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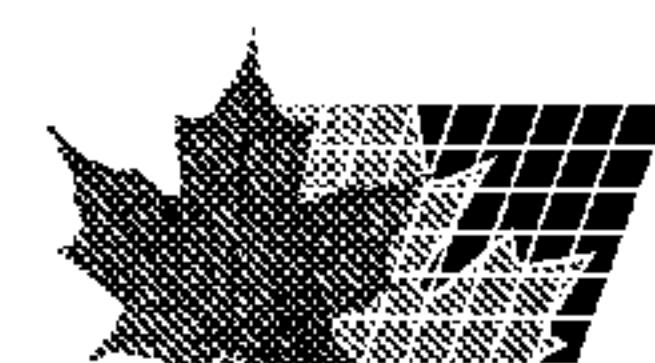
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(54) Titre : PROCEDE DE CRAQUAGE CATALYTIQUE LIQUIDE POUR LA PRODUCTION D'OLEFINES LEGERES

(54) Title: FLUID CATALYTIC CRACKING PROCESS FOR PRODUCING LIGHT OLEFINS

(57) **Abrégé/Abstract:**

A fluid catalytic cracking process for producing propylene, butylene, and exceptionally high levels of ethylene. The feedstock is relatively low in nitrogen and aromatics and high in hydrogen content. The catalyst contains a mixture of zeolite-Y and ZSM-5. The feedstock can be characterized as having less than about 1500 wppm nitrogen and greater than about 12 wt.% hydrogen.



2103230

ABSTRACT OF THE DISCLOSURE

A fluid catalytic cracking process for producing propylene, butylene, and exceptionally high levels of ethylene. The feedstock is relatively low in nitrogen and aromatics and high in hydrogen content. The catalyst contains a mixture of zeolite-Y and ZSM-5. The feedstock can be characterized as having less than about 1500 wppm nitrogen and greater than about 12 wt.% hydrogen.

Background of the Invention

The present invention relates to a fluid catalytic cracking process for producing propylene, butylene, and exceptionally high levels of ethylene. The feedstock is relatively low in nitrogen and aromatics and relatively high in hydrogen content. The catalyst contains a mixture of zeolite-Y and ZSM-5. The feedstock can be characterized as having less than about 1500 wppm nitrogen and greater than about 12 wt.% hydrogen.

Catalytic cracking is an established and widely used process in the petroleum refining industry for converting petroleum oils of relatively high boiling point to more valuable lower boiling products, including gasoline and middle distillates, such as kerosene, jet fuel and heating oil. The pre-eminent catalytic cracking process now in use is the fluid catalytic cracking process (FCC) in which a pre-heated feed is brought into contact with a hot cracking catalyst which is in the form of a fine powder, typically having a particle size of about 10-300 microns, usually about 100 microns, for the desired cracking reactions to take place. During the cracking, coke and hydrocarbonaceous material are deposited on the catalyst particles. This results in a loss of catalyst activity and selectivity. The coked catalyst particles, and associated hydrocarbon material, are subjected to a stripping process, usually with steam, to remove as much of the hydrocarbon material as technically and economically feasible. The stripped particles containing non-strippable coke, are removed from the stripper and sent to a regenerator where the coked catalyst particles are regenerated by being contacted with air, or a mixture of air and oxygen, at an elevated temperature. This results in the combustion of the coke which is a strongly exothermic reaction which, besides removing the coke, serves to heat the catalyst to the temperatures appropriate for the endothermic cracking reaction. The process is carried out in an integrated unit comprising the cracking reactor, the stripper, the regenerator, and the appropriate ancillary equipment. The catalyst is continuously circulated from the reactor or reaction zone, to the stripper and then to the regenerator and back to the reactor. The circulation rate is typically adjusted relative to the feed rate of the oil to maintain a heat balanced operation in which the heat produced in the regenerator is sufficient for maintaining the cracking reaction with the circulating regenerated catalyst being used as the heat transfer medium. Typical fluid catalytic cracking processes are described in the monograph Fluid Catalytic Cracking with Zeolite Catalysts, Venuto, P.B. and Habib, E.T., Marcel Dekker Inc. N.Y. 1979. As described in this monograph, catalysts which

are conventionally used are based on zeolites, especially the large pore synthetic faujasites, zeolites X and Y.

Typical feeds to a catalytic cracker can generally be characterized as being a relatively high boiling oil or residuum, either on its own, or mixed with other fractions, also usually of a relatively high boiling point. The most common feeds are gas oils, that is, high boiling, non-residual oils, with an initial boiling point usually above about 230°C, more commonly above about 350°C, with end points of up to about 620°C. Typical gas oils include straight run (atmospheric) gas oil, vacuum gas oil, and coker gas oils.

While such conventional fluid catalytic cracking processes are suitable for producing conventional transportation fuels, such fuels are generally unable to meet the more demanding requirements of low emissions fuels. To meet low emissions standards, the fuel products must be relatively low in sulfur and nitrogen. Furthermore, to augment the volume of low emission fuels, it is desirable to increase the amounts of light olefins such as propylene, iso- and normal butylenes, and isoamylene. The propylene, isobutylene, and isoamylene can be reacted with methanol to form methyl-propyl-ethers, methyl tertiary butyl ether (MTBE), and tertiary amyl methyl ether (TAME). These are high octane blending components which can be added to gasoline to satisfy oxygen requirements mandated by legislation. In addition to enhancing the volume and octane number of gasoline, they also reduce emissions. Ethylene, which can also be increased, is valuable as a chemical raw material. Conventional fluid catalytic cracking does not produce large enough quantities of these light olefins. Also, the fuels are not low enough in sulfur and nitrogen content to meet such standards. These standards will require either further changes in the FCC process, catalysts, or post-treating of all FCC products. Since post-treating to remove aromatics from gasoline or distillate fuels is particularly expensive, there are large incentives to limit the production of aromatics in the FCC process. Consequently, there exists a need in the art for methods of producing larger quantities of light olefins and low emissions transportation fuels, such as gasoline and distillates.

Summary of the Invention

In accordance with the present invention, there is provided a fluid catalytic cracking process for producing light olefins and low emissions fuel products, which process comprises:

(a) introducing a hydrocarbonaceous feedstock into a reaction zone of a catalytic cracking unit comprised of a reaction zone, a stripping zone, and a regeneration zone, which feedstock is characterized as having: an initial boiling point from about 230°C to about 350°C, with end points up to about 620°C; a nitrogen content less than about 1500 wppm and greater than about 12 wt.% hydrogen;

(b) catalytically cracking said feedstock in said reaction zone at a temperature from about 450°C to about 700°C, by causing the feedstock to be in contact with a cracking catalyst for a contact time of about 0.5 to 5 seconds, which cracking catalyst contains an effective amount of a mixture of zeolite-Y and ZSM-5 zeolitic component, thereby producing lower boiling products and catalyst particles having deposited thereon coke and hydrocarbonaceous material;

(c) stripping said partially coked catalyst particles with a stripping medium in a stripping zone to remove therefrom at least a portion of said hydrocarbonaceous material;

(d) recovering said hydrocarbonaceous material from the stripping zone;

(e) regenerating said coked catalyst in a regeneration zone by burning-off a substantial amount of the coke on said catalyst, optionally with an added fuel component to maintain the regenerated catalyst at a temperature which will maintain the reaction zone at a temperature from about 450°C to about 700°C; and

(f) recycling said regenerated catalyst to the reaction zone.

In preferred embodiments of the present invention, the added fuel component in the regeneration zone is selected from: C₂-saturated light gases from the catalytic cracking unit, and natural gas.

Detailed Description of the Invention

Feedstocks which are suitable for being converted in accordance with the present invention are any of those hydrocarbonaceous feedstocks which are conventional feedstocks for fluid catalytic cracking and which have an initial boiling point of about 230°C to about 350°C, with an end point up to about 620°C. The feedstocks of the present invention must also contain no more than about 1500 wppm nitrogen, and at least about 12 wt.% hydrogen. Non-limiting examples of such feeds include the non-residual petroleum based oils such as straight run (atmospheric) gas oil, vacuum gas oil, and coker gas oil.

-4-

Oils from synthetic sources such as coal liquefaction, shale oil, or other synthetic processes may also yield high boiling fractions which may be catalytically cracked, either on their own or in admixture with oils of petroleum origin. Feedstocks which are suitable for use in the practice of the present invention may not be readily available in a refinery. This is because typical refinery streams in the boiling point range of interest, and which are conventionally used for fluid catalytic cracking, generally contain too high a content of undesirable components such as nitrogen, sulfur, and aromatics. Consequently, such streams will need to be upgraded, or treated to lower the level of such undesirable components. Non-limiting methods for upgrading such streams include hydrotreating in the presence of hydrogen and a supported Mo containing catalyst with Ni and/or Co; extraction methods, including solvent extraction as well as the use of solid absorbents, such as various molecular sieves. It is preferred to hydrotreat the streams.

Any suitable conventional hydrotreating process can be used as long as it results in a stream having the characteristics of as previously mentioned. That is nitrogen levels of less than about 1500 wppm, preferably less than about 1000 wppm, more preferably less than about 500 wppm, and most preferably less than about 100 wppm, e.g., less than 50 or even less than 20 wppm; a hydrogen content of greater than about 12 wt.%, preferably greater than about 12.5 wt.%, more preferably greater than 13 wt.% and most preferably greater than 13.5 wt.%. Preferably, the 2+ring aromatic core content is less than 7.5 wt.%, more preferably, less than 4 wt.%, and the overall aromatic core content is less than 15 wt.%, more preferably, less than 8 wt.%.

Suitable hydrotreating catalysts are those which are typically comprised of a Group VIB (according to the Sargent-Welch Scientific Company Periodic Table of the Elements) metal with one or more Group VIII metals as promoters, on a refractory support. It is preferred that the Group VIB metal be molybdenum or tungsten, more preferably molybdenum. Nickel and cobalt are the preferred Group VIII metal with alumina being the preferred support. The Group VIII metal is present in an amount ranging from about 2 to 20 wt.%, expressed as the metal oxides, preferably from about 4 to 12 wt.%. The Group VIB metal is present in an amount ranging from

4a

about 5 to 50 wt.%, preferably from about 10 to 40 wt.%, and more preferably from about 20 to 30wt.%. All metals weight percents are based on total weight of catalyst. Any suitable refractory support can be used. Such supports are typically inorganic oxides, such as alumina, silica, silica-alumina, titania, and the like. Preferred is alumina.

Suitable hydrotreating conditions include temperatures ranging from about 250° to 450°C, preferably from about 350°C to about 400°C; pressures from about 250 to 3000 psig; preferably from about 1500 to 2500 psig; hourly space velocities from about .05 to 6 V/V/Hr; and a hydrogen gas rate of about 500 to 10000 SCF/B; where SCF/B means

standard cubic feet per barrel, and V/V/Hr means volume of feed per volume of the catalyst per hour.

A hydrocarbonaceous feedstock which meets the aforementioned requirements for producing light olefins and a low emissions fuel is fed to a conventional fluid catalytic cracking unit. The catalytic cracking process may be carried out in a fixed bed, moving bed, ebullated bed, slurry, transfer line (dispersed phase), riser or dense bed fluidized bed operation. It is preferred that the catalytic cracking unit be a fluid catalytic cracking (FCC) unit. Such a unit will typically contain a reactor where the hydrocarbonaceous feedstock is brought into contact with hot powdered catalyst particles which were heated in a regenerator. Transfer lines connect the two vessels for moving catalyst particles back and forth. The cracking reaction will preferably be carried out at a temperature from about 450° to about 700°C, more preferably from about 480° to about 650°C; pressures from about 5 to 60 psig, more preferably from about 5 to 40 psig; contact times (catalyst in contact with feed) of about 0.5 to 15 seconds, more preferably about 1 to 6 seconds; and a catalyst to oil ratio of about 0.5 to 10, more preferably from about 2 to 8. During the cracking reaction, lower boiling products are formed and some hydrocarbonaceous material, and non-volatile coke are deposited on the catalyst particles. The hydrocarbonaceous material is removed by stripping, preferably with steam. The non-volatile coke is typically comprised of highly condensed aromatic hydrocarbons which generally contain about 4 to 10 wt.% hydrogen. As hydrocarbonaceous material and coke build up on the catalyst, the activity of the catalyst for cracking, and the selectivity of the catalyst for producing gasoline blending stock, is diminished. The catalyst particles can recover a major proportion of their original capabilities by removal of most of the hydrocarbonaceous material by stripping and combustion of the coke by a suitable oxidative regeneration process. Consequently, the catalyst particles are sent to a stripper and then to a regenerator.

Catalyst regeneration is accomplished by burning the coke deposits from the catalyst surface with an oxygen-containing gas such as air. Catalyst temperatures during regeneration may range from about 560°C to about 760°C. The regenerated, hot catalyst particles are then transferred back to the reactor via a transfer line and, because of their heat content, are able to maintain the reactor at the temperature necessary for the cracking reactions. Coke burn-off is an exothermic reaction, therefore in a conventional fluid catalytic cracking unit with conventional feeds, no additional fuel needs to be added. The feedstocks used in the practice of the present invention, primarily because of their low levels of aromatics, and also due to the relatively short contact times in the reactor or transfer line, may not deposit

enough coke on the catalyst particles to achieve the necessary temperatures in the regenerator. Therefore, it may be necessary to use an additional fuel to provide increased temperatures in the regenerator so the catalyst particles returning to the reactor are hot enough to maintain the cracking reactions. Non-limiting examples of suitable additional fuel include C_2 -saturated gases from the catalytic cracking process itself; natural gas; and any other non-residual petroleum refinery stream in the appropriate boiling range. Such additional fuels are sometimes referred to as torch oils. Preferred are the C_2 -gases.

Catalysts suitable for use in the present invention are mixtures of zeolite-Y and ZSM-5 in a porous matrix material. The zeolite portion of the mixture will typically contain from about 5 wt.% to 95 wt.% zeolite-Y and the balance being of the zeolite being ZSM-5. For example, the catalyst may contain: from 2.5 wt.% to 57.5 wt.% zeolite-Y and from 57.5 wt.% to 2.5 wt.% ZSM-5 zeolite; or from 12 wt.% to 24 wt.% zeolite-Y and from 8 wt.% to 15 wt.% ZSM-5. By zeolite-Y is meant those zeolites which are isostructural with zeolite-Y, or faujasite, and have a steamed (16 hours at 1400°F) or equilibrated unit cell size equal to or less than about 24.35 Å. The preferred unit cell size is from about 24.21 to 24.30 Å. The particle size of the zeolite may range from about 0.1 to 10 microns, preferably from about 0.3 to 3 microns. The zeolite will be mixed with a suitable porous matrix material when used as a catalyst for fluid catalytic cracking. Non-limiting porous matrix materials which may be used in the practice of the present invention include alumina, silica-alumina, silica-magnesia, silica-zirconia, silica-thoria, silica-beryllia, silica-titania, as well as ternary compositions, such as silica-alumina-thoria, silica-alumina-zirconia, magnesia and silica-magnesia-zirconia. For example, the non-zeolitic portion of the catalyst is an amorphous silica-alumina material containing from 15 to 25 wt.% alumina. The matrix may also be in the form of a cogel. The relative proportions of zeolite component and inorganic oxide gel matrix on an anhydrous basis may vary widely with the zeolite content, ranging from about 10 to 99, more usually from about 10 to 80, percent by weight of the dry composite. The matrix itself may possess catalytic properties, generally of an acidic nature.

6a

Suitable amounts of zeolite component in the total catalyst will generally range from about 1 to about 60, preferably from about 1 to about 40, and more preferably from about 5 to about 40 wt.%, based on the total weight of the catalyst. Generally, the particle size of the total catalyst will range from about 10 to 300 microns in diameter, with an average particle diameter of about 60 microns. The surface area of the matrix material will be about $< 350\text{m}^2/\text{g}$, preferably $100\text{m}^2/\text{g}$, more preferably from about 50 to $100\text{m}^2/\text{g}$. While the surface area of the final catalysts will be dependent on such things as type and amount of zeolite material used, it will usually be less than about $500\text{m}^2/\text{g}$, preferably from about 50 to $300\text{m}^2/\text{g}$, more preferably from about 50 to

- 7 -

250 m²/g, and most preferably from about 100 to 250 m²/g.

The following examples are presented to illustrate preferred embodiments of the present invention and should not be taken as being limiting in any way.

Example 1 (Comparative)

Cracking tests were conducted in a fixed bed microactivity (MAT) testing unit. Such a test unit is described in the Oil and Gas Journal, 1966 Vol.64, pages 7, 84, 85 and November 22, 1971, pages 60-68. Run conditions are listed as follows:

Temperature, °C	527
Run Time, Sec.	30
Catalyst Charge, gr.	4.1 to 7.5
Amount Feed, cc.	1.5
Cat/Oil ratio	3.0 to 5.5

The feed for these tests was a conventional, commercially distilled VGO used as a commercial FCC feed. This FCC feed is designated by RA and had a sulfur content of 2.09%, a nitrogen content of 0.0671%, and a hydrogen content of 12.03%.

Two catalysts were used in these tests. The first was a commercial equilibrium catalyst initially containing about 30% USY (ultrastable zeolite Y), which is designated as catalyst ZA. The other catalyst was a fresh steamed ZSM-5 (Intercat's ZCAT+) which contains about 15% ZSM-5 zeolite in a silica-alumina matrix. This ZSM-5 catalyst was designated ZZ.

The total liquid product from the MAT tests which amounted to about 0.3 to 0.7 grams, was analyzed on two different GC instruments. A standard analysis is the boiling point distribution determined by gas chromatographic distillation (GCD) to evaluate: (1) the amount of material boiling less than 15°C; (2) naphtha between 15°C and 220°C; (3) light cat cycle oil (LCCO) boiling between 220°C and 345°C; and (4) bottoms boiling above 345°C.

Detailed cracking data are given in Table I below for cracking the conventional VGO feed with catalyst ZA alone and with a mixture of catalysts 92 wt.% ZA and 8 wt.% ZZ. The comparative data of Table I was made at a constant coke yield of 4 wt% on feed, reflecting the need to heat balance commercial fluid catalytic cracking units.

TABLE I

<u>Catalyst</u>	<u>ZA</u>	<u>ZA+ZZ</u>
Catalyst/Oil Ratio	5.2	5.1
Conversion (220°C)	65.8	65.8
<u>Yields, Wt%</u>		
Coke	4.0	4.0
C ₂ - Dry Gas	2.7	2.9
C ₂ H ₄	0.74	0.95
C ₃ H ₆	4.1	8.4
C ₃ H ₈	0.9	1.4
C ₄ H ₈	5.1	7.6
Iso C ₄ H ₁₀	3.2	4.8
N-C ₄ H ₁₀	1.0	0.8
15/220°C	44.9	36.0
LCCO	19.7	18.3
Bottoms	14.5	15.9

These results show the expected appreciable increase in propylene and butylene yields for using a modest amount of ZSM-5 catalyst with a conventional fluid cracking catalyst at conventional fluid catalytic cracking conditions. These olefins are produced at the expense of 15/220°C naphtha yields. Note also that C₂- dry gas yields are not substantially boosted by use of the ZSM-5 catalyst at this level. Finally, the bottoms yield was higher with use of the ZSM-5 catalyst. ZSM-5 addition in conventional fluid catalytic cracking operations must be limited to prevent larger increases in these undesirable 345°C+ products.

This example shows that adding conventional levels of ZSM-5 additive to a conventional fluid catalytic cracking operation does not significantly increase ethylene yields.

Example 2

Further cracking tests were conducted in the microactivity test unit of Example 1 above. The catalytic cracking conditions used for this example were substantially the same as those described in Example 1 except that a higher temperature of 566°C was used. The feed used for these experiments was a commercially hydrotreated, VGO catalytic cracking feed. This feed is designated Feed HA and its properties are given below.

HA Feed Properties

Wppm N	1210
Wt% S	0.249
Wt% C	87.19
Wt% H	12.43

Wt% Con Carbon* 0.19

*Conradson carbon content as defined in ASTM D-189-65

Two catalysts were used in this example. The first was a fresh, steamed, commercially available catalyst (Davison's Octacat 50+) which is an ultra stable Y zeolite in a silica matrix. This catalyst is designated herein as catalyst ZB. It was steamed 16 hours at 760°C to simulate commercially deactivated catalysts. It has a relatively low unit cell size after steaming, or commercial deactivation. Tests were also made with a fresh, steamed ZSM-5 catalyst of Example 1 above. This catalyst is designated as Catalyst ZW. The characteristics of both catalysts are set forth below.

<u>Catalyst</u>	<u>ZB</u>	<u>ZW</u>
<u>Wt%</u>		
Al ₂ O ₃	25.5	35.31
SiO ₂	73.0	53.96
RE ₂ O ₃	0.57	0.0
Na ₂ O	0.20	0.2
TiO ₂	0.67	n/a
<u>Calc. 4 hrs @ 537°C</u>		
S.A., M ² /g	271.0	34.0
P.V., cc/g	0.173	0.068
Unit Cell, A	24.47	n/a
<u>Steamed 16 hrs @ 760°C</u>		
S.A., M ² /g	230.0	46.0
P.V., cc/g	0.154	0.061
Unit Cell, A	24.26	n/a

Tests were made with catalyst ZB alone and with mixtures of 60 wt.% ZW and 40 wt.% ZB at catalytic cracking conditions similar to the conditions used in Example 1. The tests were made at a 3 to 6 catalyst to oil ratio. Detailed cracking data are given in Table II below for cracking the hydrotreated VGO feed HA at 566°C and at a constant coke yield of 4 wt% on feed.

TABLE II

Catalyst	ZB	40 wt.%ZB+ 60 wt.% ZW
Catalyst/Oil Ratio	4.6	7.0
Conversion (220°C)	73.8	74.7
<u>Yields, Wt%</u>		
Coke	4.0	4.0
C ₂ - Dry Gas	4.4	6.7
C ₂ H ₄	1.37	4.45
C ₃ H ₆	6.6	17.8
C ₃ H ₈	1.6	2.7
C ₄ H ₈	7.6	13.8
Iso-C ₄ H ₁₀	4.2	4.2
N-C ₄ H ₁₀	0.8	1.0
15/220°C	44.8	24.3
LCCO	16.6	14.0
Bottoms	9.7	11.3

These results show that cracking a relatively clean catalytic cracking feed at relatively high temperatures with catalyst mixtures containing 60 wt.% ZSM-5 not only boosts the C₃ and C₄ olefin yields, but also boosts ethylene yields. Yields of C₂- dry gas increased, but the increase was all ethylene. Yields of saturated C₂- dry gas are actually lower than with catalyst ZB alone.

These results are unexpected in view of the results at lower catalytic cracking temperatures with lower levels of ZSM-5. It is also unexpected that conversion to 345°C and 220°C products were maintained, at a higher catalyst to oil ratio, using higher levels of ZSM-5. This is apparently due to a low coke producing factor for the additive itself at these conditions. In any event, these results show that high conversions can be obtained in heat balanced fluid catalytic cracking operations with catalyst mixtures containing relatively high levels of ZSM-5 additive. This is accomplished at high cracking temperatures with relatively clean feeds.

Example 3

Further cracking tests were conducted in the microactivity unit used in the above examples. The feed and catalysts were the same as in Example 2. The catalytic cracking conditions were substantially the same as the conditions used in Example 1 except that a higher cracking temperature, 621°C, was used. This example represents a preferred embodiment of the present invention.

Detailed cracking data are given in Table III below for cracking the hydrotreated VGO feed HA at a constant coke yield of 4 wt% on feed.

TABLE III

<u>Catalyst</u>	<u>ZB</u>	<u>ZW</u>
Catalyst/Oil Ratio	3.8	6.0
Conversion (220°C)	75.3	75.9
<u>Yields, Wt%</u>		
Coke	4.0	4.0
C ₂ - Dry Gas	9.0	11.4
C ₂ H ₄	3.30	7.10
C ₃ H ₆	8.2	21.3
C ₃ H ₈	2.0	2.6
C ₄ H ₈	10.0	13.3
Iso-C ₄ H ₁₀	2.4	2.2
N-C ₄ H ₁₀	0.4	0.5
15/220°C	39.3	20.6
LCCO	13.9	12.8
Bottoms	10.8	11.3

Comparing these results with Example 2 shows that increasing cracking temperatures to 621°C from 566°C resulted in modest increases in light olefins yields produced with catalyst ZB alone. However, the ZSM-5 additive ZW had even more impact on light olefins at the higher temperature. Ethylene yields were boosted to 3.8 wt% vs a 3% boost at 566°C. Since the ZSM-5 additive boosted dry gas yields by only 2.4% C₂-saturate yields were reduced by the additive. Additive ZW also boosted propylene yields by more than 13% vs an 11% increase at 566°C. On the other hand, the additive produced less butylene at 621° than at 566°C, suggesting C₄ olefins were cracked to produce lighter olefins at the higher temperature.

Example 4

Further cracking tests were conducted in the same small fixed bed, MAT type testing unit which was described in Example 1 above. Feed and catalysts were the same as in Example 2. Catalytic cracking conditions used for these tests were similar to the conditions used in Example 3. However, some tests were made at higher cracking temperatures, while others were made at even higher catalyst to oil ratios. This example illustrates a preferred method for increasing light olefins yields.

Detailed cracking data are given in Table IV below for these more severe cracking conditions.

Table IV

**Higher Severity Cracking
of Hydrotreated VGO HA on 40% ZB/60%ZW**

<u>Cracking Temperature, °C</u>	<u>620</u>	<u>650</u>	<u>675</u>
Catalyst/Oil Ratio	15	6.0	6.1
Conversion (220°C)	81.7	79.0	79.5
<u>Yields, Wt%</u>			
Coke	9.9	5.7	7.2
C ₂ - Dry Gas	17.7	17.4	22.5
C ₂ H ₄	9.54	9.73	11.76
C ₃ H ₆	20.1	22.3	20.9
C ₃ H ₈	4.2	3.1	2.7
C ₄ H ₈	10.2	11.7	10.1
Iso-C ₄ H ₁₀	3.2	2.1	0.9
N-C ₄ H ₁₀	1.0	0.6	0.5
15/430°C	15.2	15.9	14.4
LCCO	10.4	11.4	10.5
Bottoms	7.9	9.6	9.9

Comparing these results with Example 3 shows that increasing cracking severity by boosting cracking temperatures is preferred to increasing cat to oil ratio. Higher C/O ratios and higher cracking temperatures boost conversion and ethylene yields. However, increasing cat to oil ratio results in higher coke yields than those resulting from higher cracking temperatures. Increasing cat to oil ratio also tends to produce more propane and butane vs. propylene and butylene.

Example 5

Further cracking tests were conducted in the same small fixed bed, MAT type testing unit which was described in Example 1 above. Feed and catalysts were the same as in Example 2. Catalytic cracking conditions used for these tests were similar to the conditions used in Example 4 above. However, all tests were made at a cracking temperature of 650°C and a catalyst to oil ratio of 6. In these tests, the proportion of additive ZW ranged from 70 to 100% as compared to the 60% additive level used in Examples 3 and 4. This example illustrates a preferred ZSM-5 additive to cracking catalyst ratio.

Detailed cracking data are given in Table V below for these experiments with even higher additive levels.

2103230

- 13 -

Table V

High Temperature Cracking of Hydrotreated VGO HA
with Higher Additive "ZW": Catalyst ZB Ratios

Wt% Additive ZW	<u>70</u>	<u>80</u>	<u>90</u>	<u>100</u>
Conversion (220°C)	77.0	77.4	74.3	63.0
<u>Yields, Wt%</u>				
Coke	4.7	4.3	3.4	3.7
C ₂ - Dry Gas	17.5	18.3	17.5	17.3
C ₂ H ₄	10.9	11.1	10.7	10.0
C ₃ H ₆	21.5	22.1	22.7	17.5
C ₃ H ₈	2.9	2.8	2.5	1.9
C ₄ H ₈	11.0	11.5	11.8	8.4
Iso-C ₄ H ₁₀	1.9	1.0	1.1	0.5
N-C ₄ H ₁₀	0.6	0.7	0.4	0.3
15/220°C	16.9	16.3	14.5	13.0
LCCO	12.0	11.9	12.2	14.0
Bottoms	11.0	10.7	13.6	23.0

Comparing these results with Example 4, shows that increasing the level of Additive ZW from 60 to 80 or 90% provided higher ethylene yields and lower coke yields, while maintaining conversion, propylene and butylene yields. Further increases in additive ZW levels, along with further reductions in catalyst ZB levels, resulted in significant reductions in conversion to 220°C- and particularly 345°C- products.

THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. A fluid catalytic cracking process for producing low emission fuel products, which process comprises the steps of:

(a) introducing a hydrocarbonaceous feedstock into a reaction zone of a catalytic cracking unit comprised of a reaction zone, stripping zone, and a regeneration zone, which feedstock is characterized as having: an initial boiling point from 230°C to 350°C, with end points up to 620°C; a nitrogen content less than 50 wppm; a hydrogen content in excess of 13 wt.%; a 2+ring aromatic core content of less than 7.5 wt.%; and an overall aromatic core content of less than 15 wt.%;

(b) catalytically cracking said feedstock in the catalytic cracking unit operated at a temperature from 450°C to 700°C, by causing the feedstock to be in contact with a cracking catalyst for a contact time of 0.5 to 5 seconds, which cracking catalyst contains an effective amount of a mixture of zeolite-Y and ZSM-5 zeolitic component, thereby producing lower boiling products and partially coked catalyst particle containing hydrocarbonaceous material;

(c) stripping said partially coked catalyst particles with a stripping medium in a stripping zone to remove therefrom at least a portion of said hydrocarbonaceous material;

(d) recovering said hydrocarbonaceous material from the stripping zone;

(e) regenerating said coked catalyst in a regeneration zone by burning-off a substantial amount of the coke on said catalyst, to maintain the regenerated catalyst at a temperature which will maintain the reaction zone at a temperature from 450°C to 700°C; and

(f) recycling said regenerated catalyst to the reaction zone.

2. The process of claim 1 wherein the catalyst contains from 2.5 wt.% to 57.5 wt.% zeolite-Y and from 57.5 wt.% to 2.5 wt.% ZSM-5 zeolite.

3. The process of claim 2 wherein the catalyst contains from 12 wt.% to 24 wt.% zeolite-Y and 8 wt.% to 15 wt.% ZSM-5.

4. The process of claim 1, 2 or 3 wherein the hydrocarbonaceous feedstock contains: less than 20 wppm nitrogen, greater than 13.5 wt.% hydrogen, less than 4 wt.% of 2+ring aromatic cores, and an overall aromatic core content of less than 8 wt.%.

5. The process of any one of claims 1 to 4 wherein the non-zeolitic portion of the catalyst is an amorphous silica-alumina material containing from 15 to 25 wt.% alumina.

6. The process of any one of claims 1 to 5 wherein the catalyst is zeolitic material in an inorganic matrix, which zeolitic material is a Y type zeolite having a unit cell size of 24.30 Å or less.

7. The process of any one of claims 1 to 6 wherein an added fuel component is used in step (e) in the regeneration zone for burning-off coke from the catalyst.