

[54] **MULTIPLE REACTOR FCC SYSTEM
RELYING UPON A DUAL CRACKING
CATALYST COMPOSITION**
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208/79, 208/155, 208/164, 208/159, 252/417**
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[58] Field of Search **208/80, 74, 71, 79, 155,
208/159, 164**

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[57] **ABSTRACT**
A multistage hydrocarbon conversion operation in the presence of a dual cracking catalyst composition comprising ZSM-5 type material is described for the production of gasoline and olefinic components. In a particular aspect an integrated refinery operation for producing gasoline by converting straight run hydrocarbons and recycle products of cracking in the presence of the dual cracking component catalyst is discussed with a view to identifying the operating methods relied upon for enhancing the operation.

9 Claims, 3 Drawing Figures

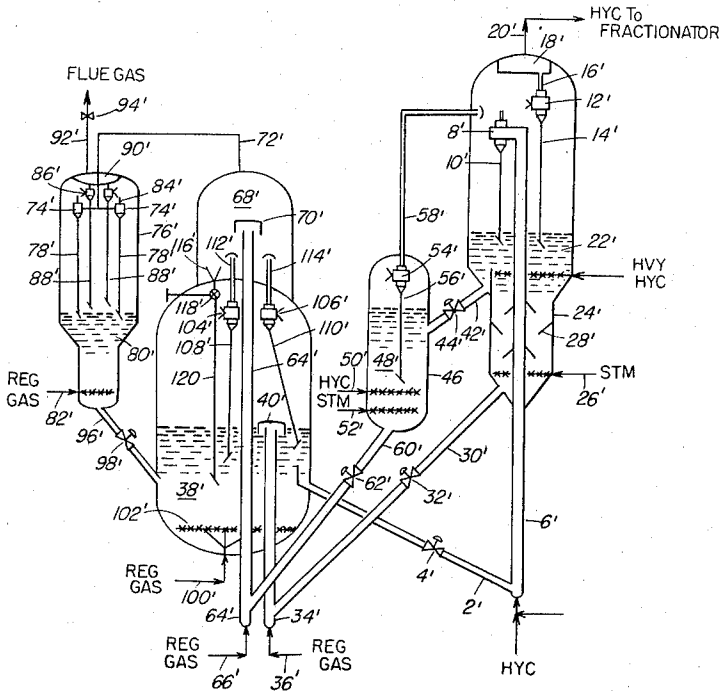


FIGURE 1

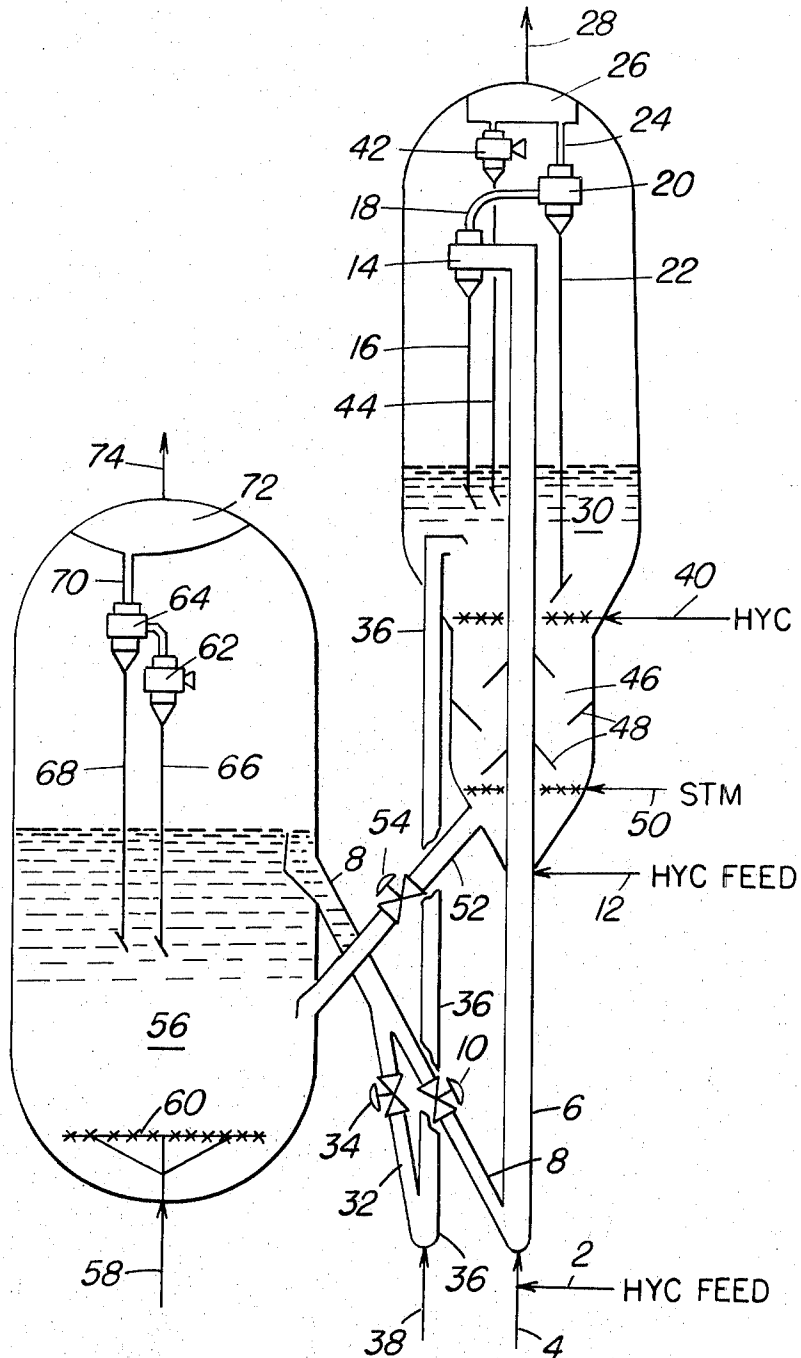


FIGURE 2

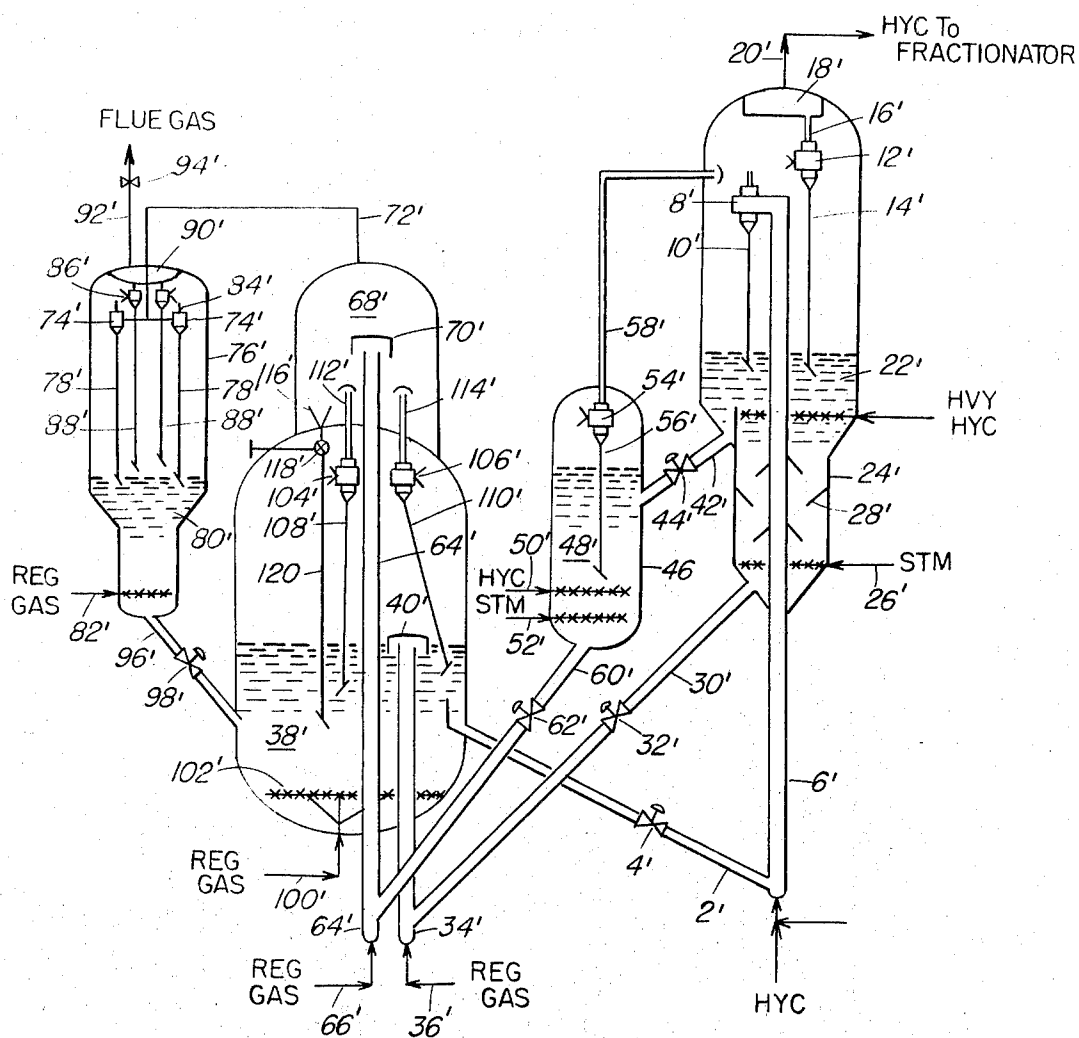
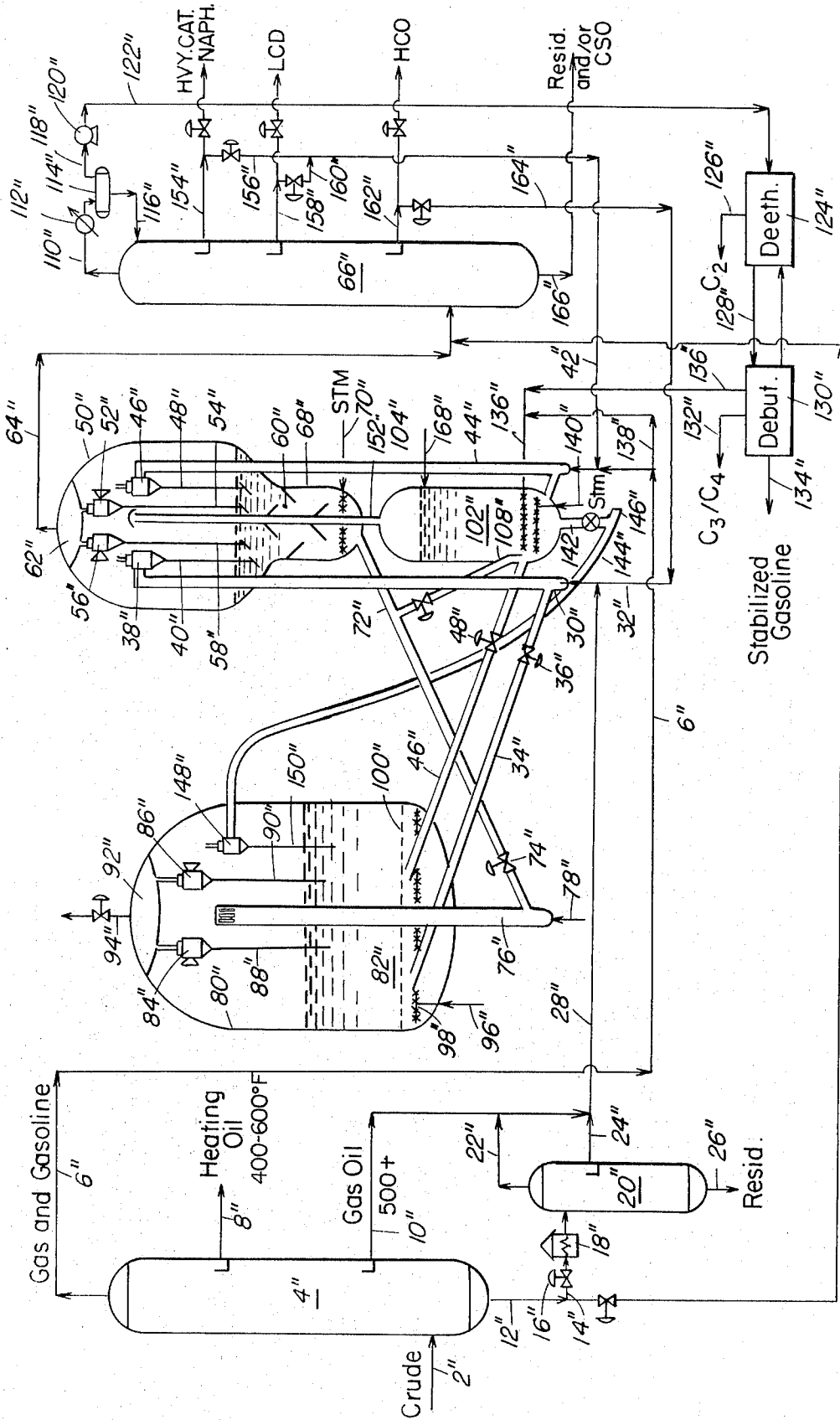


FIGURE 3



MULTIPLE REACTOR FCC SYSTEM RELYING UPON A DUAL CRACKING CATALYST COMPOSITION

BACKGROUND OF THE INVENTION

The field of catalytic cracking and particularly dense or dilute fluid phase catalytic operations have been undergoing progressive development since early 1940. Thus as new experience was gained in operating and design parameters, new catalyst compositions were developed which required a further refinement of known operating and design parameters so as to extract maximum efficiency from the combination operation. With the advent of high activity crystalline zeolite cracking catalyst development, we once again find ourselves in a new area of operation requiring even further refinements in order to take advantage of the new catalyst activity, selectivity and operating sensitivity. The present invention is concerned with a combination operation which relies upon a combination of catalyst functions mutually contributing to accomplish upgrading of available refinery feed material.

SUMMARY OF THE INVENTION

The present invention relates to the method and combination of process steps comprising catalytic hydrocarbon conversion reactions and regeneration of the catalyst employed therein. In a more particular aspect the present invention is concerned with a hydrocarbon conversion operation employing one or more riser reactors in parallel flow arrangement in combination with a dual function catalyst comprising large and smaller pore catalytic cracking materials working substantially independently in their restructuring of hydrocarbon constituents coming in contact therewith under particularly selected operating conditions.

The invention contemplates the combination of a first relatively high temperature short contact time hydrocarbon conversion step comprising the cracking of hydrocarbon in a dispersed fluid catalyst phase relying primarily upon the large pore component of the catalyst followed by restructuring of hydrocarbon constituents obtained from the cracked products thereof and other available sources in the presence of the small pore component of the catalyst in a separate zone so as to emphasize the production of relatively high quality cracked naphtha and cyclic compounds from particularly gaseous components comprising at least C_3 and C_4 hydrocarbons. In a more particular aspect a first hydrocarbon feed material contacts a dual cracking catalyst composed of small and larger pore cracking components in a dispersed catalyst phase conversion zone such as a riser conversion zone and then the dual cracking catalyst is contacted with a second hydrocarbon feed material more refractory than said first hydrocarbon feed under conditions to substantially deactivate the cracking activity of said large pore cracking component without undesirably influencing the activity of said small pore cracking component so that it can then be contacted particularly with low boiling hydrocarbon components comprising C_3 and C_4 hydrocarbons under temperature conditions within the range of 700°F. up to about 1,200°F. to effect a restructuring of the low boiling hydrocarbon components to cyclic compounds of relatively high octane rating.

In the combination particularly comprising this invention a first hydrocarbon feed such as virgin gas oil and a second hydrocarbon feed material comprising a more refractory material such as residual oils and recycle hydrocarbons of catalytic cracking are contacted simultaneously or sequentially as a suspension or relatively dispersed catalyst phase in a riser reactor at a riser inlet temperature equal to or above about 1,000°F. and operating conditions selected to obtain a substantial deactivation of the large pore cracking components of the dual component cracking catalyst used therein. The suspension is discharged from the riser as a hydrocarbon phase separate from a catalyst phase and the separated catalyst phase is then contacted under the same or different temperature conditions with at least low boiling gaseous components comprising C_3 and C_4 hydrocarbons to obtain cracking and restructuring thereof to cyclic hydrocarbon compounds and/or alkyl aromatic compounds of a higher octane rating particularly by the small pore component of the catalyst.

In the process combination of this invention and system used therefor, it is contemplated providing a separate vessel for effecting the restructuring reactions with the small pore catalyst component as shown in the drawings. In any event provisions are made for adding freshly regenerated catalyst to the collected catalyst from the riser reactors and used for restructuring the low boiling gaseous hydrocarbon components, whether effected in a separate vessel or effected in the dense catalyst phase collected about the upper end of the riser. Thus freshly regenerated catalyst may be passed with a suitable fluidizing gas, whether it be essentially an inert gas phase or a mixture of C_3 and C_4 low boiling hydrocarbons, through a suitable transfer conduit to the bed of collected catalyst to be used primarily for restructuring low boiling hydrocarbons to form cyclic compounds of a higher octane rating. On the other hand, in the event a relatively inert gas is used to convey regeneration catalyst directly to the dense fluid bed of restructuring catalyst, then the low boiling gaseous hydrocarbons comprising C_3 and C_4 hydrocarbons may be introduced to the lower portion of the fluid bed for upflow therethrough under desired temperature, space velocity and residence time conditions as herein provided. Also in the event that a separate zone is employed for the restructuring reactions, then provisions are made for passing catalyst collected about the upper end of the riser directly to the regenerator as well as to the separate zone. Furthermore provisions are made for deactivating the large pore catalyst collected in the bed in the manner herein taught before stripping the catalyst after hydrocarbon conversion use and before return to the regeneration stage of the process.

The catalyst system of the combination operation herein described comprises a dual function catalyst composed of distinctly different average pore size crystalline aluminosilicate materials. In particular the catalyst system comprises in combination a crystalline zeolite cracking component of the X or Y faujasite variety in operational combination with a ZSM-5 type of crystalline aluminosilicate conversion catalyst. This dual function cracking catalyst is used to convert a virgin and recycle oil feed to gasoline boiling range products in combination with lower and higher boiling hydrocarbon materials and sufficient recycle oil is added to a downstream portion of the riser to considerably reduce

the activity, if not, substantially deactivate the faujasite component of the catalyst mixture. In the combination operation comprising this invention it is proposed to operate a riser reactor at an inlet temperature of at least about 900°F. and preferably at least about 1,000°F. with an upper temperature limit in an inlet portion of the riser of about 1,400°F. being contemplated. Generally the riser reactor will operate at a pressure in the range of atmospheric pressure up to 100 or more pounds of pressure and a space velocity to provide a hydrocarbon residence time in the riser from about 0.5 seconds up to about 10 or more seconds. Hydrocarbon residence time in the riser of 1 to 5 seconds is particularly contemplated.

The reaction conditions contemplated in the fluid bed of catalyst with the ZSM-5 type component of the catalyst include temperatures in the range of 600°F. up to about 1,100° or 1,200°F. at hydrocarbon residence time in the catalyst bed in the range of 15 seconds up to 10 or 15 minutes at pressures in the range of atmospheric pressure up to several hundred pounds of pressure.

It will be recognized from the above that in the combination operation comprising this invention, the catalyst to oil ratio will vary over a considerable range. For example, in the dispersed phase riser reactor the catalyst to oil ratio may vary from 3 to 20 and in the fluid bed operation the catalyst to oil ratio may vary from 10 to 200 or more. In any event, in the upper portion of the riser reactor, the catalyst to oil ratio will be considerably lower than that provided in the central and lower portion of the riser.

The catalyst mixture and/or compositions suitable for use in this invention comprise a mixture of small pore and large pore crystalline aluminosilicate in combination with one another as separate discrete particles and these may be composited from substantially any high activity large pore crystalline zeolite cracking component in admixture with, for example, a ZSM-5 type of catalyst composition. The ZSM-5 type catalyst composition is a relatively small average pore diameter material smaller than, for example, a rare earth exchanged X or Y crystalline zeolite.

The large and small pore crystalline zeolites above discussed may be dispersed within a separate or a common matrix material suitable for encountering relatively high temperatures contemplated in the fluid cracking operation of this invention with its attendant catalyst regeneration operation. The catalyst mixture or composition contemplated for use in this invention will catalyze the conversion of the various components comprising the hydrocarbon feed including normal paraffins to produce for example gasoline as well as LPG types of gaseous materials. Thus the catalysts suitable for this invention have activity for cracking several different kinds and types of hydrocarbons found in gas oil boiling range materials in combination with a very selective cracking of normal paraffins and singly branched hydrocarbons which are restructured and/or upgraded to desired higher boiling components.

The novel process combination of this invention relies upon using a catalyst system comprising a mixture of separate catalyst particles or a homogeneous composition thereof containing at least two separate crystalline zeolite components, wherein each component acts substantially independently as herein defined upon given hydrocarbon components and each catalyst com-

ponent is relied upon substantially to support the function of the other. Thus it is contemplated employing in the catalyst system of this invention, a large pore crystalline aluminosilicate having a pore size in excess of about 9 Angstroms as a major component with the minor component being a small pore crystalline component having a maximum pore size not exceeding about 9 Angstroms and preferably being less than about 7 Angstroms. On the other hand, the large and small pore zeolites may be used in substantially equal amounts or the smaller pore crystalline zeolite may be in a major proportion. The small pore crystalline zeolite is preferably a ZSM-5 type of crystalline material such as that described in U.S. Pat. No. 3,702,886 issued Nov. 14, 1972. The large pore crystalline zeolite may be any of the now known crystalline aluminosilicates which are suitable for cracking hydrocarbons and providing a pore size in excess of 8 Angstroms. Such a composition has the structure and capability to act upon substantially all the components usually found in a gas oil feed boiling in the range of 500°F. up to 950° or 1,100°F. Large pore zeolites of this type are well known and include materials or synthetic faujasite of both the X and Y type as well as zeolite L. Of these materials zeolite Y is particularly preferred.

The crystalline zeolites above identified may be exchanged, combined, dispersed or otherwise intimately admixed with a porous matrix. By porous matrix it is intended to include inorganic and organic compositions with which the crystalline aluminosilicates may be affixed. The matrix may be active or substantially inactive to the hydrocarbon conversion reactions encountered. The preferred porous matrix may be selected from the group comprising inorganic oxides such as clay, acid treated clay, silica-alumina etc. A description of a catalyst composition comprising ZSM-8 type materials which may be used with advantage in this invention and their method of preparation may be found in application Ser. No. 257,983, a continuation of Ser. No. 865,418 filed Oct. 10, 1969, both now abandoned.

In the combination of this invention the small pore crystalline zeolite component of the catalyst is relied upon for promoting new ring formations by cyclization or aromatization thereof and the formation of alkyl aromatics. These reactions proceed as a function of reaction severity controlled by temperatures and residence time.

In yet a further embodiment it is contemplated combining the ZSM-5 type catalyst with a porous matrix as suggested above and an oxidation catalyst suitable for converting carbon monoxide to carbon dioxide. Thus separate particles of catalyst, one comprising ZSM-5 and the oxidation catalyst dispersed in a suitable matrix material are provided with the other comprising catalytically active X or Y faujasite dispersed in a suitable matrix material from a mixture of catalyst particles which are circulated in the system herein discussed for the reasons discussed.

In an investigation going to the very essence of this invention it has been found that C₉ aromatics formed by the interception of C₃ fragments of cracking with monocyclic aromatics were the predominant primary reaction products and as the reaction severity is increased by either raising the temperature or increasing the contact time, redistribution of alkyl groups takes place yielding aromatics both lighter and heavier than the primary product.

A further significant observation contributing to the operational concepts of this invention is the finding that the high temperature cracking of the gas oil feed does not significantly deactivate the activity and selectivity of a smaller pore ZSM-5 crystalline component with or without a carbon monoxide oxidation component as by coke deposition and thus particles of this composition can function independently to perform its unusual and desirable reaction mechanisms in the overall combination operation relying upon the total mass of catalyst particles as a heat sink for promoting the encountered endothermic conversion reactions. On the other hand, when the oxidation component is combined therewith a heat benefit is realized by virtue of the exothermic conversion of CO to CO₂ during regeneration of catalyst.

The small pore crystalline zeolite catalyst material preferred in the combination of this invention is preferably of the ZSM-5 type and as such the small pore has a uniform pore size varying because of its elliptical shape from about 5.5 Angstroms up to about 6 and about 9 Angstrom units.

One embodiment of this invention resides in the use of a single porous matrix material as the sole support for the two different pore size crystalline zeolites hereindefined. Thus the catalyst may comprise an aluminosilicate of the ZSM-5 type dispersed with an aluminosilicate having a pore size generally larger than that of ZSM-5 and more usually greater than 8 Angstrom units in a porous matrix as a homogeneous mixture in such proportions that the resulting product contains from about 1% up to about 95% by weight and preferably from about 7 to 50% by weight of total crystalline aluminosilicates in the final composite.

The particular proportions of one aluminosilicate component to the other in the catalyst system or composition herein defined is not narrowly critical and even though it can vary over an extremely wide range it has been found that the weight ratio of the ZSM-5 type aluminosilicate to the large pore size aluminosilicate can range from 1:10 up to 3:1 and preferably should be from about 1:3 to 1:1.

Hydrocarbon charge stocks which may be converted by the combination and method of this invention comprise petroleum fractions having an initial boiling point of at least 400°F. and an end point of at least 600°F. and as high as 950° to 1,100°F. The present invention also contemplates the cracking of naphtha boiling in the range of C₅ hydrocarbons up to about 400°F. to improve its octane rating in combination with producing significant quantities of LPG type materials which then can be used as part of the charge to the ZSM-5 contact stage of the combination. Hydrocarbons boiling above 400°F. include gas oils, residual oils, cycle stocks, whole topped crudes and heavy hydrocarbon fractions derived by destructive hydrogenation processes. These may be used alone or in combination as the first riser reactor hydrocarbon charge.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a diagrammatic arrangement in elevation of a hydrocarbon conversion regenerator system providing means for converting hydrocarbons in a riser reactor and a second riser for passing regeneration catalyst to the fluid bed of catalyst separated from the hydrocarbon conversion riser reactor.

FIG. 2 is a diagrammatic arrangement in elevation of a hydrocarbon conversion-catalyst regeneration system which encompasses multi catalyst contact steps for hydrocarbon conversion and catalyst regeneration arranged to take advantage of a dual function catalytic cracking composition.

FIG. 3 provides a diagrammatic arrangement in elevation of an integrated refinery process scheme comprising a crude atmospheric and vacuum tower, a reactor-regenerator catalyst system, a product fractionator arrangement and interconnecting conduits for directing different fluid streams as desired to and from the reactor-regenerator system.

DESCRIPTION OF SPECIFIC EMBODIMENTS

Referring now to FIG. 1 there is shown a side-by-side hydrocarbon conversion-catalyst regeneration system which may be used to advantage in processing different hydrocarbon feed material in the presence of a dual function cracking catalyst comprising large and small pore crystalline zeolites wherein the small pore zeolite is a ZSM-5 type of crystalline aluminosilicate. In the arrangement of FIG. 1 a first hydrocarbon feed such as a virgin oil feed material boiling above about 400°F. is introduced by conduit 2 with or without gasiform diluent material introduced by conduit 4 to the base of a first riser reactor 6. Freshly regenerated dual function catalyst above identified in either a homogenous mixture or a mixture of separate discrete particles of large and small pore particles is introduced to the base of riser reactor 6 by conduit 8 containing flow control valve 10 in such an amount to provide a desired and predetermined catalyst to oil ratio within the range of 3 to about 20 in a catalyst to oil suspension providing a mix temperature of at least about 1,000°F. and up to as high as about 1,400°F. depending upon products of reaction desired. In the initial portion of riser reactor 6 the virgin oil feed is converted to products including gasoline boiling products as well as higher and lower boiling products. The suspension is then further contacted in a downstream portion of the riser with a more refractory hydrocarbon feed material introduced by conduit 12. A recycle product of cracking or some other residual or aromatic oil material of high coke forming characteristics may be used to contact and coke up the large pore component of the cracking catalyst. The residual oil is charged in an amount sufficient to cause substantial deactivation if not complete deactivation of the large pore crystalline component of the cracking catalyst. The catalyst-hydrocarbon suspension moves upwardly through the riser reactor and then is discharged into a cyclone separator 14. Cyclonic separation of the suspension is accomplished in separator 14 with the separated catalyst withdrawn by dipleg 16. The hydrocarbon vapors with entrained catalyst pass overhead by conduit 18 to a second separator 20. In separator 20, the hydrocarbon vapors are freed further from entrained catalyst fines which are collected and withdrawn by dipleg 22. Hydrocarbon vapors or gasiform material is removed from separator 20 by conduit 24, passed to plenum chamber 26 and thence to conduit 28 for transfer to suitable fractionation equipment not shown. Separated catalyst in diplegs 16 and 22 is discharged into a dense fluid bed of catalyst particles 30. Provisions are also made for passing regenerated catalyst withdrawn by conduit 8 to branch conduit 32 containing flow control valve 34 to a riser 36. Fluidiz-

ing gas is introduced to the base of riser 36 by conduit 38. The fluidizing gas which may be inert or comprise low boiling C_3 and C_4 hydrocarbons alone or in combination with a hydrocarbon feed comprising cyclic compounds forming a suspension with the catalyst, transfers the catalyst upwardly through the riser for discharge in fluid bed 30. The amount of regeneration catalyst transferred through riser 36 will of course depend upon the temperature desired to be maintained in the dense fluid bed 30. In dense fluid bed 30, maintained at a temperature selected from within the range of 800°F. up to about 1,200°F. the small pore crystalline component is relied upon to effect a restructuring of low boiling hydrocarbons such as C_3 and C_4 hydrocarbons alone or in combination with a hydrocarbon feed comprising cyclic compounds suitable for forming alkyl aromatics. Thus the feed material to be restricted as herein defined is introduced by conduit 40 to the dense fluid catalyst bed 30. In fluid bed 30 the hydrocarbon feed comprising C_3 and C_4 hydrocarbons is caused to flow upwardly through the descending fluid bed of catalyst under conditions providing a hydrocarbon residence time within the range of 15 seconds up to about 15 minutes. Thus the hydrocarbon space velocity may be selected from within the range of about 0.11 to about 20 liquid hourly space velocity (LHSV). Vaporous products of reaction and stripping gas pass overhead from the dense fluid bed of catalyst and pass through one or more cyclone separators represented by separator 42 provided with dipleg 44. In separator 42 gasiform material comprising hydrocarbon products of the restructuring reactions herein defined along with stripping gas is separated from catalyst particles with the catalyst being withdrawn by dipleg 44 and returned to the dense bed 30. Separated gasiform products are passed to plenum chamber 26 and thence to fractionating equipment by conduit 28. Under some operating conditions it is contemplated passing C_3 and C_4 hydrocarbons into bed 30 by way of riser 36 alone or in combination with conduit 40. Thus riser reactor 36 may be operated under temperature conditions generally higher than that desired in dense fluid bed 30 so as to particularly promote the cyclization of low boiling olefin hydrocarbon components within catalyst bed 30 maintained under temperature conditions particularly promoting the formation of aromatics. The fluid bed of catalyst 30 moves generally downwardly and into a stripping section 46 provided with baffles 48. Stripping gas such as steam is introduced to the lower portion of the stripping zone by conduit 50. The stripped catalyst is withdrawn from the lower portion of the stripping zone and passed by conduit 53 provided with flow control valve 54 to a dense fluid bed of catalyst 56 in a catalyst regeneration zone.

The regeneration of the catalyst may be accomplished in any one of a number of different catalyst regeneration operations known in the art and defined in this and copending applications. For example the catalyst may be regenerated in one or more riser regenerators in parallel or sequential flow arrangement and with or without a dense fluid bed of catalyst undergoing regeneration being in the combination. In any event the regeneration operation should be one which will restore the activity of the individual catalyst components comprising the dual function catalyst herein defined in combination with maximizing the recovery of available heat developed and provided by the combustible mate-

rials introduced to the regeneration zone. In the simplified regeneration arrangement of FIG. 1 regeneration air is introduced to a lower portion of the bed by conduit 58 provided with a distributor manifold 60. Regeneration flue gases pass from the catalyst bed 56 through cyclone separators 62 and 64 provided with catalyst diplegs 66 and 68. In cyclone separators 62 and 64 catalyst particles are separated from regeneration flue gases and the separated catalyst is returned by diplegs 66 and 68 to the fluid catalyst bed 56. Flue gas is withdrawn by conduit 70, plenum chamber 72 and conduit 74.

FIG. 2 provided herewith departs from FIG. 1 in several significant aspects, the most notable being associated with the method of regenerating the catalyst used in the system and locating the catalytic reactions promoted in bed 30 of FIG. 1 in a separate vessel 46. Another significant departure in the operating system of FIG. 2 over that provided in FIG. 1 is concerned with the source of catalyst passed to the separate vessel above identified.

In the arrangement of FIG. 2, freshly regenerated catalyst is passed by standpipe or conduit 2' provided with flow control valve 4' to the lower portion of a riser reactor 6'. Hydrocarbon feed such as a virgin gas oil is introduced to the lower portion of riser 6' wherein it mixes with the hot regenerated catalyst to form a catalyst-oil suspension having a temperature in the range of from about 900°F. up to about 1,200°F. or higher. In riser reactor 6' the hydrocarbon feed is cracked particularly by the faujasite component of the dual component catalyst under temperature conditions which may be particularly selected to maximize gasoline yield. Of course higher temperature operating conditions may also be selected for riser reactor 6' and particularly those conditions producing a high octane gasoline product in conjunction with lower boiling components which may be recovered and recharged for contact with small pore component of the dual component cracking catalyst described hereinbefore. The suspension in riser 6' passes to one or more cyclone separators represented by separator 8' provided with dipleg 10'. Hydrocarbon vapors separated from catalyst in separator 8' is caused to pass into another separator 12' provided with dipleg 14'. In separator 12', hydrocarbon vapors are separated from catalyst particles and the separated hydrocarbon vapors pass into plenum 18' by conduit 16' and thence to conduit 20' connected to suitable fractionation equipment not shown. Catalyst separated in cyclone separators 8' and 12' is conveyed by the dipleg of each to a dense fluid bed of catalyst 22' therebelow. In dense fluid bed 22' the catalyst is contacted with a high coke producing hydrocarbon charge such as a recycle product of cracking or other suitable material at a temperature within the range of 900°F. up to 1,100°F wherein the feed is cracked primarily by the large pore component of the catalyst, the faujasite component, thereby considerably deactivating this large pore component by the deposition of a relatively large amount of carbonaceous deposits on the cracking sites. As identified herein, the smaller pore component comprising the ZSM-5 type component remains relatively active catalytically and relies upon the large pore component as its heat sink for effecting the restructuring of low boiling C_3 and C_4 components. Thus the dense fluid catalyst bed 22 is withdrawn as two separate portions; one portion being passed to a stripping zone 24' supplied with stripping gas by conduit 26'. The

stripping zone is provided with baffles 28'. The stripped catalyst is withdrawn from the stripping zone by conduit 30' provided with flow control valve 32' and conveyed to the lower end of riser regenerator 34' to which regeneration or lift gas is supplied by conduit 36'. Under some circumstances the regenerator may be so positioned with respect to the stripping zone that catalyst may be passed directly to a dense fluid bed of catalyst in the regenerator without first traversing a riser regeneration stage. Riser regenerator 34' shown in the figure may discharge at the bed 38' interface as shown or above or below the bed interface. Also other methods and systems for effecting catalyst regeneration as shown in FIGS. 1 and 3 may be employed. A cap 40' is shown positioned above the discharge end of riser 34' to change the direction of flow of the suspension discharge therefrom. However other known devices may be used for this purpose such as a cyclone separator should the riser discharge above the dense fluid catalyst bed interface.

Catalyst is also caused to flow from fluid bed 22' by conduit 42' containing valve 44' to vessel 46' retaining a dense fluid bed of catalyst 48'. The operating conditions selected for use in aromatizing vessel 46' may be the same as those discussed with respect to zone 104' in FIG. 3. Reactant hydrocarbons comprising C₃ and C₄ low boiling hydrocarbons alone or in combination with hydrocarbon feeds providing monocyclic hydrocarbon compounds is introduced to a lower portion of bed 48' by conduit 50' and above stripping gas inlet 52'. Hydrocarbon vapors comprising products of restructuring reactions performed in vessel 46' pass overhead into cyclone 54' provided with recovered catalyst dipleg 56'. Hydrocarbon vapors separated in cyclone 54' pass overhead by conduit 58' and are discharged into the upper portion of the vessel housing cyclone separators 8' and 12'. Hydrocarbon vapors introduced by conduit 58' pass into cyclone 12' with the other hydrocarbon vapor as discussed above. As mentioned above the primary reactions effected in vessel 46' are those accomplished with the ZSM-5 type restructuring catalyst which include the cyclization of olefins and the formation of alkyl aromatics. Thus in the absence of heat from an outside source, the temperature of the catalyst bed 48' in vessel 46' will be substantially that but usually lower than that discharged by diplegs 10' and 14'. On the other hand if greater temperature flexibility control is desired in this system, it is contemplated positioning vessel 46' with respect to the regeneration vessel so that hot freshly regenerated catalyst may be passed directly by gravity to vessel 46' or lifted by a riser as provided for in FIG. 1. In vessel 46', temperature conditions, reaction time and space velocity are selected within the broad range of conditions hereinbefore described which will be most suitable for effecting the restructuring reactions contemplated.

Catalyst is withdrawn from the lower portion of vessel 46' by conduit 60' containing flow control valve 62' and conveyed to the lower portion of a riser regenerator 64' to which regeneration gas is introduced by conduit 66'. Thus the regeneration gas introduced to risers 34' and 64' by conduits 34' and 64' may be air alone or gaseous material containing a more restricted and controlled amount of oxygen in the regeneration gas.

One of the significant advantages of the processing combination of this invention is related to the use of the catalyst composition in such a manner that the reten-

tion of carbonaceous deposits on the catalyst is increased above that normally accomplished in prior art process without undesirably decreasing the conversion characteristics of the catalyst. Furthermore the heat developed and utilized in the combination operation of this invention is accomplished with a greater efficiency than known prior art processes. Thus the overall operation is enhanced not only by the products obtained therefrom but the operating efficiency of the process is greatly improved over prior art processes.

In riser regenerator 64', a partial regeneration of the catalyst is accomplished by burning of carbonaceous material deposited on the catalyst in the various hydrocarbon conversion steps through which the catalyst is passed. The partially regenerated catalyst is discharged from riser 64' into an upper chamber 68'. A cap 70' is placed above the riser discharge for the purpose of changing the direction of the suspension passed through the riser and discharged from the end thereof. In chamber 68', the catalyst suspension discharged from riser 64' is further contacted with oxygen containing regeneration gas to effect a burning of carbon monoxide to carbon dioxide thus generating additional heat which is adsorbed by the catalyst in the suspension passed from chamber 68' by conduit 72' to separator cyclones 74' in the upper portion of vessel 76'. Diplegs 78' attached to cyclone separators 74' pass separated catalyst to a dense fluid bed of catalyst 80' maintained in the lower portion of vessel 76'. Regeneration gas is introduced to the lower portion of bed 80' by conduit 82'. Gaseous products of regeneration are discharged from cyclones 74' by open end conduits 84' and pass along with gaseous products of regenerating bed 80' into cyclone separators 86' provided with diplegs 88' for returning separated catalyst fines to the dense fluid end of catalyst 80'. Regeneration flue gas pass from separators 86' to plenum chamber 90' and are removed therefrom by conduit 92' provided with valve 94'.

Hot regenerated catalyst obtained in bed 80' and being at an elevated temperature in the range of 1,200°F. to about 1,400°F. is withdrawn by conduit 96' provided with flow control valve 98' for passage thereof to dense fluid bed 38'. In dense fluid bed 38' the hot regenerated catalyst from bed 80' is combined with partially regenerated catalyst discharged from riser 34' and regeneration of the catalyst is completed at an elevated temperature with oxygen rich regeneration gas introduced by conduit 100' to a distributor manifold 102'. Gaseous products of regeneration obtained from regenerating catalyst bed 38' commingle with regeneration gases discharged from riser 34' and passed into cyclone separators 104' and 106' provided with diplegs 108' and 110' wherein catalyst fines are separated from regeneration flue gases for return by the diplegs provided to the fluid bed 38'. Regeneration flue gases pass by open ended conduits 112 and 114 into chamber 68' wherein combustion of CO in the flue gases is particularly promoted. Catalyst is withdrawn by conduit means 116' provided with valve 118' and dipleg 120' as required to eliminate catalyst from chamber 68' not carried overhead through conduit 72'.

It is to be understood that the processing arrangement described with respect to FIG. 2 may also be employed in the arrangement of FIG. 1 at least with respect to passing stripped catalyst as withdrawn by conduit 52 in FIG. 1 upwardly through riser 64' of FIG. 2 thereby eliminating the withdrawal conduit 30' and

riser 34' as shown in FIG. 2. Furthermore cyclone separators may be placed in an upper portion of chamber 68' of FIG. 2 arranged to provide the desired heat exchange between catalyst and flue gases before return of the separated catalyst to fluid bed 38' by suitable diplegs. Therefore the system comprising vessel 76' can be eliminated or replaced by the cyclone separators positioned in the upper portion of chamber 68' as above briefly discussed. In any of these arrangements it is important to provide for conversion of CO to CO₂ and heat exchange the catalyst with the hot gases thus obtained.

In the arrangement of FIG. 2 it is contemplated passing all or a portion of the catalyst collected in zone 76' as catalyst bed 80' directly to aromatizing zone 46' containing catalyst bed 48'. In this embodiment catalyst may be added by conduit 42' to the aromatizing zone for purposes of temperature control as required. On the other hand it is also contemplated passing catalyst from bed 80' directly to the inlet of riser 6' in combination with freshly regenerated catalyst in conduit 2'.

Referring now to FIG. 3 there is shown in diagrammatic arrangement an integrated refinery operation for the production of stabilized gasoline of desired volatility and quality without the need for prior art alkylation and reforming processes. In the combination operation of FIG. 3 the conversion of hydrocarbon charge materials boiling over substantially the entire crude boiling range is accomplished by contacting under selected reaction conditions particular fraction of the crude oil charged to the process with a dual catalyst composition comprising a faujasite cracking catalyst in admixture with a small pore crystalline material of the ZSM-5 type. In the integrated refinery operation of FIG. 3 the catalyst circulated in the system may be a homogenous mixture of the large pore faujasite cracking component and the smaller pore ZSM-5 type component or they may be formed as separate discrete catalyst particles on suitable support material for convenience of handling and each component may be added separately in the process as make up catalyst as required thereby further contributing to the overall flexibility of the process. For example the ZSM-5 particle component may be added to the olefin cyclization step hereinafter defined with the faujasite cracking component being added to take advantage of its activity in one or more of the riser cracking stages defined below. In the processing combination of FIG. 3, gasoline quality and volatility are controlled by the temperature cut points made on the crude atmospheric and the catalytic fractionation towers, the temperatures employed in the riser reactors, the amount of recycle employed and the quantity of principally C₃ and C₄ hydrocarbons cyclized and/or converted to alkyl aromatics as herein defined. On the other hand heavy naphtha separated from the product of catalytic cracking in the catalytic fractionator may be recycled to a high temperature riser reactor for improving its octane and volatility.

Referring now to FIG. 3 a crude oil charge is introduced by conduit 2'' to an atmospheric fractionation tower 4''. In tower 4'', the crude oil is separated into an overhead gas and gasoline fraction withdrawn by conduit 6'', a heating oil fraction boiling in the range of about 400° to 600°F. withdrawn by conduit 8'', a gas oil fraction boiling above 500°F. withdrawn by conduit 10'' and a bottom residual oil fraction boiling above about 800°F. being withdrawn from the bottom of the

tower by conduit 12''. In one operational arrangement, the atmospheric tower bottoms withdrawn by conduit 12'' is passed by conduit 14'' containing valve 16'' to furnace 18'' wherein the residual oil is heated to a temperature within the range of 650°F. to 800°F. The thus heated residual oil is then passed by conduit 20'' to a vacuum tower 20''. In vacuum tower 20'' maintained at a bottom temperature of about 750°F. and a pressure in the range of 40 to 100mmHg gas oil boiling material is recovered and withdrawn by conduits 22'' and 24''. Higher boiling resid is withdrawn from the bottom of the vacuum tower by conduit 26''. The gas oil streams 10'', 22'' and 24'' are combined and passed by conduit 28'' to the inlet of a first riser reactor 30''. Heavy cycle oil of catalytic cracking boiling from about 400°F. to about 1,000°F. and obtained as hereinafter defined is passed by conduit 32'' to the inlet of the first riser reactor 30''. Hot regenerated catalyst in conduit 34'' provided with flow control valve 36'' is introduced to the lower portion of riser 30'' for admixture with the gas oil charge thereto thereby forming a suspension having a catalyst to oil ratio in the range of 3 to about 20 and a suspension mix temperature within the range of 900°F. to about 1,300°F. The thus formed suspension passes upwardly through riser 30'' at a space velocity selected to provide a hydrocarbon residence time within the range of 1 second to about 10 seconds. In riser 30'' the gas oil is cracked particularly by the large pore faujasite component of the catalyst to form products including gasoline and lower boiling hydrocarbons as well as higher boiling components of cracking including carbonaceous material deposited on the catalyst particles. The suspension in riser 30'' is discharged into a cyclone 38'' provided with catalyst dipleg 40''. Cyclone separator 38'' may be a plurality of separators in parallel or sequential flow arrangement. The suspension discharged into the cyclone is separated into a hydrocarbon phase and a catalyst phase, with the catalyst phase passed to a dense fluid bed of catalyst by dipleg 40''.

Straight run gasoline separated from the crude atmospheric tower with or without gaseous products withdrawn by conduit 6'' is combined with for example heavy naphtha product of catalytic cracking obtained from the fractionating tower downstream of the cracking operation, alone or in combination with a light cycle oil product of catalytic cracking in conduit 42''. The combined gasoline containing feed is passed to the lower portion of a second riser 44''. Hot regenerated catalyst withdrawn from the regenerator by conduit 46'' provided with flow control valve 48'' is passed to the lower portion of riser 44'' for admixture with the gasoline containing charge materials to form a suspension at a temperature in the range of 900°F. to 1,300°F. The thus formed suspension in a catalyst to oil ratio in the range of 3 to about 20 is passed at a space velocity selected to provide a hydrocarbon residence time in the riser within the range of 1 sec. to about 10 seconds. In riser 44'' the gasoline boiling hydrocarbons and lower boiling hydrocarbon components are subjected to contact with the dual component cracking catalyst wherein at least one of the components is a ZSM-5 type of crystalline aluminosilicate. The catalyst particles may be a homogenous mixture of the dual cracking components or separate particles of each crystalline material disposed in matrix material may be employed. In this conversion step the gasoline component of the

charge is improved in octane rating and volatility characteristics in conjunction with ZSM-5 upgrading of at least some of the low boiling olefin and paraffin components of the charge. To facilitate the reactions accomplished in riser 44" it is contemplated sizing the riser reactor and/or selecting operating conditions which will provide for a relatively dense phase of catalyst being transferred through the riser thereby significantly increasing the residence time of the hydrocarbon reactants up to as high as about 15 minutes. The catalyst-hydrocarbon suspension in riser 44" is discharged into one or more cyclone separators 46" provided with dipleg 48" such as a plurality of cyclone separators arranged in parallel or sequential flow arrangement. In cyclone separator 46" the suspension is separated into a catalyst phase which is passed by dipleg 48" to a fluid bed of catalyst therebelow and the hydrocarbon phase passed overhead and into the upper portion of chamber 50" housing the cyclone separators. Additional cyclone separators represented by separators 52" and 56" provided with diplegs 54" and 58" respectively are provided in the upper portion of chamber 50" for effecting separation of gasiform material comprising hydrocarbon products of reaction and stripping gas as herein defined from catalyst particles entrained therein. Separated catalyst particles are passed to a lower fluid bed of particles 60" maintained in the lower portion of vessel 50" by diplegs 48", 54", 58" and 40". Gasiform products of reaction separated and collected in separators 52" and 56" pass overhead into chamber 62" and are withdrawn therefrom by conduit 64" for passage to a product fractionator 66" more fully discussed below.

The fluid bed of catalyst 60" in the lower portion of vessel 50" moves generally downwardly into a lower stripping section 68" supplied with stripping gas by conduit 70" connected to a suitable distributing manifold within the bed of catalyst. The stripping zone may be provided with a plurality of sloping baffles as shown. Stripped catalyst is withdrawn by conduit 72" provided with flow control valve 74" for passage thereof to the lower end of a riser regenerator 76". Regeneration gas of desired oxygen content and temperature is supplied to the base of riser 76" to form a suspension with the catalyst which then moves upwardly through riser regenerator 76" under temperature conditions suitable to effect at least partial burning of carbonaceous material deposited on the catalyst particles during the hydrocarbon conversion steps herein defined. The temperatures encountered in riser 76" may be within the range of 1,000° to 1,400°F. The suspension moved upwardly through riser 76" is discharged from the upper end thereof through a bird cage or other suitable device which will change the direction of the upwardly flowing suspension as its velocity is reduced upon discharge into the upper enlarged section of regenerator 80". The discharged suspension separates with the catalyst particles falling into a dense fluid bed of catalyst 82" with gaseous products of combustion passing with entrained catalyst particles into two or more cyclone separators 84" and 86" provided with diplegs 88" and 90". Gaseous products of combustion or flue gases are separated from combined catalyst fines in cyclone separators 84" and 86" and then move by suitable provided conduits into chamber 92" for withdrawal therefrom by conduit 94". The catalyst collected in fluid bed 82" undergoes further regeneration by contact

with regeneration gas such as air is introduced by conduit 96" and manifold 98" to the lower or bottom portion of bed 82". A distributor grid 100" may be positioned above manifold 98" in the lower portion of the regenerator. Regenerated catalyst is withdrawn by conduits 34" and 36" for use as above discussed.

A separate fluid bed of catalyst 102" is provided in a separate vessel 104". Vessel 104" may be positioned in any convenient location from that shown in the drawing where it is convenient to pass catalyst thereto and therefrom as herein described. In the arrangement of FIG. 3, vessel 104" is positioned below stripping section 68" so that catalyst withdrawn by conduit 72" may be partially transferred by connecting conduit 108" provided with a suitable flow control valve to vessel 104" to form bed 102". Of course a separate stream of catalyst may be passed directly by a separate conduit, not shown, from stripping zone 68" to vessel 104" instead of in the manner shown by the drawing.

In vessel 104" the ZSM-5 type component of the catalyst is particularly relied upon to effect restructuring reaction of low boiling hydrocarbon components and particularly gaseous materials comprising C₃ and C₄ hydrocarbons. Thus in the processing scheme of FIG. 3 hydrocarbon products of catalytic cracking and those products formed by the ZSM-5 type restructuring catalyst lower boiling than heavy cracked naphtha boiling at least about 200°F. are withdrawn from the upper portion of fractionating tower 66" by conduit 110", passed through cooler 112" and thence to knockout drum 114" maintained at a temperature of about 90°F. Condensed liquid is withdrawn from knock-out drum 114" and returned to tower 66" as reflux by conduit 116". The remaining material comprising gasoline and lower boiling products above identified are passed by conduit 118", pump 120" and conduit 122" to deethanizing zone 124". In deethanizing zone 124", C₂ and lower boiling gaseous material such as fuel gas is withdrawn by conduit 126" for use as desired. Higher boiling materials are then sent by conduit 128" to debutanizing zone 130" wherein C₃ and C₄ hydrocarbons are separated to provide a stabilized gasoline product boiling in the range of about 40°F. up to about 380°F. and an octane rating of at least 80 research octane clear and up to 105 octane research clear. C₃ and C₄ hydrocarbons may be withdrawn by conduit 132" for other use than herein provided with the stabilized gasoline being withdrawn by conduit 134".

In the processing arrangement of FIG. 3, separated C₃ and C₄ hydrocarbons are preferably withdrawn by conduit 136" and passed to the lower portion of bed 102" wherein these hydrocarbon components are upgraded by the ZSM-5 type catalyst component as by cracking and cyclization to form alkyl aromatics. The processing combination of FIG. 3 also contemplates passing all or a portion of the combined gas and gasoline material removed from the crude atmospheric tower by conduit 6" by way of conduit 138" and 136" to catalyst bed 102". In yet a further embodiment, it is contemplated separating the material in conduit 6" in equipment not shown into primarily a gas phase and a gasoline phase so that only the gasoline phase is passed to riser 44" and the separated gas phase is passed to catalyst bed 102" in vessel 104" in contact with the ZSM-5 type catalyst component. It is also contemplated suppressing the activity of the large pore component of the catalyst mixture passed to fluid bed 102"

in the event that such is required by contacting the catalyst in bed 60'' above the stripping zone with a high coke producing residual oil as discussed with respect to FIGS. 1 and 2.

The temperature of the fluid bed of catalyst 102'' maintained in zone 104'' may be restricted within the range of 600°F. up to about 1,500°F. with it being preferred to limit the temperature thereof within the range of 800°F. up to about 1,200°F. Also a hydrocarbon residence time within the range of 15 seconds up to about 15 minutes is contemplated. Generally the hydrocarbon residence time will be at least 1 minute. For example when cyclization reactions are of primary interest because of the hydrocarbon in the feed thereto, the reaction temperatures will be in the high end of the temperature range, however when the formation of alkyl aromatics is particularly sought, the reaction temperature will be restricted to low temperatures below about 750°F. The reactions accomplished over the ZSM-5 type material are primarily those of cracking of non-cyclic compounds to form olefins and cyclization of formed olefins. Also, depending on temperature and other conditions, alkyl aromatics may be considerably formed. The temperature conditions sustained in bed 102'' may be provided by catalyst previously used for hydrocarbon conversion, reactant preheat temperature and the amount of regenerated catalyst added to the bed. Thus by a proper selection of reactant temperature charged and catalyst temperature forming bed 102'', a balance in the reaction temperature conditions may be maintained substantially as desired.

A stripping gas such as steam is introduced to the lower portion of the catalyst bed 102'' by conduit 140'' for stripping the catalyst of hydrocarbon components before withdrawal therefrom by conduit 142 provided with a catalyst flow control valve. The withdrawn catalyst is combined with regeneration gas introduced by conduit 146'' in the lower portion of riser regenerator 144'' to form a suspension. The suspension in riser 144'' undergoes at least partial regeneration of the catalyst by burning of carbonaceous deposits before discharge into a cyclone separator 148'' provided with catalyst dipleg 150''. In cyclone separator the suspension is separated into a gaseous phase and a catalyst phase with the catalyst phase passed to fluid bed 82''. The gaseous phase passes overhead from the separator for eventual withdrawal by cyclones 84'' and 86''.

In vessel or zone 104'', gasiform products of reaction and stripping gas separated from the upper catalyst bed surface are passed by open end conduit 152'' into the upper portion of vessel 50'' for removal by cyclone separator 52'' and 54'' along with products of cracking as above discussed. A cap or bird cage may be used about the upper open end of conduit 152''.

The products of riser cracking, ZSM-5 type reactions and stripping gas are removed from the upper portion of vessel 50'' by conduit 64'' and are passed to product fractionator 66''. Product fractionator 66'' is operated at a bottom temperature of about 710°F. so that low boiling gasoline product in combination with lower boiling gaseous components may be removed from the upper portion of the tower by conduit 110'' for recovery and use as above provided. A heavy naphtha product of cracking boiling in the range of 200°F. to about 440°F. is removed by conduit 154'' and a portion thereof may be conveyed by conduit 156'' to riser 44'' for reprocessing as above discussed. A light cycle oil

(LCO) is removed from fractionator 66'' by conduit 158'' and a portion or all thereof may be recycled by conduits 160'' and 156'' to riser 44'' for reprocessing as above discussed. A heavy cycle oil (HCO) is removed from the fractionator by conduit 162'' and all or a portion thereof may be recycled to riser 30'' for reprocessing to gasoline and lighter boiling product. A resid and/or catalyst slurry oil (CSO) is removed from the bottom of the tower by conduit 166'' for processing as desired. This resid product may be used to coke up the faujasite cracking component of the catalyst before passage thereof to zone 104''. In the processing combination of FIG. 3 it is contemplated adding separate discrete particles of fresh ZSM-5 type crystalline aluminosilicate dispersed in matrix material to the bed of catalyst 102'' by conduit 168''. Also fresh cracking catalyst particles comprising the large pore faujasite cracking component may be added to the dense fluid bed of catalyst 82'' being regenerated or to a catalyst conduit conveying spent catalyst to the regenerator. In yet a further embodiment it is contemplated discharging the spent catalyst in conduit 72'' into an enlarged zone about the base of riser 76'' wherein the spent catalyst is mixed with hot freshly regenerated catalyst to achieve a mix temperature of at least about 1,250°F. and thereafter the mixture is conveyed upwardly through riser 76'' under catalyst regenerating conditions to remove carbonaceous deposits by burning thereby heating the catalyst to an elevated temperature.

In accordance with the concepts hereinbefore presented, it has been visually observed of a catalyst mixture comprising separated particles of "Y" faujasite cracking component in admixture with particles of ZSM-5 type catalyst that essentially the major portion of the deposited coke forms on the particle containing the "Y" faujasite cracking component. The ZSM-5 type catalyst particles on the other hand appeared clean by comparison and could be hand separated. Accordingly adding an oxidation catalyst such as chromium oxide to the ZSM-5 type particle to promote the conversion of carbon monoxide to carbon dioxide without appreciably affecting the hydrogen in the coke laid down on the faujasite cracking component was pursued. The oxidation promoter is effective in yielding a higher carbon dioxide to carbon monoxide ratio in the flue gases and therefore a greater heat release in the regenerator to the catalyst is realized. Thus by restricting the amount of oxidation promoter in the catalyst as identified above no appreciable effect on the cracking operation is observed even though the amount of oxidation promoter is large enough to achieve an advantage in the conversion of carbon monoxide in the regeneration system.

EXAMPLE A

A concept of the invention herein described is concerned with regeneration of the catalyst in a manner which will enhance the recovery of available heat as by increasing the ratio of carbon dioxide to carbon monoxide in the regenerator flue gas through combustion and recovering the heat thus generated as by direct heat exchange with catalyst particles. To promote the conversion of carbon monoxide to carbon dioxide an oxidation catalyst promoter was combined with the ZSM-5 type catalyst particle component because of low coke deposition thereon. From the Arthur Curve

(Arthur, J. R. Transactions, Faraday Society, Vol. 47, page 164, 1951) it is ascertained that from burning coke the CO_2/CO ratio at 1,100°F. is 0.6. However, when subjecting a cracking catalyst comprising 15% by weight REY zeolite dispersed in a silica-zirconia clay matrix to regeneration at the same temperature of 1,100°F. after deposition of coke thereon, a CO_2/CO ratio of 0.57 was obtained. However, the same cracking catalyst in admixture with separate particles comprising Cr_2O_3 in an amount equivalent to 0.34% by weight Cr_2O_3 produced during regeneration a CO_2/CO ratio of 0.75. On the other hand, providing the REY zeolite cracking catalyst particle with 0.34% by weight Cr_2O_3 , produced during regeneration, a CO_2/CO ratio of 0.87. The higher CO_2/CO ratio obtained is indicative of the enhanced conversion of carbon monoxide by the oxidation catalyst thereby improving upon the generation of heat available in the process. The regeneration steps of the present invention are directed to recovering by direct heat exchange with the catalyst, the increased heat released by the exothermic conversion of CO to CO_2 .

EXAMPLE B

The concepts going to the essence of the present invention were tested using a catalyst composition containing about 15 wt. % REY (rare earth exchanged "Y" faujasite) and 5 wt. % ZSM-5 dispersed in a matrix as defined in Table 2. This catalyst after steam treating for 4 hours at 1,400°F. was used to crack a sour Middle East gas oil feed boiling in the range of 520°F. up to about 1,000°F. of the composition defined in Table 1, relying upon a cracking temperature of about 96°F. at a 4 catalyst to oil weight ratio and an on-stream time of 2.4 minutes thereby depositing substantial amounts of carbonaceous material on the catalyst amounting up to about 2.7 wt. %. The cracking activity of the catalyst was reduced to less than 40% by volume conversion by a standard test defined in Table 1 and by operating until 2.7% carbon was deposited on the catalyst. The coked catalyst was then contacted with a commercial grade gasoline product at a temperature of about 960°F. relying upon a 5 catalyst to oil weight ratio for an hour on-stream time. The data obtained are compared in tables 2 and 3 below for results obtained using an uncoked catalyst containing only ZSM-5. With the uncoked catalyst containing only ZSM-5, the results clearly show that the ZSM-5 cracks paraffins and olefins giving predominantly C_3 and C_4 olefins, forms aromatics as shown by the increase in mols of benzene rings from 28.5×10^{-2} in the charge to 33.7×10^{-2} in the cracked products and reduces the average molecular weight of the alkylbenzenes. These reactions resulted in the 1.7 gasoline octane number improvement. The cracking results with the coked catalyst containing both ZSM-5 and REY show that the ZSM-5 is active even in the presence of coked catalyst and gives large amounts of C_3 and C_4 olefins by cracking paraffins and olefins in the charge. It also reduces the average molecular weight of the alkylbenzenes. These reactions resulted in a 1.6 gasoline octane number improvement. The comparison shows that the two catalysts are similar in their cracking of the gasoline feed and improvement in octane number thereof and the data show that both catalyst display shape-selective cracking in that there is no significant loss in alkyl benzenes.

The results above obtained and identified supports the concepts comprising the invention herein defined in the following manner:

- a. A catalyst containing both shape-selective and non-shape selective zeolites can have its nonshape selective activity substantially reduced by coking without changing its shape selectivity activity and
- b. A shape-selective catalyst maintained in a dense fluid bed of catalyst will selectively crack a gasoline boiling material and increase its octane rating.

In view of the above findings, it is thus clear that the active shape selective component of the catalyst may be relied upon to perform the reactions of selective cracking and olefin cyclization provided reaction temperatures within the range of 900° to 1,100°F. are made available in combination with a proper hydrocarbon charge and residence time as herein described.

EXAMPLE C

It has been found that light C_6 - C_8 olefins and/or paraffin mixtures are converted over ZSM-5 type catalysts to a liquid fraction which, under preferred conditions, is largely aromatic and a gaseous fraction which is largely a mixture of C_1 - C_3 paraffins and olefins along with hydrogen. Several catalysts which catalyze the aromatization reaction such as metal exchanged, metal loaded and plain HZSM-5 zeolites were examined. The liquid product obtained was found largely aromatic containing C_6 to C_{11} aromatic compounds having an average gram molecular weight of 90-100 (toluene molecular weight is 92). The remaining liquid was identified as C_7 -paraffins (or olefins). The gaseous product was identified as hydrogen and a mixture of C_1 - C_3 paraffins and olefins. Table 1 below presents the accumulated data obtained in this investigation. With Zn ZSM-5 in example 2 of Table 1, hydrogen is formed in addition to methane and ethane. Examples 3 and 4 illustrate the conversion levels of HZSM-5 where methane and ethane are big products. In example 5 where propylene is passed over steamed HZSM-5, ethylene, propylene and butylenes make up much of the gaseous mixture and the paraffinolefinic concentration in the liquid is up to 38% weight. In example 6 using a ZnZSM-5 catalyst, a liquid yield of 74.8% was obtained.

It was found in this investigation that the best yields with non-hydrogen forming catalysts with propylene-propane mixtures arises when methane and ethane yields are high, as for HZSM-5 in example 7 and CrZSM-5 in example 8 of Table 2. With CrZSM-5 in example 8, a calculated yield of 47.7 wt. % aromatic yield is very close to the observed 45.4 wt. % aromatic yield assuming zero hydrogen make. NiZSM-5 catalyst also does not make hydrogen as shown by example 9, Table 3. Both CrZSM-5 and NiZSM-5, examples 9 and 8 in Table 3 have very similar activities. The ZnZSM-5 catalyst gives very good aromatic yields from propane/propylene mixtures without producing excessively large amounts of methane and ethane. Example 12, Table 4 and Example 13, Table 5, illustrate the excellent conversions obtainable with ZnZSM-5. In these examples, hydrogen was vigorously made.

The current interest in aromatization of paraffins/olefins over ZSM-5 type zeolites arises because of the increased demand for more high octane components in gasoline. Such a process for aromatizing paraffins/ole-

finds use in combination with fluid cracking operations and the olefinic gas streams obtained therefrom

as a complementary or an alternative process to the known acid alkylation process.

Table 1

Aromatization Over ZSM-5 Catalysts						
Charge Example	Propane 1	Propane 2	Propylene 3	Propylene 4	Propylene 5	Propylene 6
Catalyst	Cr/ZSM-5	Zn/ZSM-5	HZSM-5	----->HZSM-5		Zn/ZSM-5
Hrs. on Stream	1.3	17	1	1	1	1
Temperature	1100	1100	1100/950 ⁽¹⁾	1100	1100/950	1100/950
WHSV	0.78	0.85	0.4/0.4	0.81	0.51/0.51	3.29
Wt.% Recovered	120 ⁽²⁾	85.4	102.2	102.1	91.1	100.6
Based on Recovered Product						
Wt.% Liq. Prod.	31.2	47.0	61.9	59.6	40.8	74.8
Wt.% Arom. in Liq.	97.9	99.7	98.7	98.6	62.1	98.5
Av. Mol Wt. Arom.	91.0	89.7	92.7	92.2	101.8	91.1
Wt.% Olefins to Arom.	—	—	70.9	61.6	41.1	81.6
Calc. Based on 100 g. Recovered						
C ₁	29.1	15.8	10.8	9.9	2.3	6.1
C ₂ =	8.0	0.8	1.6	2.7	11.3	1.9
C ₂	18.9	19.3	10.0	12.2	1.9	6.4
C ₃ =	3.0	16.2	7.1	5.3	19.0	1.8
C ₃	8.2	—	7.2	9.2	9.2	8.4
C ₄ =	0.8	—	0.6	0.5	8.7	0.3
C ₄	0.8	—	0.6	0.5	4.8	0.1
C ₅ =	—	—	—	—	1.3	0.1
C ₅	—	—	0.2	—	0.6	0.1
Paraffins in Liq.	0.6	0.1	0.8	0.8	15.7	1.1
Benzene	9.9	18.6	18.8	17.9	2.4	23.5
Toluene	13.3	18.3	24.8	24.9	7.5	31.3
Xylene	4.6	5.5	8.9	9.0	8.2	12.5
Total C ₉	1.0	0.8	2.1	2.0	4.8	2.4
Indane	0.1	0.2	0.4	0.2	0.5	0.3
Total C ₁₀	0.4	0.2	0.8	0.8	1.2	0.7
Naphthalene	0.4	1.5	1.4	1.3	—	1.1
Total C ₁₁	0.9	0.8	3.7	2.6	0.4	1.8
					91% H ₂ in off gas	

⁽¹⁾ Where the temperature is listed as 1100/950 the catalyst bed is split in two halves; the first at 1100°F., the second at 950°F.

⁽²⁾ Based on charge rate during hour preceding balance.

Table 2

Aromatization of Propylene/Propane Mixtures at Atmospheric Pressure		
Example	7	8
Propylene/Propane	53/44	41/52
Catalyst	HZSM-5	Cr/HZSM-5
Temperature	1100/950	1100/950
WHSV	0.43/0.43	0.41/0.41
Wt.% Recovered ⁽¹⁾	99.0	102.3
Wt.% Liq. in Prod.	43.1	46.4
Wt.% Arom. in Liq.	97.7	97.9
Av. Mole Wt. Arom.	92.8	93.3
Wt. % Olefins to Arom.	80.2	110.3
Calc. Based on 100 g Recovered Product		
C ₁	14.6	17.8
C ₂ =	1.7	2.2
C ₂	11.6	12.2
C ₃ =	11.2	6.7
C ₃	15.5	13.8
C ₄	0.2	0.2
C ₄ =	1.0	0.8
C ₅ =	—	—
C ₅	—	—
Paraffins in Liq.	1.0	1.0
Benzene	11.9	13.1
Toluene	17.8	18.5
Xylene	7.1	7.1
Total C ₉	1.8	1.8
Indane	0.3	0.3
Total C ₁₀	0.7	0.8
Naphthalene	0.7	1.0
Total C ₁₁ +	1.7	2.7

⁽¹⁾ Based on a blank collected prior to time of material balance.

Table 3

Propane/Propylene Conversion				
Example	9	10	8	11
C ₃ =/C ₃	49/50	49/50	41/52	48/49
Catlyst	Ni/ZSM-5	Ni/ZSM-5	Cr/ZSM-5	Cr/ZSM-5
Carrier gas	He	H ₂	He	H ₂
Gas/HC (mol Ratio)	0.3/1.0	—	—	—
Temperature	1100/950	1100/950	1100/950	1100/950
WHSV	3.51	3.46	0.83	0.85
Wt.% Recovered	99.2	99.3	102.3	102.8
Based on Recovered				
Wt.% Liq. Prod.	41.1	35.2	46.4	28.8
Wt.% Arom. in Liq.	99.1	98.7	97.9	94.0
Av. Mol Wt. Arom	93.3	95.1	93.3	96.2
Wt.% Olefins to Arom	86.0	69.4	110.3	59.3
Calc. Based on 100 g Recovered				
C ₁	14.9	14.9	17.8	7.5
C ₂ =	2.2	2.4	2.2	4.4
C ₂	8.9	10.4	12.2	6.4
C ₃ =	1.5	5.7	6.7	7.5
C ₃	28.9	30.4	13.8	40.2
C ₄ =	—	0.4	0.2	1.2
C ₄	0.3	0.5	0.8	3.2
C ₅ =	0.1	0.1	—	0.4
C ₅	0.1	—	—	0.3
Paraffins in Liq.	0.4	0.5	1.0	1.7
Benzene	11.5	7.1	13.1	4.4
Toluene	17.5	15.3	18.5	12.1
Xylene	7.3	8.0	7.1	6.8
Total C ₉	1.4	1.6	1.8	2.0
Indane	0.2	0.2	0.3	0.2
Total C ₁₀	0.8	0.5	0.8	0.8
Naphthalene	1.2	0.4	1.0	0.2
Total C ₁₁ +	2.0	1.7	2.7	0.7

Table 4

Aromatization of 50/50 Wt. % Mix of Propylene/Propane						
Zn/ZSM-5 Example 12	Regenerated - Air - 950°F R-1		Regenerated - Air - 950°F R-2		Regenerated - Air - 950°F R-3	
Time on Stream	18.5	6	26	18.5	18.5	18.5
Sample No.	1	2-R1	3-R1	4-R2	5-R3	6-R4
Temperature	1100					
WHSV	1.74	1.95	1.82	1.87	1.75	1.63
Wt.% Recovered	105.3	85.2	103.2	103.5	87.6	89.2
Based on Recovered						
Wt.% Liq. Prod	54.9	57.4	47.0	57.2	49.4	47.2
Wt.% Arom in Liq.	99.8	92.2	99.4	99.0	99.0	98.8
Av. Mol Wt. Arom	90.8	90.5	91.0	90.9	91.9	90.5
Wt.% Olefins to Arom	105.5	118.1	97.5	120.1	107.1	103.9
Calc. Based on 100 g Recovered						
C ₁	8.0	10.9	7.9	7.1	8.2	8.8
C ₂ =	3.0	2.6	3.6	3.0	3.2	3.8
C ₂	9.0	12.0	9.2	7.5	7.9	7.1
C ₃ =	10.4	4.3	5.3	7.0	6.6	4.7
C ₃	14.2	12.8	26.8	17.5	24.2	27.2
C ₄ =	0.4	—	0.2	0.1	0.1	0.2
C ₄	—	—	—	0.5	0.3	0.9
C ₅ =	0.1	—	—	0.1	—	0.1
C ₅	—	—	—	—	—	—
Paraffins in Liq.	0.1	0.5	0.2	0.6	0.5	0.6
Benzene	19.5	20.5	15.8	19.6	15.7	15.8
Toluene	22.6	24.1	19.7	24.2	19.5	20.6
Xylene	6.7	6.8	6.6	7.1	8.8	6.4
Total C ₉	1.0	0.6	0.9	1.0	0.8	1.1
Indane	—	—	0.1	—	—	0.1
Total C ₁₀	0.8	0.9	0.9	0.8	0.6	0.7
Naphthalene	1.7	1.7	1.3	1.3	1.0	0.7
Total C ₁₁ +	2.3	2.4	1.5	2.7	2.4	1.3
		Hydrogen 1.4%				

Table 5

Conversion of 50/50 Wt.% Mix of Propylene/Propane at 1000°F - Example 13		
Hours on Stream	19.8	44.2
Catalyst	Zn/ZSM-5	Zn/ZSM-5
Sample Number	1	2
Temperature	1000	1000
WHSV	1.71	1.72
Wt.% Recovered	82.4	84.0
Based on Recovered Product		
Wt.% Liq Prod	43.2	41.4
Wt.% Arom in Liq	99.2	98.9
Av Mole Wt. Atom	92.5	92.0
Wt.% Olefins to Arom	88.7	86.0
Calc. Based on Recovered		
C ₁	5.5	5.2
C ₂ =	2.6	1.3
C ₂	7.0	7.0
C ₃ =	5.4	2.1
C ₃	35.3	42.0
C ₄ =	0.6	0.3
C ₄	0.2	0.6
C ₅ =	0.2	—
C ₅	—	—
Paraffins in Liq	0.4	0.4
Benzene	11.4	11.5
Toluene	19.1	18.2
Xylene	8.5	8.0
Total C ₉	1.4	1.3
Indane	—	0.1
Total C ₁₀	0.3	0.3
Naphthalene	0.7	0.6
Total C ₁₁	1.3	1.0

Having thus provided a general discussion of the improved methods comprising hydrocarbon conversion to form gasoline boiling products and regeneration of the catalyst employed therein and described specific processing arrangements which may be employed to accomplish the methods of this invention, it is to be understood that no undue limitations are to be imposed by reason thereof except as hereinafter defined.

I claim:

1. A method for converting hydrocarbons to gasoline product with a dual component cracking catalyst comprising a large pore cracking component in combination with a ZSM-5 type of crystalline aluminosilicate which comprises passing a suspension comprising a gas oil feed boiling above 450°F. in admixture with said dual component cracking catalyst upwardly through a riser reactor at a temperature in the range of 1,000°F. up to 1,400°F., introducing a high coke producing oil feed into a downstream portion of said riser under conditions to substantially subdue the cracking activity of the large pore crystalline aluminosilicate, separating the suspension into a hydrocarbon phase and a catalyst phase, recovering the separated hydrocarbon phase, collecting the separated catalyst phase as a dense fluid bed of catalyst, beneath the riser conversion outlet, combining freshly regenerated catalyst with said collected dense fluid bed of catalyst to provide a bed of catalyst with a temperature in the range of 800°F. to 1,200°F., introducing a hydrocarbon feed comprising C₃ and C₄ hydrocarbons to a lower portion of said dense fluid bed for cyclization thereof to aromatic components, withdrawing catalyst from said dense fluid bed, stripping the withdrawn catalyst, regenerating the stripped catalyst to remove deposited carbonaceous material and returning regenerated catalyst to said riser reactor.

2. A method for converting hydrocarbons in the presence of a dual cracking component catalyst comprising a large pore crystalline aluminosilicate and a ZSM-5 type of crystalline aluminosilicate which comprises combining said dual component catalyst with a gas oil feed under conditions to form a suspension at a temper-

ature in the range of 1,000°F up to about 1,400°F., passing the suspension thus formed through a dispersed catalyst phase riser reaction zone for a hydrocarbon residence time in the range of 0.5 seconds to 10 seconds to form cracked products of reaction comprising gasoline and olefinic constituents of cracking, separating the suspension after traversing said riser reaction zone into a hydrocarbon phase and a catalyst phase, recovering the hydrocarbon phase, recovering the catalyst phase as a dense fluid bed of catalyst, contacting the dense fluid bed of catalyst under temperature conditions in the range of 900°F. to 1,100°F. with a high coke producing feed material at a catalyst residence time in the range of 0.5 minutes up to 5 or 10 minutes and sufficient to effect substantial deactivation of the large pore CAS component, passing a portion of the dense fluid bed of catalyst to a stripping zone, stripping the catalyst and passing the stripped catalyst to catalyst regeneration, passing another portion of said dense fluid bed of catalyst to a separate olefin aromatization zone maintained at a temperature in the range of 800°F. to 1,200°F. passing a C₃ and C₄ olefin rich feed in contact with the catalyst in said aromatization zone, stripping and withdrawing catalyst from said aromatization zone, regenerating catalyst withdrawn from said stripping zone and passing regenerated catalyst to said riser reactor above identified.

3. The method of claim 2 wherein the catalyst withdrawn from the stripping zone is regenerated in a first riser regenerator and the catalyst withdrawn from the aromatizing zone is regenerated in a second riser regeneration zone, gasiform products of combustion discharged from the first and second riser regeneration zone are combined in a zone promoting the combustion of carbon monoxide, gasiform products of combustion with catalyst separated from the first riser regeneration zone are passed in direct heat exchange relationship to a separate catalyst accumulation zone, separating catalyst from gases products of combustion in said accumulation zone, combining catalyst separated in said accumulation zone with catalyst discharged from said second riser regeneration zone, subjecting the catalyst thus recovered and combined to further regeneration in the presence of oxygen containing regeneration gases and passing regeneration catalyst to said hydrocarbon riser reactor.

4. A method of regenerating catalyst which comprises passing a cracking catalyst comprising crystalline aluminosilicate contaminated with carbonaceous material upwardly through separate first and second riser regeneration zones, burning gaseous components discharged from said first and second riser regenerators to convert carbon monoxide to CO₂ and produce hot combustion gases, passing catalyst discharged from said first riser regenerator with hot combustion gases in direct heat exchange to a catalyst accumulation zone, separating catalyst from hot combustion gases in said accumulation zone, combining catalyst separated in said accumulation zone with catalyst separated from said second riser regeneration zone and subjecting the combined catalyst to regeneration with oxygen containing gas.

5. A method for converting a crude oil to gasoline product of acceptable octane rating which comprises, separating a crude oil having a gravity in the range of 15 API to 40 API by atmospheric and vacuum distillation into gas oil fractions, a heating oil fraction and an overhead fraction comprising hydrocarbon gases and

straight run gasoline, passing said overhead fraction through a first riser reactor in contact with a dual function cracking catalyst comprising a ZSM-5 type crystalline aluminosilicate component suspended therein at a temperature in the range of 1,000°F. up to 1,400°F. for a hydrocarbon residence time in the range of 1 to 10 seconds, passing gas oil fractions of atmospheric and vacuum distillation through a second riser reactor in contact with said dual function cracking catalyst as a suspension at a temperature in the range of 900°F. to 1,300°F. for a hydrocarbon residence time in the range of 1 to 10 seconds, separating the suspensions after traverse of said riser reaction zones into a hydrocarbon phase and a catalyst phase, passing the hydrocarbon phase to a fractionation zone, stripping the catalyst phase separated from each riser reaction zone and passing the stripping products to said fractionation zone, passing a portion of the stripped catalyst to catalyst regeneration, passing another portion of the stripped catalyst to a separate aromatization zone, passing gasiform material rich in C₃ and C₄ hydrocarbons in contact with the catalyst in said aromatization zone maintained at a temperature in the range of 600°F. to 1,500°F., and a hydrocarbon residence time in the range of 15 seconds to 15 minutes, separating product hydrocarbons from the catalyst in said aromatization zone and passing the thus separated products of aromatization to said fractionation zone, passing catalyst from said aromatizing zone to catalyst regeneration, in said fractionation zone separating the hydrocarbon passed thereto into a gasoline and lower boiling hydrocarbon fraction comprising olefins, a heavy naphtha fraction, a light cycle oil fraction, a heavy cycle oil fraction and a bottoms residual fraction, passing the overhead fraction through a deethanizing zone and a debutanizing zone, recovering debutanized gasoline, passing a gaseous fraction rich in C₃ and C₄ hydrocarbons separated from the gasoline product to said aromatizing zone, passing heavy naphtha product to said first riser reactor with said straight run gasoline feed and passing heavy cycle oil product to said second riser with said gas oil feeds.

6. A method for upgrading a crude oil to useful products comprising

- a. separating a crude oil by atmospheric and vacuum distillation into a gas oil fraction boiling from about 500°F. up to about 1,100°F., a higher boiling residual fraction, a light oil fraction boiling from about 400°F. up to about 600°F. and a lower boiling fraction comprising straight run gasoline and lower boiling gaseous hydrocarbons,
- b. cracking said gas oil fraction in a first dispersed catalyst phase reaction zone at a temperature of at least 900°F. in the presence of a dual cracking component catalyst comprising ZSM-5 type crystalline aluminosilicate and a larger pore size cracking component,
- c. contacting the straight run gasoline and lower boiling gaseous hydrocarbon comprising C₃ and higher boiling gaseous hydrocarbons in a second dispersed catalyst phase reaction zone under hydrocarbon conversion conditions in the presence of said dual cracking component catalyst recited above,
- d. separating hydrocarbons from catalyst after traverse of said first and second reaction zones within a hydrocarbon residence time within the range of 0.5 to 10 seconds and passing separated hydrocarbons to a product fractionation zone,
- e. collecting and stripping the catalyst recovered

from said first and second reaction zones to remove entrained hydrocarbons therefrom,

- f. passing stripped catalyst to a separate dense fluid bed of catalyst maintained at a temperature within the range of 600°F. up to 1,200°F. to which is passed straight run gasoline and product gasiform hydrocarbons comprising C₃ and C₄ hydrocarbons under conditions to provide a hydrocarbon residence time within the range of 15 seconds up to about 15 minutes,
 - g. passing reaction products of said separate dense fluid catalyst bed along with stripped products to said product fractionation zone,
 - h. recovering from said product fractionation zone a heavy cycle oil recycled in part to said first reaction zone, a light cycle oil recycled in part to said second reaction zone, a heavy naphtha fraction recycled in part to said second reaction zone, a gasoline and lower boiling C₃ and C₄ hydrocarbons which are further separated to recover stabilized gasoline therefrom and
 - i. passing C₃ and C₄ hydrocarbons separated from the gasoline product to said separate dense fluid bed of catalyst.
7. The method of claim 6 wherein the straight run gasoline fraction comprising C₃ and C₄ gaseous hydrocarbons is separated so that the C₃ and C₄ gaseous hydrocarbons may be passed to said separate dense fluid catalyst bed and said straight run gasoline may be passed to said second dispersed phase reaction zone.
8. An integrated refinery operation for upgrading a crude oil and products of cracking which comprises,
- a. separating from a crude oil and products of cracking, a hydrocarbon fraction boiling above about 500°F. and thereafter cracking the separated fraction in the presence of a catalyst mixture comprising a large pore crystalline aluminosilicate and a smaller pore ZSM-5 type crystalline aluminosilicate at a temperature above 1,000°F. employing a hydrocarbon residence time in the presence of said catalyst mixture not exceeding about 10 seconds,
 - b. separating from said crude oil a straight run gasoline fraction and from the product of catalytic cracking a heavy naphtha fraction which fractions are combined and passed in contact with a catalyst mixture comprising a large pore crystalline aluminosilicate and a smaller pore ZSM-5 type catalyst at a temperature of at least 1,000°F. using a hydrocarbon residence time less than 10 seconds,
 - c. passing a gasiform stream comprising C₃ and C₄ hydrocarbons separated from the cracked products obtained in steps (a) and (b) above in contact with a ZSM-5 type catalyst at a temperature in the range of 600°F. up to 1,200°F. using a hydrocarbon residence time sufficient to crack and aromatize said gasiform stream and
 - d. recovering from the combined products of steps (a), (b) and (c) above recited, a stabilized gasoline fraction of desired octane rating.
9. In a hydrocarbon conversion process wherein the gas oil components of a crude oil are converted by cracking with a crystalline zeolite cracking catalyst to products comprising gasoline in combination with lower and higher boiling products including gaseous products comprising C₃ and C₄ hydrocarbons, the method for improving the octane rating and yield of gasoline product therefrom which comprises, mixing a ZSM-5 type crystalline catalyst with a larger pore size crystalline zeolite cracking catalyst, using the mixture

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to crack gas oil to products including gasoline and gaseous C₃ and C₄ hydrocarbons, using the mixture to crack straight run gasoline and heavy naphtha product of cracking to improve the octane and volatility thereof and form C₃ and C₄ hydrocarbons, using the ZSM-5 component of the mixture for cracking and aromatizing

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olefins formed from said gaseous C₃ and C₄ hydrocarbons and relying upon the catalyst mixture to convey heat to the combination of steps above recited from a catalyst regeneration zone.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,856,659 Dated December 24, 1974

Inventor(s) HARTLEY OWEN

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

Column 17, line 41 : After "2.7%" insert --wt.%--

Column 18, line 21 : "C₁₁" should be --C₂--

Column 23, line 52 : After "conversion" insert
--zone--

Signed and Sealed this

second Day of September 1975

[SEAL]

Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents and Trademarks