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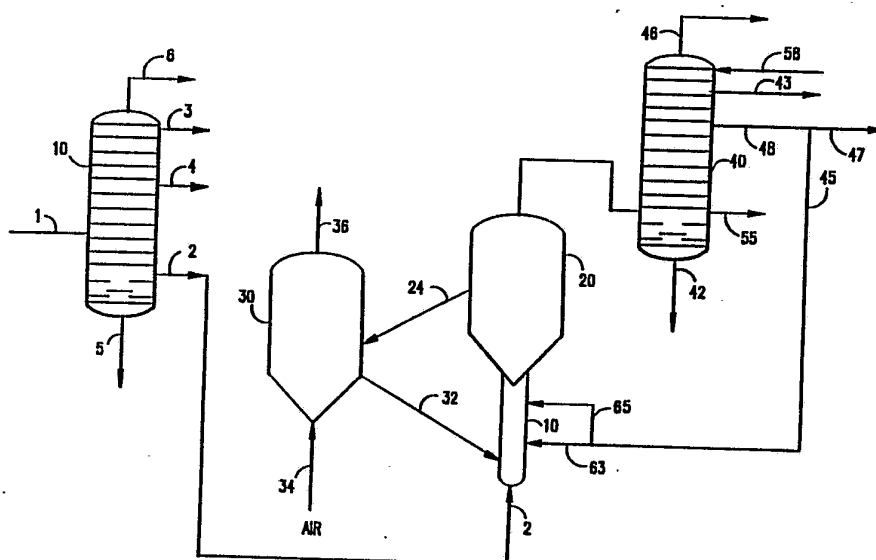
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(54) Title: CATALYTIC CRACKING OF DISTILLED FEEDS



(57) Abstract

A catalytic cracking process for converting distilled heavy hydrocarbon feed to lighter products comprising mixing the distilled heavy hydrocarbon feed and a hot stream of regenerated cracking catalyst from a catalyst regenerator (30) to the base section of the riser reactor (10). At least 95 wt % of said distilled feed is vaporized within 0.24 second of the vapor residence time in said riser reactor (10) the amount and temperature of the hot regenerated catalyst being sufficient to effect both catalytic and thermal cracking of said vaporized distilled feed in the base section of said riser (10). A quench fluid is injected onto the catalyst/vaporized feed mixture, in a quench zone (63) or (65) within said riser reactor (10) downstream of the base section thereof and more than 15 % of the length of the riser upstream of the riser outlet, to lower the temperature in the riser at least 6 °C.

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CATALYTIC CRACKING OF DISTILLED FEEDS

The invention relates to catalytic cracking of distilled hydrocarbon feeds.

Processes for cracking hydrocarbon feeds by
5 contact with fluidized catalyst particles at high temperature are known generically as "fluid catalytic cracking" (FCC) processes.

Gas oils and vacuum gas oils, which are obtained by distillation, are preferred feeds for FCC. They
10 have less contaminants and make less coke during cracking than heavier hydrocarbons which are left behind in distillation columns as residual fractions.

The FCC process can produce large quantities of gasoline and, in most FCC units operating for maximum
15 gasoline production, roughly 50 LV % of the feed is converted into gasoline. The FCC gasoline has high octane, and most of it can be added to the refinery gasoline blending pool. There is, however, a continuing need to increase the octane number of the
20 gasoline product from the FCC unit and simultaneously increase the gasoline yield. Unfortunately, this poses a problem with existing FCC processes since anything that increases gasoline octane usually decreases gasoline yield.

25 Another problem with existing FCC processes is FCC heavy naphtha, which is one fraction of FCC gasoline and which often has too much sulfur and is too heavy (too high an end point, or sometimes a 90 or 95% boiling point) to permit all of it to be added to
30 the gasoline blending pool. Legislation in many countries restricts the amount of sulfur and/or aromatics which may be present in gasoline and puts additional constraints on the volatility of the gasoline boiling range materials. Sulfur levels can be
35 reduced by hydrotreating, but this requires

considerable capital and operating expense and also saturates olefins, which reduces octane.

The FCC process itself can be used to reprocess naphtha produced by the FCC unit. For example, U.S. 4,832,825 teaches recycling FCC light naphtha to the base of an FCC riser to meet hot regenerated catalyst and reports that naphtha recycle doubles the production of light olefins.

U.S. 3,928,172 teaches that cracking FCC heavy naphtha in a separate riser reactor removes essentially all of the olefins, producing a highly aromatic gasoline product. Table III shows multiple examples of cracking FCC naphtha in a riser pilot plant, to produce a gasoline product having 76.7 to 99.3 vol % aromatics.

However, no completely satisfactory way is available to upgrade FCC heavy naphtha using existing technology.

According to the present invention, it has now been found that, in an FCC process using a distilled feed, the octane number and the yield of the gasoline product can simultaneously be increased by raising the temperature in the base of the FCC riser and then injecting a quench fluid at a specific distance along the riser.

Moreover, it has been found that, if FCC heavy naphtha is used as the quench fluid, the heavy naphtha not only undergoes conversion to lighter products but also its sulfur content is decreased.

U.S. 4,818,372 discloses the injection of a quench fluid in an FCC process but in combination with a resid-containing feed where the problems addressed are the the vaporization and conversion of the heavy products. By definition, FCC units cracking distilled feeds have no problem vaporizing the feed.

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The present invention resides a catalytic cracking process for converting a distilled heavy hydrocarbon feed to lighter products comprising:

5 a) charging said distilled heavy hydrocarbon feed to a lower base section of a riser catalytic cracking reactor having an upper outlet section;

b) charging a stream of hot, regenerated cracking catalyst from a catalyst regenerator to the base section of the riser reactor to mix with and vaporize at least 95 wt % of said distilled feed within 0.25 seconds of vapor residence time in said riser reactor, the amount and temperature of the hot regenerated catalyst being sufficient to effect both catalytic cracking and thermal cracking of said vaporized distilled feed in the base section of said riser;

15 c) injecting a quench fluid into the catalyst/vaporized feed mixture, in at least one quench zone within said riser reactor downstream of the base section thereof and more than 15% of the length of the riser upstream of the riser outlet, to lower the temperature in the riser by at least 6°C (10°F) and thereby reduce thermal cracking, without terminating catalytically cracking, of the quenched mixture;

25 d) discharging a mixture of catalytically cracked products and spent cracking catalyst from said outlet of said riser reactor;

e) separating said discharged mixture into a cracked product rich vapor phase and a spent catalyst rich phase; and

30 f) regenerating the spent catalyst in a catalyst regeneration zone and recycling the hot regenerated catalyst to the base of said riser reactor.

35 Preferably, the quench fluid is a heavy naphtha fraction including hydrocarbons boiling in the range

150 to 200°C (300 to 400°F) separated from the cracked product.

5 The invention will now be more particularly described with reference to the accompanying drawing, which is a simplified schematic process flow diagram of a part of a oil refinery including an FCC unit operating with heavy naphtha quench.

10 Referring to the drawing, crude oil flows via line 1 to an atmospheric distillation column 10, where the crude is distilled to produce streams ranging from light overhead vapor products removed via line 6, light overhead liquid products removed via line 3, to a naphtha fraction removed via line 4, and a gas oil fraction removed via line 2. Non-distillables, at
15 least those hydrocarbons not recoverable by conventional distillation at atmospheric pressure, are removed via line 5 as resid fraction.

20 In most refineries the resid fraction 5 is charged to a vacuum column, not shown, to produce a vacuum gas oil fraction and a vacuum resid. This produces more distilled feed for the FCC unit, and reduces the size of the resid stream, while preserving the principle of sending only distilled feeds to the FCC. In most units there is some contamination of the
25 distilled feed, either due to entrainment in the fractionator, or because a minor amount of residual material is blended with the distilled feed.

30 The FCC unit comprises FCC riser 10, a separator 20, a regenerator 30, and FCC main column 40. The gas oil from the atmospheric distillation column 10 and the vacuum gas oil from the vacuum column are charged to the base of riser reactor 10, where it contacts hot regenerated catalyst which is fed from regenerator 30 via line 32 to the base of the riser 10.

A quench stream, preferably a recycled heavy naphtha from line 45, is added to one or more quench points via lines 63 or 65 at various elevations in the riser. The optimum quench point, and number of quench points, can vary based on product demands, unit constraints, and catalyst activity.

Feed and hot catalyst pass up the riser 10, are quenched, and then are catalytically cracked at a lower temperature in the remainder of the riser. Cracked products and spent catalyst enter separator 20, where spent catalyst is separated from cracked products by conventional means. Spent catalyst is stripped in a catalyst stripping means within vessel 20, then charged via line 24 to FCC regenerator 30, which receives regeneration air via line 34. Coke is burned from the spent catalyst in the regenerator, producing flue gas, which is removed via line 36, and hot regenerated catalyst, which is recycled via line 32 to the base of riser reactor 10.

Hot cracked product withdrawn from vessel 20 passes via line 26 to the base of the FCC main column 40, which operates conventionally. Trays or packing fractionate the cracked product vapor into a main column bottom stream 42, sometimes called a slurry oil, one or more cycle oil products, such as a light cycle oil or LCO product withdrawn via line 55, a heavy naphtha stream withdrawn via line 48, a light naphtha stream withdrawn via line 43, and an overhead vapor stream withdrawn via line 46. Light liquid reflux returns to the column via line 58.

The heavy naphtha fraction withdrawn via line 48 may be removed as a product via line 47, but preferably some of the FCC heavy naphtha is recycled via line 45 to one or more quench points in the FCC riser reactor.

Cracking a distilled feed, followed by quenching with an FCC heavy naphtha produces a number of advantages. The temperature in the base of the riser can be increased so as to promote the cracking reaction and thereby increase the yield and octane number of the gasoline product fraction. Use of FCC heavy naphtha quench brings about some unexpected upgrading of the heavy naphtha; the heavy naphtha is desulfurized and converted to lighter gasoline, but dry gas make is minimal.

Riser Cracking Conditions - Pre Quench

The conditions in the base of the riser are very similar to conventional FCC riser cracking conditions, but the temperature is preferably 6 to 30°C (10 to 50°F) hotter than that normally employed.

In general, the mix temperature at the base of the riser is 510-590°C (950-1100°F), and catalyst:oil ratios is from 1:1 to 10:1, preferably greater than 4:1.

For efficient cracking in the riser, it is beneficial to atomize the feed well. Atomizing feed nozzle(s) which produce droplets of oil having an average particle size below 2000 microns, preferably below 1000 microns, and most preferably below 500 microns, are desirable. Nozzle exit velocities above 15 m/s (50 fps), preferably above 30 m/s (100 fps), and most preferably above 61 m/s (200 fps) should be used. The nozzles preferably vaporize the distilled feed in the riser within less than 10 meters of travel, and more preferably within 1 to 5 meters of riser travel or even less.

Regardless of the nozzle velocity, or droplet size, it is essential for best results that complete feed vaporization be achieved within 0.25 seconds of vapor residence time, preferably within 0.1 seconds,

and most preferably within 0.05 seconds of vapor residence time. Such rapid feed vaporization promotes high temperature catalytic cracking in the base of the riser reactor.

5 Riser Top Temperature

Although conditions at the base of the riser are more severe than those associated with conventional FCC operations, the FCC unit at the top of the riser can operate conventionally. In fact, it will
10 frequently be beneficial to operate with somewhat lower than normal riser top temperatures. Riser top temperatures of 480 to 565°C (900 to 1050°F) will be satisfactory in many instances.

Quench

15 In the process of the invention the use of high temperatures in the base of the riser promotes catalytic cracking of the feed, especially since the catalyst is in its most active state at the base of the riser. In view of the higher temperatures, thermal
20 cracking is also promoted in the base of the riser, but is reduced in the upper part of the riser by the injection of quench fluid.

Quenching can be effected rapidly after feed injection, that is within less than a second or even
25 within 0.5 seconds or less of feed injection. However, rapid quenching requires large amount of quench fluid, that is sufficient quench fluid to reduce temperatures by 6 to 56°C (10 to 100°F), and preferably by 11 to
30 42°C (20 to 75°F), presuming all streams are well mixed and that quench is instantaneous. The drawback of adding such large amounts of quench fluid is loss of plant capacity or loss of selectivity due to increased pressure. Large amounts of water quench, on
35 the order of 10 - 15 wt % water, produce large amounts of steam, which increases the pressure drop across the

riser, the vapor traffic in the main column, and sour water production. Recycled liquid hydrocarbon quench streams unload to some extent the wet gas compressor but can load up the riser and even flood the main
5 column.

One benefit of using large amounts of quench is that the maximum promotion of catalytic cracking will be achieved while the catalyst is still highly active in the base of the riser. Short residence time riser
10 cracking can be achieved in a conventional FCC unit in the lower 10 - 50% of the riser. Cracking in the upper portions of the riser can be largely eliminated with large amounts of quench, because all reactions, both thermal and catalytic, will be suppressed
15 downstream of the quench injection point.

Rather than refer to vapor residence time, which varies greatly from unit to unit and is difficult to calculate, quenching at the following fractional riser locations may be considered. In general, it is
20 believe that quick quenching should occur no more than 1/2 way up the riser, and preferably around 1/10 to 5/10 of the way up the riser. Quenching about 2/10 to 4/10 of the way up the riser will be optimum in many installations.

25 As an alternative, it may in some cases be preferable to effect delayed quenching, involving addition of smaller amounts of quench fluid higher up in the riser. Catalytic reactions are then promoted throughout a much greater distance in the riser
30 reactor, offset by increased thermal reactions upstream of the quench point.

Quenching with modest amounts of quench fluid will usually occur after at least a second of vapor residence time in the base of the riser, and

preferably after 1.5 seconds of residence time, and most preferably after 2.0 seconds of residence time.

5 Rather than refer to vapor residence time, which varies greatly from unit to unit, and is difficult to calculate, quenching at the following fractional riser locations may be considered. In general, delayed quenching should occur at least 50% of the way up the riser, and preferably around 60 to less than 85% of the way up the riser. Quenching about 75% up the riser will be optimum in many installations.

10 In any event it is important to quench well upstream of the riser outlet and in particular at more than 15% of the length of the riser upstream of the riser outlet.

15 Quench Fluid

Any conventional quench fluids, such as cold solids, water, steam, or inert vaporizable liquids, such as light cycle oil, heavy cycle oil, slurry oils, or other aromatic rich streams, may be used. All such quench fluids will remove heat. Preferably liquids are used so that more heat can be removed from a given weight of fluid added. Use of a reactive quench liquid, such as the heavy naphtha fraction, which further promotes endothermic reactions, may be preferred in some circumstances.

25 The amount of quench fluid used is related to the quench point. Delayed quench, with only 7 wt % water, can work about as well as quick quenching with twice as much water. For units not limited by pressure, sour water or other constraints, it will be usually be preferred to use more quench fluid and quench near the mid point of the riser.

30 The preferred quench fluid is FCC heavy naphtha, which is defined herein as that portion of the FCC cracked product having an initial boiling point of 100

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to 160°C (220 to 325°F), a 5% boiling point of 120 to 150 °C (250 to 300°F), a 95% boiling point from 200 to 280°C (400 to 500°F) and an end boiling point of 220 to 270 °C (425°F to 525°F). The heavy naphtha is the fraction intermediate the FCC light naphtha (C5+ to the end point for light naphtha) and light cycle oil. Considerable variation in boiling ranges of all these materials is possible, due both to local product specifications and fractionator constraints. There is usually considerable overlap between the end point of the heavy naphtha and the initial boiling point of the light cycle oil because of imperfect fractionation.

Heavy naphtha is the preferred quench fluid because it is always available downstream of an FCC unit and its use increases FCC conversion and gasoline octane without adding to sour water production or significantly increasing dry gas production. Also, quite unexpectedly, using heavy naphtha as a quench fluid in the process of the invention reduces its sulfur content.

Heavy naphtha quench may be used in an amount equal to 2.5 to 25 wt %, preferably 5 to 15 wt %, of the fresh feed. When used in these amounts, increased conversion of feed, an increase in both gasoline yield and octane number will be achieved. The mid point, and the 90% point, of a finished gasoline product made from a blend of FCC light naphtha, and hydrotreated heavy naphtha, can usually be reduced from 3 to 6°C (5 to 10°F) or more.

Catalyst Activity

Conventional FCC catalyst can be used in the process of the invention, although it is preferred to employ highly active catalysts, with high zeolite contents, in particular high amounts of large pore zeolite cracking catalyst, such as zeolite Y. In

particular, large pore zeolite contents of the fresh makeup catalyst, exclusive of any additive catalyst, of 10 to 80 wt % are suitable, with 30 to 60% being preferred, and 35 to 55 wt % considered optimum.

Catalyst activities should be at least 55 MAT, more preferably at least 60 to 65 MAT, and most preferably above 70 or even 75 MAT. The MAT test is well known, and more details of it may be found in ASTM test method D3907.

Thermal Reactions

The extended residence time in the riser, at higher temperatures, will lead to increased thermal conversion. This has both advantages and disadvantages. Thermal cracking produces olefinic (and highly reactive) gasoline of good octane number, but usually in poor yield. Thermal cracking of light ends of the feed, and re-cracking of cracked products is especially undesirable. It is therefore important to limit thermal cracking and ensure that catalytic cracking is the predominant reaction in the riser. For this reason it is important to restrict the feed to distilled materials, since resids are more susceptible to thermal cracking.

Additive Catalysts

In many instances it will be beneficial to use one or more additive catalysts, which may either be incorporated into the conventional FCC catalyst or added to the circulating inventory in the form of separate particles of additive.

High silica, shape selective additives, such as zeolites having a Constraint Index of 1 - 12, and silica:alumina ratios above 12 are preferred. Silica:alumina ratios of 50:1, 100:1, 200:1, 300:1, 400:1, 500:1 or higher may be used.

Details of the Constraint Index test procedures are provided in J. Catalysis 67, 218-222 (1981) and in U.S. 4,711,710 (Chen et al.).

Preferred shape selective zeolites are exemplified by ZSM-5, ZSM-11, ZSM-12, ZSM-23, ZSM-35, ZSM-48, ZSM-57 and similar materials. ZSM-5 is especially preferred.

ZSM-5 is described in U.S. 3,702,886, U.S. Reissue 29,948 and in U.S. 4,061,724 (describing a high silica ZSM-5 as "silicalite").

ZSM-11 is described in U.S. 3,709,979.

ZSM-12 is described in U.S. 3,832,449.

ZSM-23 is described in U.S. 4,076,842.

ZSM-35 is described in U.S. 4,016,245.

When the catalyst inventory contains large amounts of shape selective zeolite, such as ZSM-5, the optimum quench point will shift closer to the riser outlet, because the ZSM-5 retains catalytic activity long after the large pore cracking catalyst has lost most of its activity. Thus it is preferred to employ more than 10 wt % additive catalyst (ZSM-5 plus matrix) or more than 3.0 wt % ZSM-5, on a pure crystal basis, in the equilibrium catalyst. Most preferably, more than 15 wt % shape selective additive catalyst is used, with the optimum being around 20 - 25 wt % in many instances.

Feed Composition

The present invention works with all distillable FCC feedstocks such as gas oils or vacuum gas oils. Modern fractionation technology has allowed deeper cuts to be made of feedstocks, and distilled feeds with end points in excess of 1000°F may readily be produced. Despite their high end points, such feeds were vaporized in a distillation column, are readily vaporized in an FCC riser, and are ideal for use in

the process of the present invention. Such distilled feeds are essentially free of, or contain greatly reduced amounts of, all or most of the asphaltics, or Conradson Carbon Residue. These residual materials, which are troublesome to handle and difficult to vaporize, are preferably excluded from the process of the present invention.

Light cycle oil, heavy cycle oil, or slurry oil, may be present. Recycle of such streams is common in FCC.

Examples - Computer Simulations

Although there can be great variation from refinery to refinery, or in the same refinery from summer (gasoline mode FCC) to winter (distillate mode) operation, in the same refinery it is usually possible to keep fractionator operation reasonably constant and produce a consistent product. Refineries frequently run 12 hour or 24 hour tests to confirm if all flow meters are properly calibrated and to determine the yields of a given process. It is also possible to adjust yields of, e.g., heavy naphtha, to account for imperfect fractionation. This can be done by analyzing the boiling range of the light naphtha, heavy naphtha, and light cycle oil actually produced and calculating what the yields would be if the fractionator were run at different conditions.

As used herein, liquid yield refers to those liquid yields obtained with consistent operation of the fractionator to produce on specification products or streams having a specified boiling range and suitable for use as a gasoline blending component.

Several computer simulations and some actual examples are presented below.

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EXAMPLE 1

The first experiment reported represents a test conducted at a commercial refinery processing a distilled feed.

5 The commercial scale FCC riser reactor had a throughput of about 12720 m³/day (80,000 BPD) and an initial riser diameter of about 1.1 m (3.5 feet), expanding to about 2.3 m (7.5 feet) at the riser outlet, and an overall length of about 47.2 m (155 feet). Quench nozzles for the test were installed in
10 ports which were available. The ports were perpendicular to the riser axis. Bete Fog Maxipass "off-the-shelf" nozzles were used which were compatible with the port openings. The total
15 residence time in the riser reactor was 4 seconds.

The heavy feed was a sour gas oil having the following properties:

	API	22.5
	Basic N	425 wt ppm
20	Total N	1275 wt ppm
	UOP K	11.6
	Analine Pt	165°F (74°C)
	Sulfur	2.04 wt %
	D1160 DISTILLATION	
25	10%	590°F (310°C)
	50%	760°F (404°C)
	90%	965°F (518°C)

and the naphtha quench material had the following properties:

30	NAPHTHA DISTILLATION	
	5%	283°F (139°C)
	50%	424°F (218°C)
	90%	490°F (254°C)

The catalyst was an equilibrium catalyst having 66 FAI. The equilibrium catalyst was estimated to have an average catalyst composition of 11 wt % USY on a Si-Al matrix, with 2.8 wt % rare earths. The fresh make-up catalyst had more than 30 wt % USY content. Natural aging or steaming of the makeup catalyst in the FCC unit reduced the 30+ wt % USY zeolite of the fresh catalyst to the 11 wt % USY content of the equilibrium catalyst.

Several tests were conducted: two tests to determine a base line condition, followed by recycling some heavy naphtha to mix with the riser feed followed by tests with from 5 to 15 vol % heavy naphtha quench.

The operating conditions during all tests are summarized in Table 1 and the results are summarized in Tables 2-4.

Table 1

**Heavy Naphtha Quench Test
Operating Conditions**

Case			Base Case 1	Base Case 2	Recyc 5% vol	Quench 5% vol	Quench 9% vol	Quench 15% vol
5	Fresh Feed Rate	TBD	79.7	79.8	79.7	79.7	79.7	79.7
	Hvy Naph Recycle Rate	TBD	0.0	0.0	4.0	0.0	0.0	0.0
	Hvy Naph Quench Rate	TBD	0.0	0.0	0.0	4.0	7.2	12.0
	Riser Top Temp	°F	1011	1011	1010	1011	1011	1011
10	Combined Feed Temp	°F	366	362	368	369	367	396
	Stripping Steam	M#/hr	24.9	24.9	24.9	24.9	24.9	24.9
	Air Rate	MMSCF/D	266.8	270.2	274.9	276.8	284.6	291.0
	Catalyst Circulation	TPM	84.2	87.1	86.8	90.0	92.6	93.4
15	Avg Dilute Phase Temp	°F	1329	1335	1325	1323	1320	1317
	Regen Cat to Riser Temp	°F	1253	1253	1253	1253	1253	1253

Table 2

Heavy Naphtha Quench Test
Yield and Key Product Property Shifts

Case		BASE CASES		RECYCLE, QUENCH CASES				YIELDS TO AVERAGED BASE CASE			
		Base Case #1	Base Case #2	Recyc 5%vFF	Quench 5%vFF	Quench 9%vFF	Quench 15%vFF	Recyc 5%vFF	Quench 5%vFF	Quench 9%vFF	Quench 15%vFF
5	Yields, % of FF:										
	C ₂ - wt%	5.1	5.0	5.0	5.0	5.1	5.2	(0.1)	(0.1)	0.0	0.1
	C ₃ vol%	3.6	3.6	3.5	3.5	3.6	3.7	(0.1)	(0.1)	0.0	0.1
10	C ₃ = vol%	8.0	7.7	7.5	7.9	7.9	7.8	(0.4)	0.0	0.0	(0.1)
	nC ₄ vol%	2.0	2.0	2.1	2.0	2.1	2.1	0.1	0.0	0.1	0.1
	iC ₄ vol%	6.2	6.6	6.4	6.3	6.3	6.5	0.0	(0.1)	(0.1)	0.1
	C ₄ = vol%	9.0	8.9	9.4	9.1	9.2	9.3	0.5	0.2	0.3	0.4
	Gasoline vol%	55.8	55.2	56.4	57.2	57.5	57.9	0.9	1.7	2.0	2.4
15	LOO vol%	15.9	16.7	15.3	14.6	14.3	13.5	(1.0)	(1.7)	(2.0)	(2.8)
	CSO vol%	6.2	5.5	6.0	5.7	5.7	5.7	0.2	(0.1)	(0.1)	(0.1)
	Coke wt%	6.3	6.6	6.6	6.8	6.9	7.2	0.1	0.3	0.4	0.7
	Conversion vol%	77.9	77.8	78.7	79.7	80.0	80.8	0.8	1.8	2.1	2.9
	Total Gasoline Props:										
20	RHO Octane	93.0	93.0	93.3	93.6	93.6	93.6	0.3	0.6	0.6	0.6
	MHO Octane	81.2	81.3	81.4	81.5	81.6	81.7	0.2	0.3	0.4	0.5

Table 3

Heavy Naphtha Quench Test
Gasoline Sulfur Contents

Case	Base Case 1	Base Case 2	Recyc 5% vol	Quench 5% vol	Quench 9% vol	Quench 15% vol
<u>Flow Rates, TBD:</u>						
Fresh Feed	79.7	79.8	79.7	79.7	79.7	79.7
Heavy Naphtha Recycle	0.0	0.0	4.0	0.0	0.0	0.0
Heavy Naphtha Quench	0.0	0.0	0.0	4.0	7.2	12.0
Overhead Gasoline	41.9	41.5	43.1	43.8	44.0	44.4
HDF Feed/Product	2.5	2.5	1.7	1.8	1.8	1.8
Total Gasoline	44.4	44.0	44.9	45.6	45.8	46.2
<u>As-Out Sulfur Contents, wt%</u>						
Fresh Feed	2.06	2.00	2.10	2.03	2.02	2.04
Overhead Gasoline	0.21	0.21	0.23	0.27	0.21	0.18
HDF Feed/Quench, Recyc.	1.78	1.78	2.24	2.38	2.30	2.21
HDF Product	0.11	0.11	0.14	0.25	0.27	0.18
Untreated Gasoline	0.32	0.32	0.32	0.37	0.31	0.28
Treated Gasoline	0.20	0.20	0.23	0.27	0.21	0.18
<u>Total Sulfur, M#/D</u>						
Fresh Feed	529.9	512.5	539.8	520.7	518.9	523.8
Overhead Gasoline	22.8	22.6	26.9	31.5	24.1	21.1
HDF Feed	14.7	14.4	12.2	14.3	13.8	13.4
HDF Product	0.91	0.89	0.76	1.50	1.62	1.09
Untreated Gasoline	37.5	37.0	39.0	45.8	37.9	34.4
Treated Gasoline	23.7	23.4	27.6	33.0	25.7	22.1

Notes: 1) Gasoline end points for 5% and 9% quench cases were higher than those for the other cases by 21 and 5°F, respectively.

2) Data for overhead gasoline calculated from treated gasoline, HDF feed and HDF product.

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Table 4

**Heavy Naphtha Quench Test
Gasoline Distillations**

<u>Case</u>	<u>Base</u>				<u>Quench</u>			
	<u>Case 1</u>	<u>Case 2</u>	<u>Recyc</u>	<u>5% vol</u>	<u>5% vol</u>	<u>9% vol</u>	<u>15% vol</u>	<u>15% vol</u>
5	<u>Simulated Distillation</u>							
	<u>Temp., °F @ wt% off</u>							
	74	73	73	73	74	73	73	73
	80	80	80	80	80	80	80	80
	84	82	83	83	84	82	82	82
	107	107	107	107	107	106	106	106
	145	145	146	146	146	144	142	142
	173	178	177	177	181	172	170	170
	210	212	211	211	213	210	207	207
	248	256	252	252	258	247	241	241
15	289	291	289	289	293	287	282	282
	337	338	337	337	341	336	333	333
	396	400	396	396	403	393	381	381
	429	436	431	431	442	426	413	413
	485	487	489	489	510	501	508	508
	44.4	44.0	44.9	44.9	45.6	45.8	46.2	46.2
	30.5	30.0	30.8	30.8	30.9	31.9	32.5	32.5
	33.9	32.9	33.9	33.9	34.0	35.0	35.7	35.7
20	<u>Flow Rates, TBD:</u>							
	<u>Total Gasoline</u>							
	<u>C₅ - 280 TBP</u>							
	<u>C₅ - 320 TBP</u>							

As shown in Table 2, quenching with the heavy naphtha resulted in an increase in conversion and gasoline octane as compared with the base case (no recycle or quench) and the case where the heavy naphtha was recycled to mix with the feed.

A surprising reduction in sulfur content of the finished gasoline product can be seen by reviewing the sulfur content of various products streams, reported in Table 3. The finished gasoline in this refinery is a blend of the C5+ fraction of the main column overhead and a hydrofinished heavy naphtha. The naphtha is hydrofinished to meet a target of 0.20-0.22 wt % sulfur for the blended gasoline.

When the naphtha hydrofinisher had to be taken out of service, the gasoline end point typically was reduced to meet the sulfur specification. With heavy naphtha quench it was possible to avoid this. Heavy naphtha recycle at 5 vol % of fresh feed helped meet sulfur specifications and also increased gasoline yield 1.2 to 1.7 vol %.

As shown in Table 4, gasoline distillation showed an unexpected improvement in production of relatively lighter gasoline. Most of the increased gasoline yield was in C₅-280 TBP or C₅-320 TBP.

Model Prediction

This represents a model prediction of a base case compared with riser quench operation. The model used is believed to be a reliable indicator of the results that would be achieved in commercial FCC operations. The feedstock is very light, with an endpoint of 363°C (686°F). Properties are shown in Table 5.

Table 5**Properties of Light East Texas Gas Oil (LETGO)**

	API	36.3
	Specific Gravity, 60°F(16°C)	0.8433
5	Aniline Point, °F (°C)	168 (76)
	Pour Point, °F (°C)	25 (-4)
	Conradson Carbon Residue, wt%	0.02
	Ramsbottom Carbon Residue, wt%	0.07
	Sulfur, wt%	0.13
10	Total Nitrogen, wt%	0.02
	Basic Nitrogen, wt%	0.0036
	K.V. @ 100°F(38°C)	4.04
	K.V. @ 210°F(99°C)	1.45
	Molecular Weight	242
15	Refractive Index @ 70°F	1.45092

Distillation (D86), vol%

	IBP, °F(°C)	456 (236)
	5	483 (251)
	10	494 (257)
20	20	510 (266)
	30	522 (272)
	40	535 (279)
	50	550 (288)
	60	566 (297)
25	70	585 (307)
	80	610 (321)
	90	643 (339)
	95	686 (363)

30 The model was used to predict yields for cracking the LETGO feed for a base case (no quench) and for a case with 10% quench. The model was based on a total riser height of 46.9m (154 feet), with quench injection 27.4m (90 feet) up from the base of the riser. Results are reported in Table 6.

Table 6
Quench Benefits for LETGO

	Quench Amount	--	10
	Quench Temperature, °F(°C)	--	425(218)
5	Riser Top Temperature, °F(°C)	950(510)	950(510)
	Catalyst Activity, FAI	60	60
	Yields, wt%		
	Gasoline	49.2	51.2
	C ₄ and Lighter	27.3	27.6
10	LCO	17.1	14.6
	MCB	1.9	1.8
	Coke	4.5	4.8
	Conversion	81.0	83.6

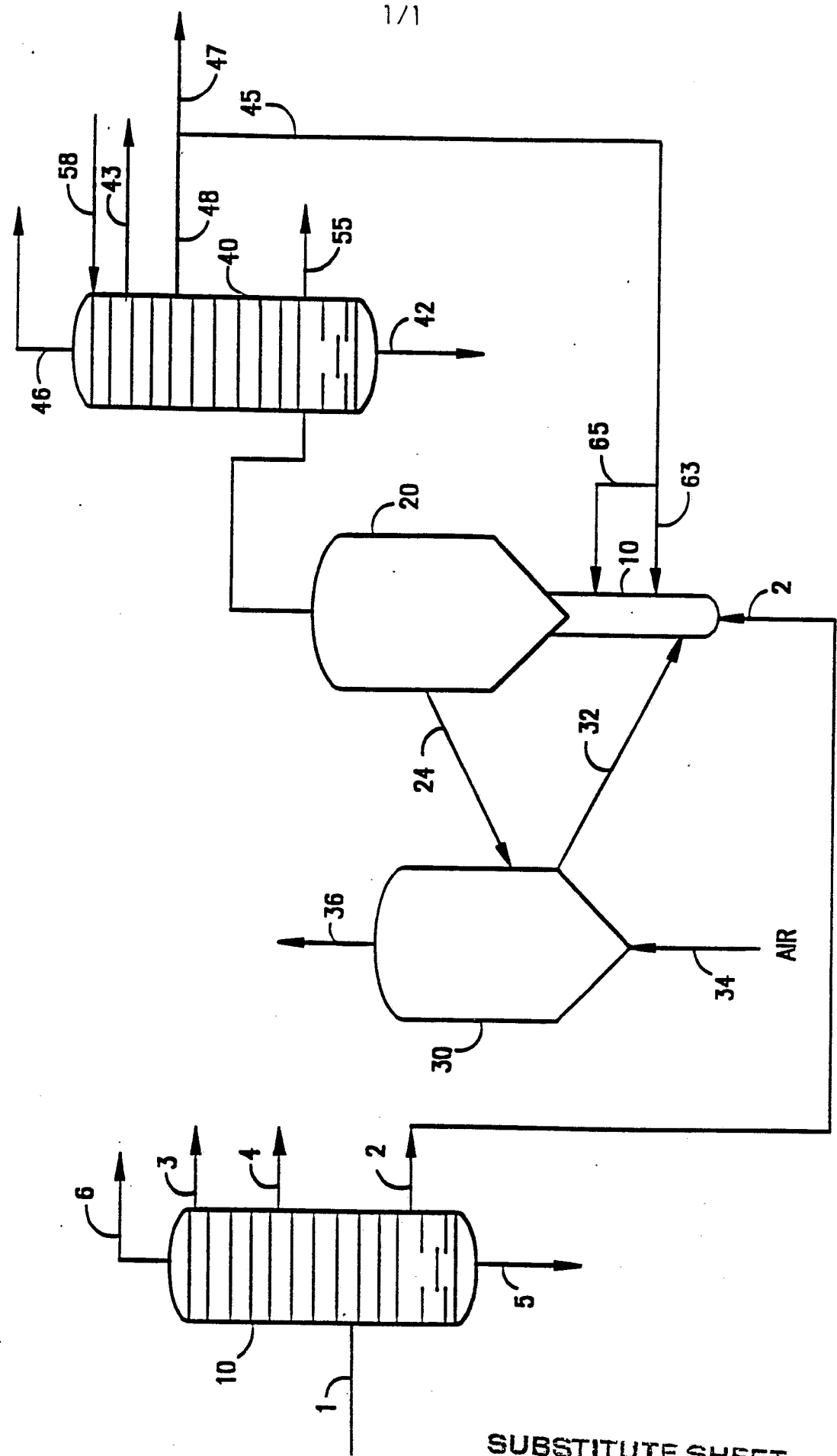
15 The LETGO feed has no heavy ends, nor non-distillables, and yet its conversion in an FCC riser reactor is considerably enhanced by addition of 10 wt% quench.

CLAIMS:

1. A catalytic cracking process for converting a distilled heavy hydrocarbon feed to lighter products comprising:

- 5 a) charging said distilled heavy hydrocarbon feed to a lower base section of a riser catalytic cracking reactor having an upper outlet section;
- b) charging a stream of hot, regenerated cracking catalyst from a catalyst regenerator to the
10 base section of the riser reactor to mix with and vaporize at least 95 wt % of said distilled feed within 0.25 seconds of vapor residence time in said riser reactor, the amount and temperature of the hot regenerated catalyst being sufficient to effect both
15 catalytic cracking and thermal cracking of said vaporized distilled feed in the base section of said riser;
- c) injecting a quench fluid into the catalyst/vaporized feed mixture, in at least one quench zone
20 within said riser reactor downstream of the base section thereof and more than 15% of the length of the riser upstream of the riser outlet, to lower the temperature in the riser by at least 6°C (10°F) and thereby reduce thermal cracking, without terminating
25 catalytically cracking, of the quenched mixture;
- d) discharging a mixture of catalytically cracked products and spent cracking catalyst from said outlet of said riser reactor;
- e) separating said discharged mixture into a
30 cracked product rich vapor phase and a spent catalyst rich phase; and
- f) regenerating the spent catalyst in a catalyst regeneration zone and recycling the hot regenerated catalyst to the base of said riser
35 reactor.

2. The process of claim 1 wherein the quench fluid is selected from water, steam and recycled cracked product.
- 5 3. The process of claim 1 wherein the quench fluid is a heavy naphtha fraction including hydrocarbons boiling in the range 150 to 200°C (300 to 400°F) separated from the cracked product.
- 10 4. The process of claim 1 wherein the cracking catalyst has a large pore zeolite content of at least 10% by weight and a M.A.T. activity of at least 55.
- 5 5. The process of claim 1 wherein the catalyst: feed ratio in the base section of the riser is at least 4:1.
- 15 6. The process of claim 1 wherein the feed is catalytically cracked for at least 1 second in the riser before the injection of the quench fluid.
7. The process of claim 1 wherein the injection of the quench fluid lowers the temperature in the riser by 8 to 56°C (15 to 100 °F).



INTERNATIONAL SEARCH REPORT

International application No.
PCT/US93/04088

A. CLASSIFICATION OF SUBJECT MATTER

IPC(5) :C10G 11/18
US CL :208/120, 208/48Q

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. :

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US,A, 3,758,403 (Rosinsici, et al) 11 September 1973 (see col. 2 lines 2 to line 55)	1-7
X	US,A, 4,818,372 (Mauleon et al) 4 April 1989, see col. 4, lines 9 to 49	1-7
X	US,A, 4,764,268 (Lane) 16 August 1988 (see col. 5, lines 24-41.	1-7
X	US,A 4,356,338 (Young) 26 October 1982 (see col. 1 line 54 to col. 2 line 12	1-7



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:		"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention	
"A"	document defining the general state of the art which is not considered to be part of particular relevance	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
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"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&"	document member of the same patent family
"O"	document referring to an oral disclosure, use, exhibition or other means		
"P"	document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search

08 JULY 1993

Date of mailing of the international search report

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