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(54) Process for cracking a hydrocarbon feedstock to obtain gasoline and olefins and upgrading the olefins to improve the total gasoline yield.

(57) Improved processes are disclosed for increasing gasoline yield from a gas oil at a constant riser top temperature by introducing a quench fluid, such as liquid water, butane, or lighter hydrocarbons or an alcohol or ether into a riser downstream of the site where the gas oil and/or catalyst are injected. In another embodiment of the invention the introduction of quench fluid, acting as a heat sink, can be used to increase octane number while avoiding significant formation of wet gas as is observed when higher octane number is achieved by generally increasing the overall riser temperature. This invention further provides an integrated process wherein the C_4- product from an FCC riser unit which is limited to a predetermined top temperature maintained by injecting a quench fluid intermediate the inlet and outlet of the FCC riser is combined and contacted with a zeolite catalyst in a turbulent fluid bed under conditions of severity to upgrade the light olefin-containing gas to heavier hydrocarbons, especially gasoline.

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Description

PROCESS FOR CRACKING A HYDROCARBON FEEDSTOCK TO OBTAIN GASOLINE AND OLEFINS AND UPGRADING THE OLEFINS TO IMPROVE THE TOTAL GASOLINE YIELD

This invention relates to an improved process for increasing gasoline octane number and total gasoline yield and an integrated process for increasing the total gasoline yield per unit of chargestock used in the process. In a most preferred embodiment the invention integrates an improved fluid catalytic cracking (FCC) process to obtain improved gasoline yield of higher octane number and olefins and to a catalytic technique for upgrading the olefins to heavier hydrocarbons, in particular, gasoline. The disclosed process will thus provide increased gasoline yields of higher octane for given volume or weight of chargestock fed to the process.

Hydrocarbon conversion processes utilizing in crystalline zeolites have been the subject of extensive investigation during recent years, as is obvious from patent and scientific literature. Crystalline zeolites have been found to be particularly effective for a wide variety of hydrocarbon conversion processes, including the catalytic cracking of a hydrocarbon, e.g., gas oil, to produce motor fuels and have been described and claimed in many patents, such as U.S. Patent Nos. 4,118,338 and 4,368,114.

Attempts have been made to improve the basic catalytic process in order to achieve higher gasoline yield, such as reported in U.S. Patent No. 3,886,060, the entire contents of which are herein incorporated by reference. The patentees utilized a dual component cracking catalyst of large and small pore size to catalytically crack feeds of residual and recycle oil. By utilizing the residual oil as a quench medium conversion of recycle oil was limited.

Other attempts at injecting one or more streams into an FCC riser are disclosed in U.S. Patents Nos. 3,692,667; 3,928,172; 4,147,617; 4,218,306; and 4,485,184, the disclosures of all of which are herein incorporated by reference. These prior art processes fail to provide solutions to the desire for increased gasoline yield and octane without the co-production of increased amounts of commercially undesirable by-products.

In order to reduce automobile exhaust emissions to meet federal and state pollution requirements, many automobile manufacturers have equipped the exhaust systems of their vehicles with catalytic converters. These converters contain catalysts which are poisoned by tetraethyl lead. Since tetraethyl lead has been widely used to boost the octane number of gasoline, refiners now have to turn to alternate methods to improve gasoline octane number.

Many methods of octane improvement, however, reduce the yield of gasoline. With the present short supply of available crude oil and the concommitant high demand for unleaded gasoline with a sufficiently high octane number, refiners are faced with a severe dilemma.

One method of increasing octane number is to raise the overall cracker reactor temperature. This method, however, is very limited, since many units are now operating at maximum temperatures due to metallurgical limitations. Raising the overall cracker reactor temperature also results in increased production of light gas, C_4^- a product of less economic value than gasoline. This increased production of gas in turn, results in increased capital requirements for the gas plant (i.e., gas compressor and separator) necessary to process the gas. Because most gas plants are now operating at or close to maximum capacity, significant increases in the gas processing are not well tolerated by the present equipment. As can well be appreciated from the foregoing, it would be extremely desirable to have a process which will provide high octane unleaded gasoline without undue sacrifice of gasoline yield. It is, of course, always desirable to increase gasoline yield. It would be even more desirable if the foregoing desires could be obtained in conjunction with an increase in operational flexibility, including use of existing equipment, and without undue use of expensive catalyst.

Other attempts at obtaining gasoline from lighter hydrocarbons through the use of a catalytic technique are disclosed in U.S. Patent No. 4,579,999. Such techniques employ gases containing light olefin, such as ethene-containing olefinic light gas, optionally containing propene or other lower alkanes, to produce C_4^+ hydrocarbons, such an olefinic liquid fuels, isobutene, aromatics and other useful products. Ethene (ethylene C2H4)-containing gases, such as petroleum cracking off gas are useful feedstocks for a continuous process of oligomerizing the olefinic-containing light gas to heavier hydrocarbons.

However, none of the foregoing processes are able to produce the desired high yield of gasoline based on unit volume or weight of chargestock fed to the integrated process of the present invention.

According to the present invention, the temperature at the inlet of a FCC unit, e.g., riser, can be increased and, by the addition of a quenching fluid, such as liquid water, intermediate to the hydrocarbon inlet and outlet a significant improvement in yield and octane number of gasoline can be obtained without raising the outlet (top) temperature of the cracking unit. Thus, there is less yield loss of gasoline to light gases (C_4^-) than occurs when the temperature of the entire FCC unit is increased.

In another embodiment of the invention it has been found that the total yield of gasoline can be increased if the quench fluid, such as liquid water, or a hydrocarbon stream such as fresh feed, recycled oil naphtha, light (LCO) or heavy (HCO) cycle oils, coker gas oils, liquified propane gas (LPG), butanes and lighter hydrocarbons, alcohols or ethers, is introduced into the cracking unit above the point where the catalyst and oil become well mixed.

At least a portion of the light olefin-containing gas obtained from the foregoing process is fed to a fluidized bed of catalytic particles, e.g., zeolite catalyst, whereby the light olefins are upgraded to heavier hydrocarbon products, C_5^+ , and especially gasoline.

The improved process of this invention affords the refiner greater flexibility in the catalytic cracking operation while improving the total yield of gasoline obtained from a unit volume or weight of hydrocarbon chargestock.

Fig. 1 is a schematic of a catalyst section for a fluid catalytic cracking plant;

Fig. 2 is a graph of normalized conversion plotted versus mix temperature (° F) of gas oil and catalyst;

Fig. 3 is a graph of increase in mix temperature plotted versus weight percent of quench fluid added to the riser.

Fig. 4 is a schematic view of a fluidized bed reactor system for upgrading light olefin gas to heavier hydrocarbons..

The process of this invention is particularly applicable to the fluid catalytic cracking (FCC) process. Although the design and construction of individual plants vary, the essential elements of an FCC unit, particularly the flow of catalyst and hydrocarbon chargestock are illustrated by Fig. 1 which show a conventional catalyst section of a fluid catalytic cracking plant.

Referring now to Fig. 1, the hydrocarbon feed 2, such as a gas oil fraction, or resid, boiling above 473°C (600°F), typically from about 473° C (600° F) up to about 538° C (1000° F) is passed, after preheating thereof, to the bottom portion of riser 4 for admixture with hot regenerated catalyst introduced by standpipe 6 provided with flow control valve 8. A suspension of catalyst and hydrocarbon vapors at a temperature of at least about 510° C (950° F), but more usually at at least 538°C (1000° F), is thus formed in the lower portion of riser 4 for flow upwardly therethrough under hydrocarbon conversion conditions. The suspension initially formed in the riser may be retained during flow through the riser for a hydrocarbon residence time in the range of about 0.5 to about 20 seconds. It is to be expressly understood that although the foregoing description refers to regenerated catalyst, it is also within the scope of the invention to substitute at least part, if not all, of the regenerated catalyst with fresh catalyst without departing from the spirit of the invention. The hydrocarbon vapor-catalyst suspension formed in the lower section of the riser is passed upwardly through riser 4 under hydrocarbon conversion conditions of at least about 482° C (900° F) and more usually at least about 538° C(f1000° F) before discharging to one or more cyclonic separation zones above the riser discharge, represented by cyclone separator 14. There may be a plurality of such cyclone separator combinations comprising first and second cyclonic separation means attached to or spaced apart from the riser discharge for separating catalyst particles from hydrocarbon vapors. Separated hydrocarbon vapors are passed from separator 4 to a plenum chamber 16 for withdrawal thereof by conduit 18. The catalyst separated from the hydrocarbon vapors in the cyclonic separation means is passed, by suitable diplegs, represented by dipleg 20, to a dense fluid bed of separated catalyst 22 retained about an upper portion of riser conversion zone 4. Catalyst bed 22 is maintained as a downwardly moving fluid bed of catalyst countercurrent to rising gasiform material. Catalyst passes downwardly through a stripping zone 24 immediately therebelow and countercurrent to riser stripping gas, introduced to a lower portion thereof by conduit 26. Baffles 28 are provided in the stripping zone to improve the stripping operation.

The catalyst is maintained in stripping zone 24 for a period of time sufficient to effect the high temperature desorption of feed deposited compounds which are then carried overhead by the stripping gas. The stripping gas with desorbed hydrocarbon passes through one or more cyclone separating means 32 wherein entrained catalyst fines are separated and returned to the catalyst 22 by dipleg 34. The hydrocarbon conversion zone comprising riser 4 may terminate in an upper enlarged portion of the catalyst collecting vessel, commonly known in the prior art as a "bird cage" discharge device, where an open end "T" connection may be fastened to the riser discharge which is not directly connected to the cyclonic separation means. Cyclonic separation means may be spaced apart from the riser discharge so that an initial catalyst separation is effective by a change in velocity and direction of the discharged suspension so that vapors less encumbered with catalyst fines may then pass through one or more cyclonic separation means before passing through the product separation step. In any of these arrangements, gasiform materials comprising stripping gas, hydrocarbon vapors and desorbed sulfur compounds are passed from a cyclonic separation means, represented by separator 32, to a plenum chamber 16 for removal with hydrocarbon products of the cracking operation through conduit 18. Gasiform material, comprising hydrocarbon vapors, is passed by conduit 18 to a product fractionation device (not shown). The hot stripped catalyst, at an elevated temperature, is withdrawan from the lower portion of the stripping zone by conduit 36 for transfer to a fluid bed of catalyst being regenerated in a catalyst regeneration zone of catalytic regenerator 40. A flow control valve 38 can be provided in the coked catalyst conduit 36 for controlling the flow of the coked catalyst into the regeneration zone. The details of the regenerator 40 are not shown as the specifics of the catalyst regeneration operation is not part of the present invention and various types of regeneration processes and apparatus known to those having ordinary skill in the art may be utilized to regenerate the catalyst utilized in the FCC unit.

The type of catalyst regeneration operation is not part of the present invention, with various types of regeneration processes and apparatus being well known to those having skill in the art. Thus, although the details of regeneration zone 40 are not set forth herein, it is to be understood that hot freshly regenerated catalyst is withdrawn from regeneration zone through conduit 6, passing through flow control valve 8 for mixture with the hydrocarbon feed 2 entering riser 4 so as to effect catalytic cracking of the hydrocarbon feed 2. The hot regenerated catalyst entering riser 4 from conduit 6 is at an elevated temperature, generally higher than 538°C (1000°F), usually in the range of about 566° C (1050°F) to above about 704° C (1300°F) when it contacts hydrocarbon feed 2. In the present invention, the combination of hot regenerated catalyst and preheated feedstock, or both, produces a mix temperature in the bottom of the FCC riser above about 552° C (1025° F), preferably in the range of about 582° C (1080° F) to about 593° C (1100° F). It is to be understood that although the regenerated catalyst may be substituted with fresh catalyst, it is preferred to use hot catalyst as a source of heat to raise the temperature in the lower section of riser 4.

Conventional fluid catalytic cracking reaction vessels or risers 4, vary in diameter and height. Typical diameters are from about 0.9 to 1.8 m (3 feet to 6 feet) with typical heights being from about 15 m to 30 m (50 feet to 100 feet).

In one embodiment of the present invention it is preferred to introduce a quenching fluid, such as liquid water, directly into the catalyst-oil mixture in riser 4 above the point where the catalyst and oil are fully mixed. The point of introduction of the quenching fluid will affect the yield of products as well as the octane number of the gasoline fraction. The point of introduction of the quenching fluid can thus be tailored to meet the requirements of specific products and specific equipment. In a particularly preferred embodiment the quenching fluid is introduced within about 7 to 1520 cm (50 feet) of the feedstock inlet.

Thus, in a FCC rise 4 as illustrated in Fig. 1, which is limited to a fixed riser top temperature (RTT) of about 538° C (1000° F) it will be possible with the addition of the quenching fluid to increase the mix temperature to any desired degree at the bottom riser 4. This can be accomplished by increasing the preheating of hydrocarbon feed 2 or raising the temperature of the catalyst entering riser 4 through conduit 6, or both.

This increase in mix temperature at the bottom of the riser has unexpectedly been observed to increase the yield of gasoline. This yield increase of gasoline is attributed to an increase in the vaporization of the hydrocarbon feed in the bottom of the riser 4 as the mix temperature is raised. Because vapor phase cracking rates are much faster than the liquid phase cracking rates, the shift toward the vapor state causes the increased conversion of a hydrocarbon feed, such as a gas oil fraction, to gasoline.

Introducing a quenching fluid, such as liquid water, at a point downstream of the oil inlet, wherein the catalyst and oil have just been mixed, will permit the attainment of a much higher mix temperature at the bottom of the riser while retaining the same top temperature of the riser. The catalyst-to-oil ratio of the prior art, typically 10:1 to 2:1, preferably 6:1 can be maintained. In this way, riser units limited by a maximum top temperature, maximum catalyst circulation rate, or maximum coke burning rate, can increase mix temperature, and hence gasoline yield, within these constraints. The amount of quenching fluid admitted is in such quantity and temperature so as to limit the top temperature of the cracking unit to a desired amount, preferably less than about 549° C (1020° F), preferably below about 538° C (1000° F). Among the aforementioned qunehcing fluids, water, butane and lighter hydrocarbons, alcohols and ethers are preferred, with water and butane and lighter hydrocarbons being more preferable. Of all quenching fluids, water is most preferred. The amount of quenching fluid admitted to quench the temperature of the catalyst oil mixture will vary depending on the desired inlet and outlet temperature, competing endo- and exo- thermic heats of reaction and temperature and type of quenching material.

In a preferred embodiment of the invention the amount of water as quenching fluid is within the range of 5-15 weight percent, preferably 7-8% based upon the total weight of the hydrocarbon charge introduced at the inlet. When the quenching fluid is liquefied petroleum gas (LPG) or mixed butanes about 15 weight percent, based on the total weight percent of the hydrocarbon charge is preferred. When LCO (e.g., sponge oil) is used as the quenching fluid in place of water, addition of about 35 weight percent based on the total weight of the hydrocarbon charge is preferred. In a further embodiment, when HCO is used as the quenching fluid, a volumetric amount equal to the aforementioned weight of LCO (sponge oil) is the preferred amount of quench fluid.

Referring now to Fig. 2 the effect of mix temperature on conversion of gas oil to gasoline is demostrated for commercial and pilot plant units. The effect in commercial units (solid line CU) is much greater than the effect observed in pilot plant units (dashed line PP). The greater sensitivity of commercial units in regard to percent conversion versus mix temperature has heretofore not been observed and is believed to be the result of poor mixing and vaporization in the larger diameter commercial units. It is readily apparent that increasing the mix temperature in both the commercial and pilot plant units result in an increase in gasoline yield based upon greater conversion of the hydrocarbon feedstock to gasoline.

By employing the invention in a commercial unit, the mix temperature at the bottom of riser 4 can be increased in the order of about 31° C (55° F) which causes conversion to increase significantly.

Fig. 3 shows the increase in mix temperature plotted versus the amount of water added intermediate the riser oil inlet and outlet as a percentage of the oil feed. This plot is at a constant riser top temperature (1000° F) and a constant catalyst-to-oil ratio of 6.0:1. The injection point of the quenching fluid, such as water, should be in the portion of the riser downstream of where the the catalyst and oil are well mixed, generally occurring from about the first 7 to about the first 20 feet, preferably from about the first 10 to about the first 20 feet of the riser. The point of introduction of the quenching fluid can occur at any point downstream of where the catalyst and oil are well mixed to about 6.1 m (20 feet) from the and outlet of the riser. The use of a quenching fluid, such as liquid water, makes the instant process economical in that liquid quenching streams are typically available from the refinery surrounding the FCC unit. The temperature of the quenching fluid is not critical and liquid water at a temperature range of from about 16° C (60° F) to about 38° C (100° F) has been found suitable although these temperatures may vary from ambient to above boiling and other liquids may be used at temperatures of from about 16° C (60° F) to about 482° C (900° F).

In a further embodiment of the invention, it has been found that increasing the temperature in the bottom of an FCC reactor followed by quenching with a quenching fluid increases gasoline research and motor octanes similar to that observed by increasing the temperature throughout the reactor but without the attendant disadvantages associated with a general temperature increase. When raising the temperature throughout the reactor, a significant increase in the conversion of gasoline to light gaseous hydrocarbon, C_4^- , occurs. By increasing the temperature only in the bottom of the reactor, then quenching according to the present invention, the amount of conversion of gasoline to light gaseous hydrocarbon is reduced for the same increase in gasoline octane obtained by generally increasing the temperature throughout the riser.

Thus, in an FCC unit, of the type shown in Fig. 1, the temperature in the bottom of the reactor can be controlled independently of the temperature in the top of the reactor by adding suitable amounts of a quenching fluid intermediate the oil inlet and outlet of the reactor. The preferred quenching fluid is liquid water, due to its ready availability, although other materials such as the aforementioned fresh feed, recycle oil napntha, etc. may be used alone or in combination. The point of introduction 5 is intermediate the oil inlet and outlet of the reactor. As stated heretofore, most FCC units are operating with the gas plant (i.e., gas compressor and separator) at or near maximum capacity, with significant increases in gas processing load not being well tolerated by the present equipment. The present invention overcomes the problems associated with increasing octane number according to the prior art process of generally raising the temperature throughout the reactor, without the attendant increase in gaseous hydrocarbon (C_4^-) production, by introducing a quenching fluid intermediate the oil inlet and outlet of the reactor so as to limit gaseous hydrocarbon,C_4^- formation, to levels tolerated by existing gas plant equipment.

The effect of increasing the temperature in the bottom of a pilot plant reactor is shown in Table 1:

Table 1

	Base	Steep Profile
Riser Bottom Zone, Temp., °C(°F)	552 (1025)	593 (1100)
Riser Mid Zone, Tem., °C (°F)	538 (1000)	538 (1000)
Riser Top Zone Tem.,°C (°F)	524 (975)	510 (950)
H_2	0.12	0.10
C_1	1.05	1.28
C_2	0.88	1.14
C_2 =	0.77	1.17
C_3	1.16	1.16
C_3 =	4.80	5.59
C_4, wt %	10.3	9.9
Gasoline, wt %	50.2	49.3
LFO, wt %	17.5	16.6
HFO, wt %	6.0	6.7
Coke, wt %	6.1	5.9
Conversion, wt %	76.5	76.7
Wet gas, M^3/sec at 100 M BBL/D	21.5	23.7
C Gasoline Octanes		
R+O	89.3	92.5
M+O	79.9	80.9

By the foregoing use of the term "base", which is a representative prior art riser, operated at a top temperature of about 524° C (975° F), it can be seen that 50.2 weight percent of gasoline is obtained with about 76.5 weight percent conversion of the total hydrocarbon charge. The use of the term "steep profile" in the foregoing table describes the present invention wherein the riser bottom zone temperature is raised over that obtainable in the prior art although by the use of quench fluid the riser top zone temperature is actually reduced to a point lower than that of the prior art. Gasoline yield remains high at 49.3% with approximately the same weight percent of conversion but higher gasoline octanes for both research and motor octane values are obtained.

Moreover, it will be appreciated from Table 1 that there is a shift in the gas yields from butenes and butylene towards ethylene and propylene. By separating the C_4^- and lighter gases from the other products exiting conduit 18 of the improved FCC process and which are used as a feed gas for the olefin to gasoline process, additional product yields of gasoline will be obtainable.

Conventional fluid catalytic cracking reaction vessels or risers 4 (Fig. 1) vary in diameter and height. Typical diameters are from about 0.9 m (3 feet) to about 1.8 M (6 feet) with typical heights being from about 15.2 m (50 feet) to about 30.5 m (100 feet). However, in such conventional fluid catalytic cracking reaction vessels the metallurgical and process requirements limit the top temperature generally from about 566° C (1050° F) to less than 538° C (1000° F), e.g., 510° C (950° F).

However, according to the present invention a hydrocarbon feed entering riser 4 through inlet 2 may be preheated to a temperature such that when it contacts the hot regenerated catalyst entering riser 4 through conduit 6 through flow control valve 8 the temperature of the catalyst-oil mix will be greater than 593° C (1100° F) whereby conversion of hydrocarbon to gasoline will be effected. At a point 5, intermediate the inlet and outlet of riser 4 a quench fluid will be injected into the hot hydrocarbon catalyst mix. The temperature and amount of injection can be controlled so that a top temperature of the riser will be about 550° C (1020° F) or below, e.g., 538° C (1000° F), preferably about 524° C (975° F), most preferably about 510° C (950° F).

The temperature of the quenching fluid is not critical and liquid water at a temperature range from about 15° C (60° F) to about 100° C (212° F) has been found suitable, preferably about 15° C (60° F) to about 38° C (100° F), although these temperatures may be varied from ambient to above boiling and other liquids may be used at temperature of from about 15° C (60F) to about 482° C (900° F).

A light olefin-containing gas, obtained from the product fractionation device (not shown), is used as the feed gas entering through conduit 110 (Fig. 4) with the main flow being directed through bottom inlet of reactor vessel 120 for distribution through grid plate 122 into the fluidization zone 124. Here the feed gas contacts a turbulent bed of finely divided catalyst particles. Reactor vessel 120 is shown provided with heat exchange tubes 126, which may be arranged in several separate heat exchange tube bundles so that the temperature control can be separately exercised over different portions of the fluid catalyst bed. The bottoms of the tubes are spaced above feed distribution grid 122 sufficiently to be free of jet action caused by the feed changed through the small diameter holes in the grid. Alternatively, reaction heat can be partially or completely removed by using cold feed. Baffles may be added to control radial and axial mixing. Although depicted without baffles, the vertical reaction zone can contain open-end tubes above the grid for controlling hydraulic constraints, as disclosed in U.S. Patent No. 4,251,484. The heat released from the reaction can be controlled by adjusting feed temperature in a known manner. Catalyst outlet means 128 is provided for withdrawing catalyst from above bed 124 and passed for catalyst regeneration into vessel 130 via flow control valve 129. A partially deactivated catalyst is oxidatively regenerated by controlled contact with air or other regeneration gas at elevated temperature in a fluidized regeneration zone to remove carbonaceous deposits and restore acid activity. The catalyst particles are entrained in a lift gas and transported, via riser tube 132, to a top portion of the vessel 130. Air is distributed at the bottom of the bed to effect fluidization, with oxidative by-products being carried out of the regeneration zone through cyclonic separator 134, which returns any entering solids to the bed. Flue gas is withdrawn via top conduit 136 for disposal; however, a portion of the flue gas may be recirculated, via heat exchanger 138, separator 140, and compressor 142, for return to the vessel with fresh oxidation gas via line 144 and as lift gas for the catalyst in riser 132.

The regenerated catalyst is passed to the main reactor 120 through conduit 146 provided with flow control valve 148. The regenerated catalyst may be lifted to the catalyst bed with pressurized feed gas through catalyst return riser conduit 150. Because the amount of regenerated catalyst, passed to the reactor is relatively small, the temperature of the regenerated catalyst does not upset the temperature constraints of the reactor operation in a significant amount. A series of sequentially connected cyclone separators 152, 154 are provided with diplegs 152a, 154a to return any entrained catalyst fines to the lower bed. These separators are positioned in an upper portion of the reactor vessel comprising dispersed catalyst phase 124. Filters, such as sintered metal plate filters, can be used alone or in conjunction with the cyclones.

The product effluent separated from the catalyst particles in the cyclone separating system can be withdrawn from the reactor vessel 120 through top gas outlet means 156. The recovered hydrocarbon product comprises C_5^+ olefins and/or aromatics, paraffins and naphthenes and may thereafter be processed as required to provide a desired gasoline or higher boiling product. The basic process heretofore described can be used to obtain higher overall yields of gasoline per unit weight or volume of hydrocarbon chargestock than heretofore obtainable prior to the present invention.

Typical results, obtained in a fluid bed reactor, of the type disclosed in 120 of Fig. 2 are shown in the following Examples 1-3:

Example 1

Reactor Conditons:	
Temperature	370°C
Pressure	410 kPa
Olefin-WHSV	0.5
No Recycle	
Feed Composition, wt. %	
Hydrogen	10.7
Ethene	89.3
Product Yields	
Methane	0.1
Ethane	1.9
Ethene	11.7
Propane	7.3
Propene	5.0
Isobutane	10.6
n-Butane	4.4
Butenes	7.6
C_5^+ Hydrocarbons	51.4
C_5^+ Hydrocarbon Properties	
R+O Octane	93.2
Specific Gravity	0.74

Example 2

Reactor Conditions:	
Temperature	370°C
Pressure	1200 kPa
Olefin-WHSV	0.4
No Recycle	
Feed Composition, wt. %	
Nitrogen	65.8
Hydrogen	0.8
Ethene	14.7
Propene	18.7
Product Yields	
Methane	0.1
Ethane	1.4
Ethene	3.6
Propane	8.9
Propene	2.8
Isobutane	12.8
n-Butane	6.0
Butenes	5.7
C_5^+ Hydrocarbons	58.7
C_5^+ Hydrocarbon Properties	
R+O Octane	93.2
Specific Gravity	0.74

Example 3

Reactor Conditions:	
Temperature	370° C
Pressure	1200 kPa
Olefin-WHSV	0.4
Recycle ratio, Mol/Mole	1.4
Feed Compsoition, wt. %	
Nitrogen	65.8
Hydrogen	0.8
Ethene	14.7
Propene	18.7
Product Yields'	
Methane	0.1
Ethane	0.7
Ethene	6.0
Propane	4.7
Propene	3.0
Isobutane	9.9
n-Butane	3.6
Butenes	6.3
C_5^+ Hydrocarbons	65.7
C_5^+ Hydrocarbon Properties	
R+O Octane	90.3
Specific Gravity	0.73

Example 1 is for a feed containing only ethene and hydrogen. Example 2 is for a feed containing nitrogen, hydrogen, ethene and propene. Similar data can be obtained by substituting lower alkanes for the nitrogen. C_4^+ yields will be higher, as some of the alkanes convert. Example 3 is for a similar feed to Example 2, but a substantial portion of the C_5^- product is recycled back to the reactor. C_5^+ yields are higher and catalyst makeup requirements are lower for Example 3 as compared to Example 2. Higher isobutane yields and higher gasoline octane numbers are possible at higher temperatures, lower pressures and higher catalyst activity. This is illustrated in the following Example 4:

Example 4

Reactor Conditions:				
Pressure	410 kPa			
Olefin-WHSV	0.4			
Feed Composition, wt. %				
Hydrogen	10.7			
Ethene	89.3			
Reactor temperature, °C	340	370	400	425
Ethene Conversion, wt. %	70.8	88.4	96.5	96.8
Yield, wt %				
Propene	5.0	4.8	3.6	3.9
Butene	9.5	7.4	4.1	3.8
Isobutane	5.9	11.4	15.3	14.4
C_5^+ HC	43.1	50.9	48.1	42.9
C_5^+ HC R+O Octane	89.0	93.4	96.8	98.3
C_5^+ plus maximum potential alkylate refinery with excess				
iC_4	74.3	77.4	65.0	59.9
iC_4 short	54.7	73.3	78.2	71.2

When the conversion of gasoline obtainable by the use of the olefin-to-gasoline process is added to the gasoline obtained from the fluid catalytic craking unit operated according to the steep temperature profile of the present invention, it will be appreciated that the total gasoline yield increases while simultaneously increasing both research and motor octane numbers for the gasoline produced. This can be seen in the following Table 2.

Table 2

	Olefin to Gasoline + Steep Profile
Riser Bottom Zone, Temp., °C (°F)	593 (1100)
Riser Mid Zone, Temp., °C (°F)	538 (1000)
Riser Top Zone Temp., °C (°F)	510 (950)
H_2	0.10
C_1	1.35
C_2	1.17
$C_2{}^=$	0.18
C_3	1.40
$C_3{}^=$	3.76
C_4, wt %	10.7
Gasoline, wt %	51.0
LFO, wt %	16.6
HFO, wt %	6.7
Coke, wt %	5.9
Conversion, wt %	76.7
Wet gas, M^3/S 0100 MBBL/D	23.7
C_5^+ Gasoline Octanes	
R+O	92.6
M+O	80.9

Existing FCC processes which will benefit from the disclosed invention utilize catalysts which are conventional in the prior art. Such catalysts are well known, per se, and reference is made to the aforementioned U.S. Patent No. 4,368,114. It is noted that the combination of an additive catalyst, such as ZSM-5 to the conventional FCC catalyst disclosed in U.S. Patent No. 4,308,114 will produce an even greater octane increase. ZSM-5 is described and claimed in U.S. Patent No. 3,702,886 and U.S. Patent Reissue No. 29,948.

Other additive catalysts which can be included in the improved process of the present invention are exemplified by ZSM-5 type catalysts such as ZSM-11 (US Patent 3,709,979), ZSM-12 (US Patent 3,832,449), ZSM-23 (US Patent 4,076,842), ZSM-35 (US Patent 4,016,245), ZSM-38 (US Patent 4,046,859) and other similar materials.

The zeolites used as the additive catalyst in the invention may be in the hydrogen form or they may be base exchanged or impregnated to contain a rare earth cation complement. Such rare earth cations comprise Sm, Nd, Pr, Ce and La. It is desirable to calcine the zeolite after base exchange. Suitable catalysts and catalyst additives are described in the aforementioned U.S. Patent No. 4,368,114, the entire contents of which are herein incorporated by reference.

Conversion of lower olefins, especially propene and butenes, over HZSM-5 is effective at moderately elevated temperatures and pressures. Product distribution for liquid hydrocarbons can be varied by controlling process conditions, such as temperature, pressure and space velocity. Gasoline (C_5- C_{10}) is readily formed at elevated temperatures, e.g., up to about 400°C, and moderate pressure from ambient to about 5500 kPa, preferably from about 250 to about 2900 kPa. Olefinic gasoline can be produced in good yield and may be recovered as a product or fed to low severity, high pressure reactor systems for further conversion to heavier distillate-range products. Operating details for typical oil to gasoline oligomerization units are described in U.S. Patents Nos. 4,456,779; 4,497,968 and 4,433,185. At moderate temperatures and relatively high pressures, the conversion conditions favor distillate-range products having a normal boiling point of at least 165°C (330°F). Lower olefinic feedstocks containing C_2-C_6 alkenes may be converted selectively; however, the low severity distillate mode conditions do not convert a major fraction of ethene. While propene, butene-1 and others may be converted to the extent of 50% to 95% in the lower severity moderate temperature distillate mode, only about 10% to 30% of the ethene component will be converted using HZSM-5 or similar acid zeolites. Ethene can be converted at moderate temperature where a bi-functional nickel catalyst is present.

It has been found that ethene-rich olefinic-light gas can be upgraded to liquid hydrocarbons rich in olefinic gasoline, isobutane and aromatics by catalytic conversion in a turbulent fluidized bed of solid acid zeolite catalyst under high severity reaction conditions in a single pass or with recycle of gas product. This technique is particularly useful for upgrading FCC light gas, particularly that obtainable by the improved steep temperature profile process previously described which usually contains significant amounts of ethene, propene, C_2-C_4 paraffins and hydrogen produced in cracking heavy petroleum oils or the like. By upgrading the by-product light gas, gasoline yield of existing and new FCC units can be significantly increased.

The C_3-C_5 alkane:alkene ratio in the hydrocarbon product exiting the fluidized bed is maintained at about 0.1:1 to about 200:1 and preferably less than 50:1 under conditions of reactions of severity to effect feedstock conversion to C_5^+ products. Advantageously, the olefin-to-gasoline process employing the fluidized bed technique can employ a single pass ethene conversion of at least 70% to provide high octane gasoline range hydrocarbon product in good yield. Although a thermodynamically heat balanced mixture of exothermic alkanes and endothermic alkanes can be converted without significant recycle and/or diluent to provide high octane gasoline range hydrocarbon product in good yield, recycle of mostly C_4^- gas can be used to increase C_5^+ yields further and lower catalyst make up requirements.

The oligomerization catalyst preferred for use in the present invention include the medium pore (i.e., about 5-7 Angstroms) shape-selective crystalline alumino-silicate zeolites having a silica-to-alumina ratio of at least 12, a constraint index of about 1 to 12 and alpha cracking activity of about 10 - 250. In the fluidized bed reactor, the coked catalyst may have an apparent activity (alpha value) of about 10 to 80 under the process conditions to achieve the required degree of reaction severity. Representative of the zeolites suitable for use in the fluidized bed include ZSM-5, ZSM-11, ZSM-12, ZSM-22, ZSM-23, ZSM-35 and ZSM-38, which have been previously described.

All suitable zeolites have a coordinated metal oxide to silica molar ratio of 20:1 to 200:1, or higher, and it is advantageous to employ a standard ZSM-5 having a silica-alumina molar ratio of about 25:1 to 70:1, suitably modified. A typical zeolite catalyst component having Bronsted acid sites may consist essentially of alumina-silicate ZSM-5 with 5 to 95 weight percent silica and/or alumina binder.

These siliceous zeolites may be employed in their acid forms, ion exchanged or impregnated with one or more suitable metals, such as Ga, Pd, Zn, Ni, Co and/or other metals of periodic groups of III-VIII. The zeolite may include a hydrogenation-dehydrogenation component (sometimes referred to as a hydrogenation component) which is generally one or more metals of group IB, IIB, IIIB, VA, VIA or VIIIA of the periodic table (IUPAC) especially aromatization metals, such as Ga, Pd, etc. Useful hydrogenation components include the noble metals of Group VIIIA, especially platinum but other noble metals, such as palladium, gold, silver, rhenium or rhodium, may also be used. Base metal hydrogenation components may also be used, especially nickel, cobalt, molybdenum, tungsten, copper or zinc. The catalyst materials may include two or more catalytic components, such as a metallic oligomerization component, e.g., ionic Ni^{+2}, and a shape selective medium pore acidic oligomerization catalyst, such as ZSM-5 zeolite, which component may be present in admixture combined in a unitary bifunctional solid particle. It is possible to utilize an ethene dimerization metal or oligomerization agent to effect oligomerization of an ethene feedstock in a continuous reaction zone.

Certain of the ZSM-5-type medium pore shape selective catalysts are sometimes known as pentasils. In addition to the preferred aluminasilicates, the borosilicate, thiosilicate, and "silicalite" materials may be employed.

The ZSM-5-type pentasils-type zeolites are particularly useful in the process because of their regenerability, long life and stability under extreme conditions of operation. Usually the zeolite crystals have a crystal size of from about 0.01 to over 2 microns or more, with 0.02-1 micron being preferred. In order to obtain the desired particle size for fluidization in the turbulent regime, the zeolite catalyst crystals are bound with a suitable inorganic oxide, such as silica, alumina, etc. to provide a zeolite concentration of about 5 to 95 weight percent. In the description of the aforementioned Examples 1-4 a 25% HZSM-5 catalyst contain within a silica-alumina matrix and having a fresh alpha value of about 80 was employed unless otherwise stated.

Particle size distribution can be a significant factor in achieving overall homogeneity in turbulent regime fluidization. It is desired to operate the process with particles that will mix well throughout the bed. Large particles having a particle size greater than 250 microns should be avoided, and it is advantageous to employ a particle size range consisting essentially of 1 to 250 microns. Average particle size is usually about 20 to 100 microns, preferably 48 to 80 microns. Particle distribution may be enhanced by having a mixture of larger and smaller particles within the operative range, and it is particularly desirable to have a significant amount of fines. Close control of distribution can be maintained to keep about 10 to 25 weight percent of the total catalyst in the reaction zone in the size range less than 32 microns. Accordingly, the fluidization regime is controlled to assure operation between the transition velocity and transport velocity. Fluidization conditions are substantially different from those found in non-turbulent dense beds or transport beds.

The reaction severity conditions can be controlled to optimize the yield of C_4-C_9 aliphatic hydrocarbons. It is understood that aromatics and light paraffin production is promoted by the zeolite catalyst having a high concentration of Bronsted acid reaction sites. Accordingly, an important criterion in selecting and maintaining catalyst inventory is to provide either fresh catalyst having acid activity or by controlling catalyst deactivation and regeneration rates to provide an apparent average alpha range of about 15 to 80. The temperature on the fluidized bed is maintained at about 315° to 510° C at a weight hourly feedstock space velocity (WHSV) (based on olefin equivalent and total reactor catalyst inventory) of about 0.1 to about 5.

Claims

1. A process for cracking a fresh hydrocarbon feedstock and increasing the octane number of a gasoline comprising:
   (a) introducing the fresh hydrocarbon feedstock boilding above 316°C and a catalyst into the bottom of a riser catalytic cracking unit having a feedstock inlet and product outlet;
   (b) mixing at a mix temperature in the riser the feedstock and catalyst and cracking said feedstock into gasoline with said catalyst as they pass upwardly through said riser cracking unit;
   (c) introducing 6-35 wt %, based on total hydrocarbon added to the base of the riser of a quenching fluid of at least one member selected from fresh feed, recycled oil naphtha, LPG, butanes and light hydrocarbons, alcohols and ethers into the cracking unit intermediate the point where feedstock and catalyst are mixed in the riser and the product outlet of the riser cracking unit; and
   (d) recovering a gasoline product having increased octane number from the unit.

2. The process of claim 1 further including the step of preheating the feedstock.

3. The process of claim 1 or 2, wherein the quenching liquid is introduced within the range of from 2 m of a feedstock inlet to 12 m from the outlet of the cracking unit.

4. The process of claim 3, wherein the quenching fluid is introduced within the range of 2 m to 15 m of the feedstock inlet.

5. The process of any one of the preceding claims wherein the top temperature of the FCC riser reactor is maintained less than 549° C.

6. The process of any one of the preceding claims, wherein the quenching liquid is at a temperature in the range of 15° C to 482° C.

7. The process of any one of the preceding claims, wherein the quenching fluid is admitted in such quantity and temperature so as to limit the cracking unit top temperature to below 538° C.

8. The process of any of the preceding claims, wherein the catalyst is ZSM-5, ZSM-11, ZSM-12, ZSM-23, ZSM-35 or ZSM-38.

9. The process of any one of the preceding claims, wherein the feedstock is gas oil or resid.

10. The process of any of the preceding claims, wherein the introducing step produces a mix temperature which is in the range of from 552° C to 621° C.

11. The process of claim 1, wherein the quench liquid comprises 6-10 wt % water.

12. An integrated process for improving total gasoline yield per unit volume of hydrocarbon chargestock comprising the steps of:
   (a) feeding a hydrocarbon chargestock to an FCC riser;
   (b) contacting the chargestock of step (a) under elevated temperature conditions with a zeolite catalyst;
   (c) introducing a quenching fluid into the riser at a point intermediate an inlet and an outlet of the riser;
   (d) recovering products including gasoline and a light olefin-containing gas;
   (e) contacting the light olefinic-containing gas of step (d) with a fluidized bed of catalyst particles at elevated temperatures; and
   (f) recovering a product containing predominant amount of C_5^+ hydrocarbons..

13. The process of claim 12, wherein the fluid of step (b) is water.

14. The process of claim 13 or 14, wherein catalyst of step (d) is a catalyst selected from ZSM-5, ZSM-11, ZSM-12, ZSM-22, ZSM-23, ZSM-35 and ZSM-38.

15. The process of claim 12, 13 or 14, wherein the riser top temperature is in the range of from 510° C to 549° C.

16. The process of claim 12, 13 14 or 15, wherein the quenching fluid is at a temperature in the range of from 16° C to 482° C.

17. The process of claim 16, wherein the quenching fluid is water and is injected in the range of 6% to 10% by weight, based upon the total weight of the hydrocarbon chargestock.

18. The process of claim 12, 13, 14, 15 or 16, wherein the quenching fluid is selected from the group consisting of water, fresh hydrocarbon chargestock, recycled oil naphtha, light cycle oil, heavy cycle oil, coke gas oils, liquified propane gas, butanes and lighter hydrocarbons, alcohols and ethers and mixtures thereof.

19. The process of claim 18, wherein the quenching fluid is introduced into the riser in an amount of up to about 35% by weight based on the weight of the hydrocarbon chargestock.

20. The process of claim 19, including the step of regenerating at least a portion of the catalyst of step (e).

21. The process of claim 20, including the step of passing at least a portion of the products of step (f) through the fluidized bed of step (e).

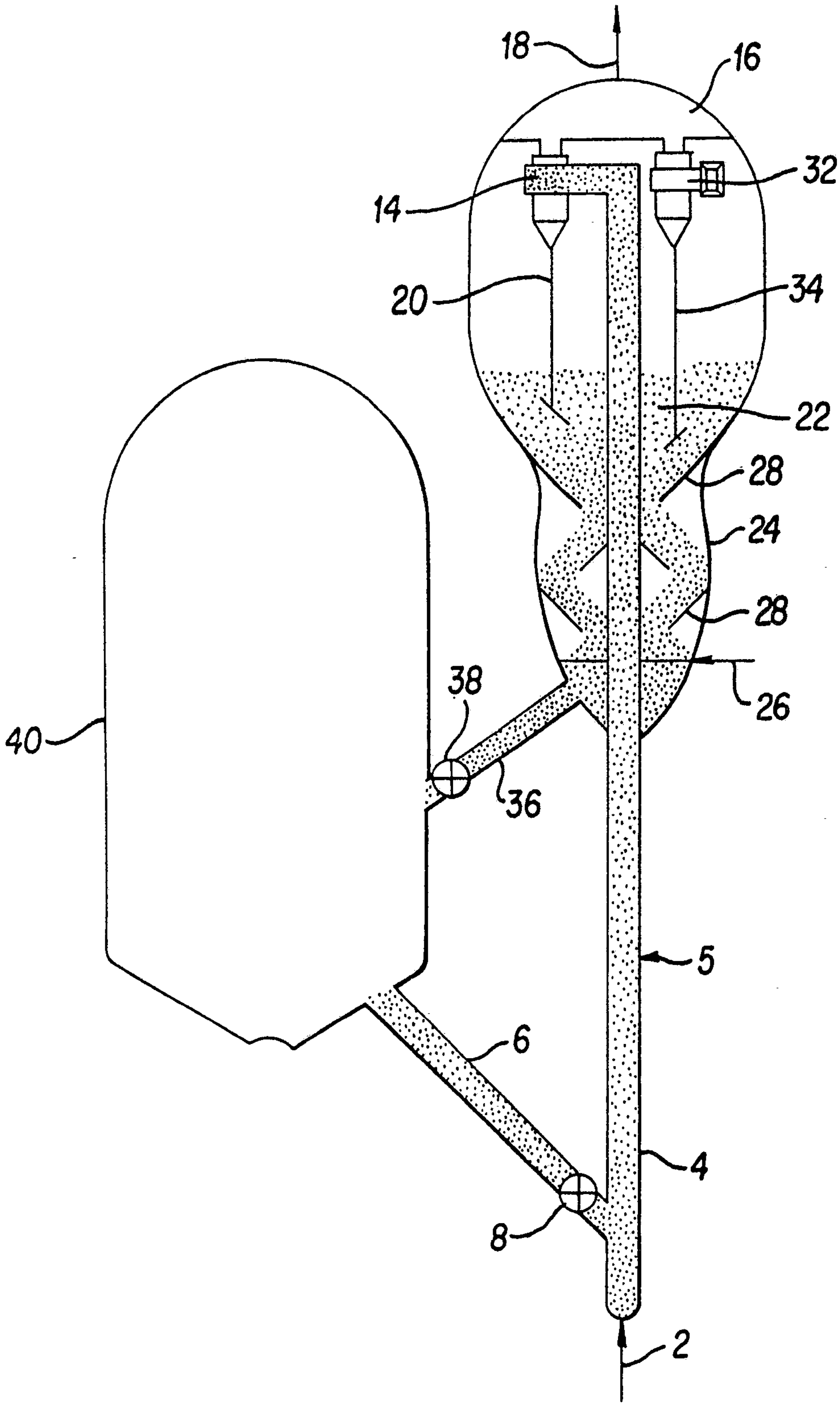

FIG. 1

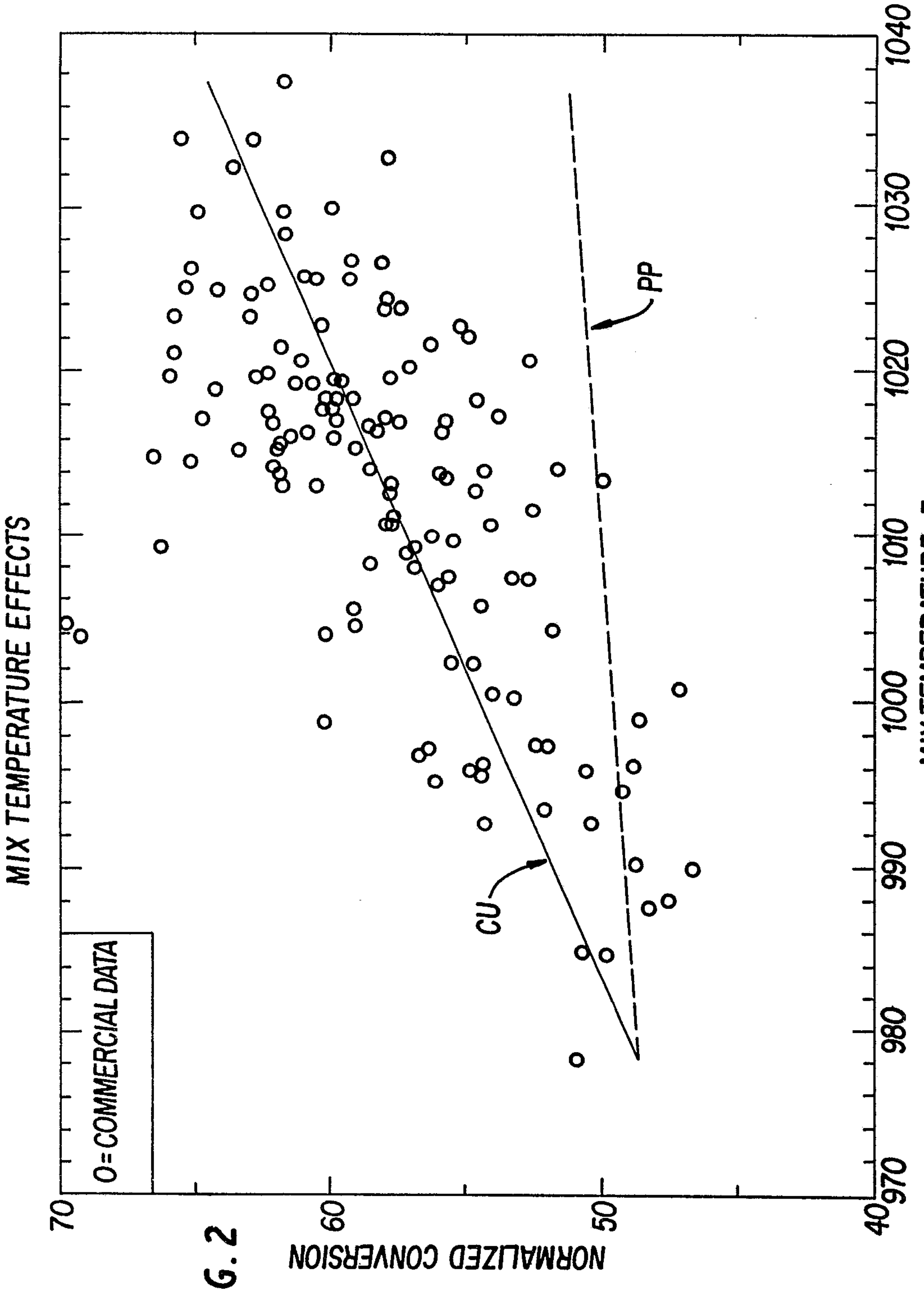
MIX TEMPERATURE EFFECTS
O=COMMERCIAL DATA
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FIG. 2

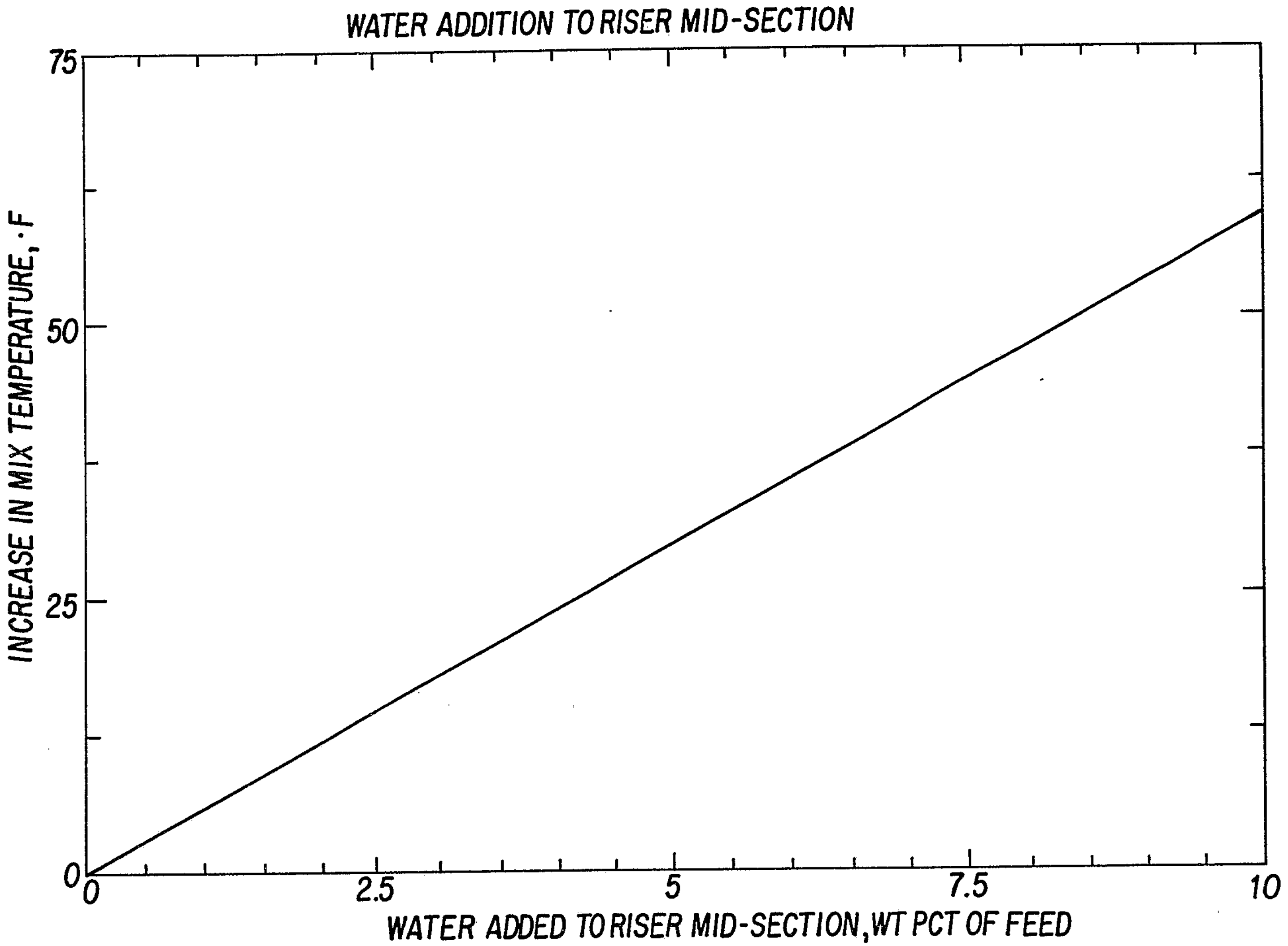
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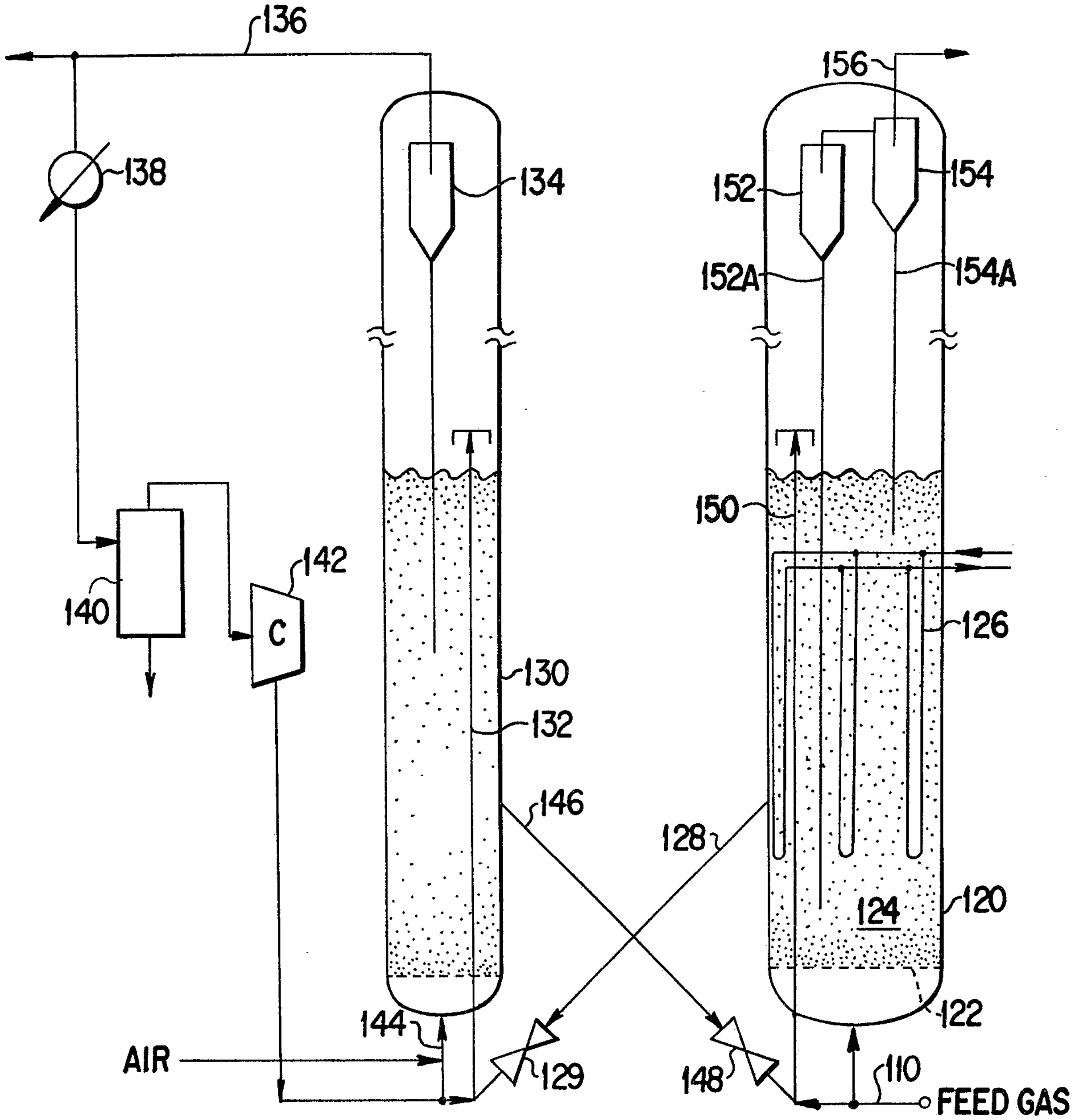
FIG. 3

FIG. 4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EUROPEAN SEARCH REPORT

Application Number

EP 88 30 9278

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
X	EP-A-0 208 609 (COMPAGNIE DE RAFFINAGE ET DE DISTRIBUTION TOTAL FRANCE) * Claims 1,3,5-9 *	1-2,4-11	C 10 G 11/18 C 10 G 57/02
Y		3,12-21	

D,X	US-A-3 692 667 (McKINNEY et al.) * Figure; claims; column 2, lines 4-25 *	1,2,5-7,9-10	

Y	EP-A-0 113 180 (MOBIL OIL) * Claims 1,5 *	12-21	

D,X	US-A-3 886 060 (OWEN) * Figure 2; claims *	1,2,5-10	

D,Y	US-A-4 218 306 (GROSS et al.) * Abstract *	3	

			TECHNICAL FIELDS SEARCHED (Int. Cl.4)
			C 10 G

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	16-01-1989	MICHIELS P.

CATEGORY OF CITED DOCUMENTS

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E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons
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& : member of the same patent family, corresponding document