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[54] **CONVERSION OF HYDROCARBONS WITH "Y" FAUJASITE-TYPE CATALYSTS**

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[51] **Int. Cl.**..... **C10g 37/02**; C10g 11/18; B01j 9/20

[58] **Field of Search**..... 208/78, 71, 62

[56] **References Cited**

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[57] **ABSTRACT**

A FCC operation is described for separately converting with faujasite conversion catalyst, a gas oil feed material and a C_3–C_4 rich hydrocarbon fraction. Conversion of the gas oil is accomplished in a normal riser reactor and conversion of the C_3–C_4 rich hydrocarbons is accomplished with catalyst separated from the gas oil riser reactor in a restricted riser reactor confined within the catalyst collecting zone about the discharge end of the gas oil riser.

7 Claims, 1 Drawing Figure

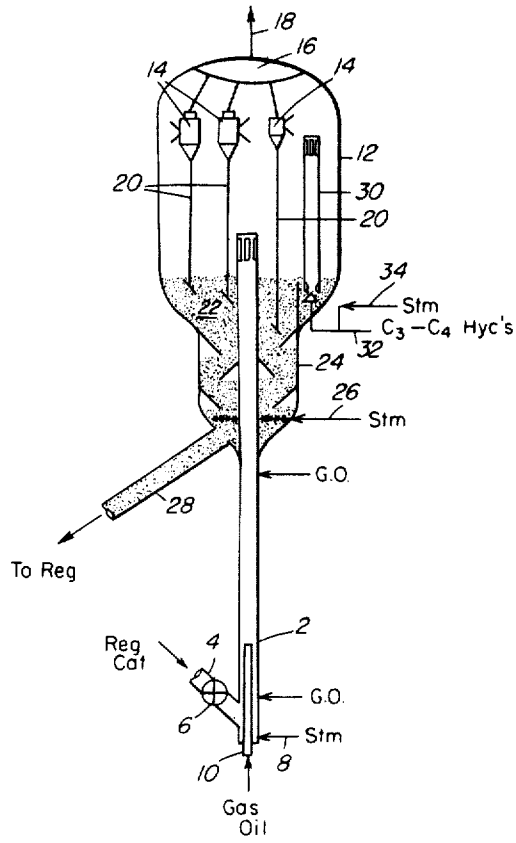
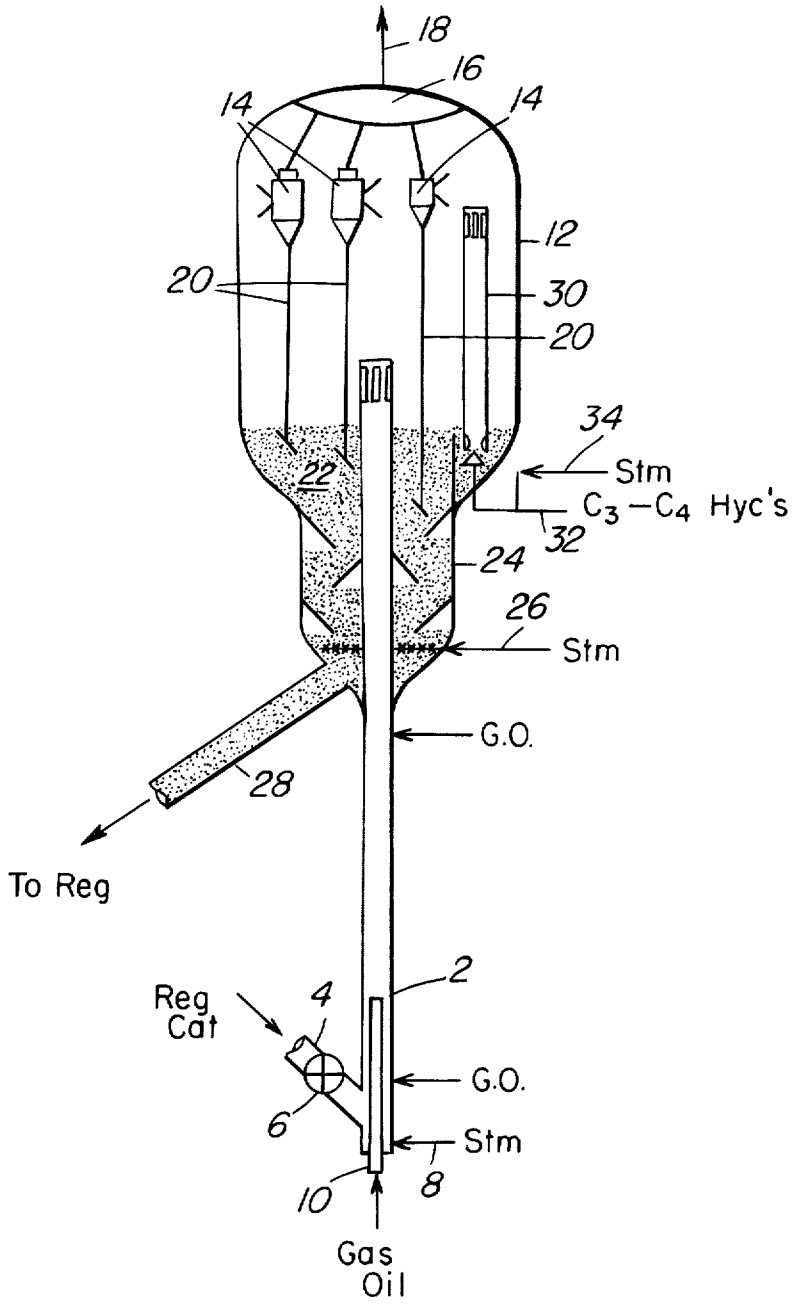


FIGURE I


18
16
14
14
12
20
30
20
34
Stm
C_3-C_4 Hyc's
22
32
24
26
Stm
G.O.
28
To Reg
2
Reg Cat
4
G.O.
6
Stm
8
10
Gas Oil

CONVERSION OF HYDROCARBONS WITH "Y" FAUJASITE-TYPE CATALYSTS

BACKGROUND OF THE INVENTION

The field of catalytic cracking and particularly the operations related to dense and dilute fluid phase catalytic operations have been undergoing progressive development since early 1940. As new experience was gained in operating and design parameters, new catalyst compositions were developed which prompted a further refinement in known operating technology. With the development of high activity crystalline zeolite catalyst, the industry found a further need to improve upon its operating parameters to take advantage of the new catalysts activity, selectivity and operating sensitivity. The present invention is thus concerned with an improved method of cracking or catalytic operation which relates to catalyst activity and selectivity to processing parameters in a manner mutually contributing to improving the conversion of available refinery feed materials.

SUMMARY OF THE INVENTION

The present invention is directed to the conversion of hydrocarbons in the presence of a relatively large pore crystalline material of the faujasite type of crystalline zeolite. In a more particular aspect, the present invention is concerned with more completely utilizing the activity and selectivity characteristics of X and Y faujasite crystalline aluminosilicate conversion catalyst to upgrade gas oil feed materials and normally gaseous hydrocarbon products such as those obtained in a gas oil conversion operation. In yet another aspect the present invention is concerned with using a faujasite cracking catalyst separated from a gas oil hydrocarbon conversion zone to upgrade particularly C_3 and C_4 rich hydrocarbon gaseous materials to higher boiling gasoline boiling material. The C_3–C_4 rich gaseous material may be the product of a high temperature hydrocarbon cracking operation or the gaseous hydrocarbons may be recovered from other available refinery sources. More particularly, the present invention is concerned with the cracking of high boiling hydrocarbons such as gas oil boiling range hydrocarbons, residual oils and hydrogenated products thereof including a hydrogenated resid material with particularly a Y faujasite cracking catalyst under elevated temperature cracking conditions selected from within the range of 900°F. to about 1,100°F. at a hydrocarbon residence time in a once through conversion zone restricted to within the range of 1 to about 12 seconds. Catalyst to oil ratios may be selected from within the range of 4 to about 20. Generally, it is preferred to accomplish cracking of the gas oil in an upflowing riser conversion zone discharging into a separation zone such as an upper portion of an enlarged catalyst separation and collection vessel wherein products of gas oil cracking are separated from the catalyst used. The riser suspension may be discharged directly into cyclonic separating means attached to the end of the riser or into the enlarged vessel under velocity reducing conditions causing catalyst particles to settle out and separate from vaporous hydrocarbons before encountering cyclonic separation of entrained catalyst fines from hydrocarbon vapors. The separated catalyst is collected in a lower portion of the enlarged vessel for passage to a lower catalyst stripping zone wherein the catalyst is stripped with countercurrent flowing stripping gas such as steam. The stripped products and products of cracking separated from the catalyst upon discharge from the riser conversion zone are combined, removed from the enlarged vessel and passed to one or more down-stream separation zones. In accordance with one aspect of this invention, a restricted or relatively short riser reactor discharging into catalyst separation means such as one or more cyclonic separators at the riser outlet is provided within the upper portion of the enlarged vessel so that the restricted riser extends upwardly from within the collected bed of catalyst to an upper portion of the vessel. In this arrangement the catalyst separated from the gas oil conversion step at an elevated temperature is available for flow upwardly through the restricted riser conversion zone suspended in normally gaseous C_3–C_4 hydrocarbon feed material. In this invention, a C_3–C_4 rich hydrocarbon mixture is combined with faujasite conversion catalyst separated from the gas oil conversion zone at an elevated cracking temperature to form a suspension of catalyst to hydrocarbon feed ratio in the range of 5 to about 40 at an elevated suspension temperature in the range of about 700 to about 1,050°F. The C_3–C_4 rich hydrocarbon feed stream may be furnace heated to an elevated temperature in the range of 550°F. to about 900°F. before entering the restricted riser conversion zone. On the other hand, to vary the catalyst to hydrocarbon ratio within the restricted riser conversion zone, steam may be used along with the C_3–C_4 hydrocarbon stream. Also steam may be used to effect the lift characteristics of the suspension to pass upwardly through the restricted conversion zone. The suspension formed as herein provided passes upwardly through the restricted riser conversion zone under conditions providing a hydrocarbon residence time within the range of 1 to about 10 seconds before discharge and separation of the suspension by cyclonic means. During this operation, the faujasite catalyst providing hydrogen transfer activity and cyclization selectivity converts the C_3–C_4 hydrocarbons to aromatics; alkyl aromatics and low boiling gaseous material.

Catalyst particles separated from the conversion zones herein identified are caused to flow downwardly to and through a stripping zone countercurrent to rising stripping gas such as steam. The stripped catalyst is then transferred to a catalyst regeneration zone not shown for the removal of deposited carbonaceous material thereby heating the catalyst to an elevated temperature.

It is contemplated providing separate stripping zones for stripping catalyst separated from each riser conversion zone and adding heat to each stripping operation. For example, either one or both stripping operation may be provided with hot regenerated catalyst to raise the temperature of the stripping zone. On the other hand, where a single stripping zone is used, it may also be advisable to bring a stream of hot regenerated catalyst into the stripping operation to maintain its efficiency at a high value. It is also contemplated passing the relatively cold catalyst of the C_3–C_4 hydrocarbon conversion step to a lower portion of the gas oil separated catalyst stripping step and providing multiple stripping gas inlets to the stripping zone.

BRIEF DESCRIPTION OF THE DRAWING

The FIGURE is a diagrammatic sketch in elevation of an arrangement of hydrocarbon conversion zones

for catalytically converting selected hydrocarbon feeds with a fluid conversion catalyst.

DISCUSSION OF SPECIFIC EMBODIMENTS

Referring now to the FIGURE, there is shown a riser conversion zone **2** supplied with hot regenerated catalyst by conduit **4** provided with a catalyst flow control valve **6.** Steam is introduced to a bottom portion of riser **2** by one or more steam inlet conduits **8** external to and about a gas oil inlet conduit **10** which projects upwardly into the bottom portion of riser **2.** A suspension of catalyst in dispersion steam is thus initially formed into which an upflowing gas oil feed is introduced providing a mix or catalyst-oil suspension temperature of at least 950°F. Steam may also be combined with the oil charge. The suspension passes upwardly through riser **2** under velocity conditions selected to provide a hydrocarbon residence time therein preferably within the range of 2 to about 10 seconds. The upflowing suspension in riser **2** is discharged from the end thereof as by slotted openings into an enlarged catalyst settling zone promoted by reduced vapor velocity. On the other hand, riser **2** may discharge directly into one or more cyclonic separating means or immediately adjacent the bell mouth opening thereto for separating fluid catalyst particles from hydrocarbon vapors. In the specific arrangement shown in the FIGURE the suspension in riser **2** is discharged into an enlarged zone or vessel **12** wherein separation of catalyst from hydrocarbon vapors is encouraged by a substantial reduction in the suspension velocity. Hydrocarbon vapors then pass through cyclonic separation means **14** for removal of entrained fines before the hydrocarbon vapors pass into a plenum chamber **16** and removal from the vessel by conduit **18.** Catalyst separated from hydrocarbon vapors by settling and in cyclonic means **14** pass by diplegs **20** to a fluid bed of catalyst **22** therebelow maintained in the lower portion of the vessel **12.** The fluid bed of catalyst **22** is in open communication with a lower stripping zone **24** to which the fluid bed of catalyst moves downwardly to and through countercurrent to rising stripping gas introduced by conduit **26.** Stripped catalyst is removed from a bottom portion of the stripping zone by conduit **28** for transfer to a catalyst regeneration zone not shown. A portion of the catalyst withdrawn by conduit **28** may be recycled to the inlet of riser **2** when a higher catalyst to oil ratio is desired. The fluid bed of catalyst **22** separated from the riser conversion zone **2** is normally (in the absence of restricted riser **30**) at an elevated temperature and from about 25°F. to about 75°F. below the temperature employed at the inlet of the riser conversion zone **2.** However, in accordance with this invention, a second restricted riser conversion zone **30** is provided within vessel **12** and the presence of such a restricted conversion zone will cause a further reduction in the catalyst bed temperature unless augmented as herein provided. Riser **30** extends from beneath the upper interface of bed **22** into an upper portion of the vessel so that a suspension of catalyst and hydrocarbon vapors discharged from the upper end of riser **30** will be substantially adjacent the inlet of a cyclonic separation means or discharge directly into cyclonic separating means. Catalyst separated as by cyclonic means **14** is then returned to a lower portion of bed **22** than the inlet to riser **30** by a dipleg **20** as shown. A catalyst withdrawal well about the inlet of riser **30** may be provided. A gaseous hydrocarbon feed such as a mixture of C_3–C_4 hydrocarbons at a suitable elevated temperature is introduced by conduit **32** with or without steam introduced by conduit **34** to the bottom of riser **30** with suspended catalyst particles from fluid bed **22** to form a mixture or suspension at a temperature within the range of 700°F. to about 1,050°F. The suspension formed in a catalyst/oil ratio in the range of 5 to about 40 is passed upwardly through riser **30** under conditions to provide a hydrocarbon residence time within the range of 1 to about 10 seconds. The upwardly flowing suspension on riser **30** is discharged from the upper end thereof adjacent the inlet to cyclonic separation means or directly into cyclonic separating means on the riser outlet and positioned in the upper portion of the enlarged settling vessel **12.** The discharged suspension is separated by catalyst settling in the specific arrangement of the FIGURE due to a drop in velocity and by the aid of cyclonic separation means such as separators **14.** The separated catalyst is returned to the fluid bed of catalyst **22** by diplegs provided. The discharge end of risers **2** and **30** may be in a T connection and provided with one or more cyclonic separation means on each end thereof so that the suspension passed upwardly through the risers will pass directly into the cyclonic separators. This method of handling the suspension discharged from the risers provides a more positive control on the contact time between hydrocarbon vapors and catalyst particles.

The method and system of the FIGURE above described may be modified to some considerable extent without departing from the concepts of the present invention. For example, riser **30** may be a separate riser, the major portion of which is external to the vessel **12** in much the same manner as riser **2** is external to the vessel. In this arrangement, the riser relied upon to upgrade C_4 and lower boiling hydrocarbons may be provided with hot freshly regenerated catalyst or catalyst separated from the gas oil riser conversion step either before or after stripping thereof. In yet another embodiment, it is contemplated initially contacting freshly regenerated catalyst in the bottom portion of riser **2** with a C_3–C_4 hydrocarbon rich mixture to form a suspension and thereafter bringing the suspension in contact with gas oil feed material in an upper portion of the riser at one or more spaced intervals before discharge thereof into catalyst-hydrocarbon vapor separating zones. In one or more of the above embodiments, the C_4 and lower boiling gaseous feed components may contact active conversion catalyst of the faujasite type at a temperature within the range of 800°F. up to about 1,100°F. and the gas oil feed may contact the catalyst preferably at temperatures in excess of 900°F. and as high as 1,100°F. In yet a further embodiment it is contemplated employing a single riser system in which system the gas oil feed initially contacts the hot freshly regenerated catalyst and a stream of C_4 and lower boiling gaseous hydrocarbons such as a C_3–C_4 rich stream is then brought in contact with the gas oil catalyst suspension in a down-stream or upper portion of the riser conversion zone. In yet another embodiment it is contemplated providing an annular conversion zone about an upper extension of the stripping zone arranged so that stripped hydrocarbons will bypass the catalyst in the annular conversion zone but all of the catalysts discharged from the riser conversion zone will pass into the annular conversion zone before

entering the stripping zone. In this arrangement the feed to either the riser or annular conversion zone may be either gas oil or a C_3–C_4 rich hydrocarbon stream.

DISCUSSION OF SPECIFIC EXAMPLE

A series of conversion runs with an isobutylene rich feed were made under selected temperature and hydrocarbon residence time conditions which simulate the operations contemplated by the present invention and variations thereon. A catalyst comprising 15% REY was contacted under the conditions identified in the table below which produced the results identified. It was observed upon examination of the product that a considerable amount of hydrogen transfer occurred along with the production of a significant amount of liquid product. The liquid product was identified as consisting chiefly of toluene, xylenes, trimethylbenzenes and naphthalenes. Runs were made at a temperature of 1,050°F. and 850°F. using a wide spread in hydrocarbon residence time. The operating conditions selected thus support the variations in operating arrangements contemplated by this invention without interfering with prior art operating conditions such as those relied upon for converting a gas oil charge under elevated temperature cracking conditions.

TABLE

Unit	Hopper (dense bed)		Riser (dilute phase, steady state)							
Run No. 180C-	193	194	195		196		197			
Temp., °F	1050°	1050°	1050°		850°		850°			
τ gas, sec.	46	22	7		8		17			
Cat/gas (wt/wt)	29	41	40		40		80			
Conversion (NLB):										
Unconv. butylene	5.4	8.7	17.4	29.3	27.4	31.7	9.1	14.6		
Propylene	3.3	4.1	11.9		4.3		5.5			
Isobutane	19.9	23.7	34.1		42.0		47.4			
C_5+ gaso.	3.3*	4.3*	19.8		13.8		17.3			
Other C_4– gases	39.1	32.4	8.0	16.8	2.5	12.5	6.5	20.6		
Coke	29.0	26.8	8.8		10.0		14.1			

*No liquid trap used

It will be observed from these data, that at the shorter residence time used for the riser conversion runs, cracking of isobutylene to lower molecular weight gases and to coke is much reduced. However, at total conversion levels of **82.6, 67.8** and **90.9%** of the isobutylene, losses to undesirable products are **12.21%** and the ratios of isobutane to butylene plus propylene range from **1.15** to **3.25.**

Thus run **195** effected at a high temperature and short residence time supports the concept of the present invention where the hot freshly regenerated catalysts contact the C_3–C_4 rich feed initially in either a separate riser reactor or in an initial portion of a single riser reactor followed by gas oil cracking. On the other hand, run **196** supports that portion of the concept of this invention wherein a previously used catalyst is contacted in a separate riser reactor or in a down-stream portion of a single gas oil riser reactor with the C_3–C_4 rich gaseous hydrocarbon feed material. Thus in any of these arrangements a Y faujasite conversion catalyst has activity and selectivity for hydrogen transfer reaction and olefin cyclization reaction leading to the production of significant quantities of isobutane and aromatics.

Having thus generally described the method and means of the present invention and discussed specific embodiments related thereto, it is to be understood that no undue restrictions are to be imposed by reason thereof except as defined by the following claims.

I claim:

1. A method for upgrading hydrocarbons with a faujasite crystalline zeolite conversion catalyst which comprises,

passing a suspension of faujasite zeolite conversion catalyst dispersed in a high boiling hydrocarbon fraction at a temperature within the range of 950°F. to about 1,100°F. upwardly through a first riser conversion zone at a hydrocarbon residence time within the range of 2 to 10 seconds,

discharging the suspension from said first conversion zone into a separation zone above a fluid bed of catalyst and passing separated catalyst into said fluid bed,

mixing catalyst particles in an upper portion of said fluid bed of catalyst with a hydrocarbon feed rich in C_4 and lower boiling hydrocarbons to form a second suspension at a temperature in the range of 700° to 1,050°F.,

passing the second suspension comprising C_4 hydrocarbons upwardly through a second riser conversion zone extending from an upper portion of said fluid bed of catalyst into the upper portion of a catalyst-hydrocarbon vapor separation zone, said second suspension maintained at a temperature, space velocity and catalyst/hydrocarbon ratio selected to convert the C_4 and lighter hydrocarbons to form aromatics,

separating hydrocarbon conversion products and catalyst upon discharge from said second conversion zone,

recovering hydrocarbon products of said conversion zones, and passing catalyst separated from each conversion zone through a stripping zone before effecting regeneration thereof.

2. The process of claim 1 wherein a high boiling hydrocarbon is added at intervals to the suspension passing through the first conversion zone.

3. The process of claim 1 wherein high boiling hydrocarbon and gasiform dispersant are mixed with hot regenerated catalyst in an annular mixing zone to form a suspension thereof which is thereafter passed upwardly through said first riser conversion zone under hydrocarbon conversion conditions.

4. The process of claim 1 wherein said high boiling hydrocarbon fraction is a hydrogenated material of at least gas oil boiling range.

5. The process of claim 1 wherein said C_4 and lower boiling hydrocarbons comprise a fraction rich in C_3 and C_4 hydrocarbons which are converted to aromatics and isobutane in said second conversion zone.

6. The process of claim 1 wherein the residence time of the low boiling hydrocarbons in the second conversion zone is restricted to within the range of 4 to 10 seconds.

7. The process of claim 1 wherein the catalyst to hydrocarbon ratio in the second conversion zone is controlled in response to relatively inert gasiform material combined with said low boiling hydrocarbon feed.

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