 0.03 lbs./lb. of charge. The results of the above experiment showed that under these drastic conditions, conversion of the gas oil was maintained at above 30% for 4.5 hours and above 20% for 6.6 hours. This catalyst treated 1900 pounds of charge stock per pound of catalyst.

EXAMPLE 10

A catalyst mixture was prepared by mixing together

(1) Seven volumes of a crystalline aluminosilicate prepared according to the following manner:

20 grams of a crystalline aluminosilicate identified as zeolite Y were placed in a Soxhlet reactor with 7.35 grams of ethylenediaminetetracetic and the mixture refluxed overnight. The product was then filtered and washed to yield a catalyst having an alpha value of about 0.6; and

(2) Three volumes of the shape-selective catalyst employed in Example 9.

This mixture of catalysts was then placed in a reactor and tested for the conversion of a mixture of helium and the hydrotreated Beaumont charge stock of Example 4 in a molar ratio of 3 to 1 at a temperature of 1150° to 1200° F., and at 420 LHSV based on the cracking catalyst oxygen was added at 0.3 lbs./lb. of charge.

After a period of 8 hours, it was calculated that under these conditions one pound of catalyst could have treated 1500 pounds of charge stock.

It is to be understood that the above description is merely illustrative of the preferred embodiments of the invention and is not intended that it be limited thereto except as necessitated by the appended claims.

What is claimed is:

1. A method of internally heating a catalytic cracking zone containing a combustible fuel component wherein a fluid hydrocarbon charge undergoes cracking in the presence of a solid porous cracking catalyst characterized by having an alpha value of from about 0.5 to about 4 and being substantially free of oxidation activity which comprises introducing into said zone together with said charge an oxidant and in admixture with said cracking catalyst a crystalline aluminosilicate having rigid three-dimensional networks bearing within the interior thereof catalytic oxidation surfaces and having a pore size of about 5 A. which are sufficiently large to admit said oxidant and said fuel component but sufficiently small to exclude at least a portion of the hydrocarbon charge, initiating combustion of said fuel component in contact with said catalytic oxidation surfaces whereby the temperature of said reaction zone ranges from about 1100° F. to about 1350° F. so as to effect cracking of said hydrocarbon charge to normally liquid hydrocarbons lighter than said charge and a gaseous product, utilizing said gaseous product as the aforementioned fuel component, the reaction being carried out at space velocities ranging from 32 to 1200 LHSV and at catalyst-to-oil ratios, based on the cracking catalyst, no higher than 0.1.

2. The process of claim 1 wherein the cracking catalyst is a crystalline aluminosilicate having a pore size greater than 6 A.

3. The process of claim 2 wherein the cracking catalyst has an alpha value of about 2.0.

4. The process of claim 2 wherein the shape selective combustion catalyst has a silicon to aluminum atomic ratio of at least 1.8.

5. The process of claim 2 wherein the gaseous oxidant is oxygen.

6. The process of claim 2 wherein the gaseous oxidant is air.

7. A method for internally heating a catalytic cracking zone containing a combustible fuel component wherein a fluid hydrocarbon charge undergoes cracking in the presence of a faujasite characterized by an alpha value of from 0.5 to 4 and substantially free of oxidation activity which comprises introducing air into said zone together with said charge and in admixture with said faujasite, a crystalline aluminosilicate having a pore size of about 5 A. and bearing within the interior thereof catalytic oxidation surfaces, initiating combustion of said fuel component in contact with said catalytic oxidation surfaces whereby the temperature of said reaction zone ranges from about 1100° to about 1300° F. so as to effect cracking of said hydrocarbon charge to normally liquid hydrocarbons lighter than said charge in a gaseous product, utilizing said gaseous product as the aforementioned fuel component, said reaction being carried out at a space velocity of from about 32 to about 1200 LHSV and a catalyst-to-oil ratio no higher than 0.1, based on the faujasite.

8. The process of claim 1 wherein the shape selective combustion catalyst having a pore size of about 5 A. is erionite.

9. The process of claim 1 wherein the shape selective combustion catalyst having a pore size of about 5 A. is zeolite T.

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U.S. Cl. X.R.

208—120

PO-1050
(5/69)

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,530,064 Dated September 22, 1970

Inventor(s) NAI YUEN CHEN and STANLEY J. LUCKI

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 3, line 35, that portion of the formula reading "$M_{\frac{2}{n}}:OAl_2O_3$" should read --$M_{\frac{2}{n}}O:Al_2O_3$--.

Column 4, line 3, "by" should read --of--.

Column 5, line 31, "resuling" should read --resulting--.

Column 7, line 27, "reaction" should read --reactor--.

Column 7, line 68, "we" should read -wt.--.

(line 3 of chart)

[illegible] read [illegible]

[illegible] read [illegible].

SIGNED AND
SEALED
DEC 15 1970

(SEAL)
Attest:

Edward M. Fletcher, Jr.
Attesting Officer

WILLIAM E. SCHUYLER, JR.
Commissioner of Patents