

HYDROCARBON CRACKING WITH POSITIVE REACTOR TEMPERATURE GRADIENT**Field of the Invention**

The invention provides a process for increasing yields of ethylene
5 and/or propylene in a catalytic cracking process by use of a positive reactor
temperature gradient.

Background of the Invention

Thermal and catalytic conversion of hydrocarbons to olefins is an
important industrial process producing millions of pounds of olefins each year.
10 Because of the large volume of production, small improvements in operating
efficiency translate into significant profits. Catalysts play an important role in
more selective conversion of hydrocarbons to olefins.

Particularly important catalysts are found among the natural and
synthetic zeolites. Zeolites are complex crystalline aluminosilicates which
15 form a network of AlO_4 and SiO_4 tetrahedra linked by shared oxygen atoms.
The negative charge of the tetrahedra is balanced by the inclusion of protons
or cations such as alkali or alkaline earth metal ions. The interstitial spaces
or channels formed by the crystalline network enable zeolites to be used as
molecular sieves in separation processes. The ability of zeolites to adsorb
20 materials also enables them to be used in catalysis. There are a large
number of both natural and synthetic zeolitic structures. The wide breadth of
such numbers may be understood by considering the work "Atlas of Zeolite
Structure Types" by W. M. Meier, D. H. Olson, and C.H. Baerlocher (4th ed.,
Butterworths/Intl. Zeolite Assoc. [1996]). Catalysts containing zeolites have
25 been found to be active in cracking light naphtha to ethylene and propylene,
the prime olefins.

Of particular interest are the acidified zeolites which are effective for
conversion of light hydrocarbons such as low boiling naphthas to the prime
olefins. Typical catalysts include ZSM-5 zeolite described and claimed in U.S.

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Pat. No. 3,702,886, and ZSM-11 described in U.S. Pat. No. 3,709,979, and the numerous variations on these catalysts disclosed and claimed in later patents.

Previous uses of multiple temperature zones in prime olefin production have used hydrocracking or hydrogenolysis to produce ethane and propane with little production of prime olefins in the first stages. Franck et al. U.S. Patent No. 4,137,147 used multiple hydrogenolysis stages to which each stage is operated at 5 to 25°C higher than the preceding stage. The light hydrocarbons up to C₃ in the effluent from the hydrogenolysis stages were then steam cracked to prime olefins while the C₄+ production was separated and at least part of it sent to further hydrogenolysis for additional ethane and propane production. The steam cracking unit was supplied a fraction consisting essentially of ethane and propane for conversion to ethylene. Lionetti et al. U.S. Patent No. 4,388,175, discloses a two stage system for production of aromatics from heavy oil. The second stage is operated at a higher temperature than the first to produce light naphtha, gasoline and needle coke. There was no indication of any application to prime olefins production. Tabak U.S. Patent No. 4,487,985 and its divisional U.S. Patent No. 4,560,536 teaches oligomerization of lower olefins in a multistage series of reactors wherein catalyst partially inactivated in the primary stage is employed at a higher temperature in a secondary stage prior to catalyst regeneration. In European patent application 0 023 802 a hydrocracking step produces C₂ to C₅ alkanes from which prime olefins are produced by downstream thermal cracking at a higher temperature. GB 2,105,362 teaches a two stage thermal cracking process in a catalyst free system wherein the first reaction zone heats the steam/feedstock from 800°C to 1000°C and then passes the feedstock to a second catalyst free zone where it is heated from 850°C to 1150°C. Mauleon et al. U.S. Patent Nos. 5,506,365 and 5,264,115 teach a multiple zone process wherein hot catalyst is used in a

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mild steam thermal cracking process and reacted further downstream with additional catalyst at a lower temperature in a process aimed at gasoline production.

European Patent Application 0 262 049 teaches steam cracking of hydrocarbons (propane is exemplified) followed by contact with a multi-component zeolite containing catalyst with added metal oxides having a hydrogenation/dehydrogenation function. The thermal cracking unit is operated at a higher temperature than the catalytic cracker. Adams U.S. Patent No. 3,360,587 also teaches a steam cracking step followed by a catalytic cracker, again the catalytic cracker is at a lower temperature than the upstream thermal cracker. In European patent application 0 023 802 a catalytic (hydrocracking) reaction stage produces mainly C₂ to C₅ paraffins which are subsequently fed to an optional higher temperature thermal cracking unit for conversion to prime olefins. Published PCT application WO 95/13255 describes an integrated system wherein a light fraction is separated from the effluent of a deep catalytic cracking unit running on a relatively heavy oil fraction and recycled to a thermal cracking unit to produce prime olefins. Published PCT application WO 86/02376 discloses heavy oil cracking including a pre-pyrolysis cracking step followed by separation of an overhead stream that is thermally cracked for prime olefin production. Burich U.S. Patent No. 3,702,292 discloses an integrated refinery apparatus wherein various streams are separated and feed to both a hydrocracking unit and a thermal cracking unit. Derwent WPI Accession No. 88-053890/08 for Japanese patent 60235890 discloses thermal cracking of hydrocarbons in a two stage system. Derwent WPI Accession No. 86-011144/02 for Japanese patent 63010693 discloses feeding by-product light oil containing olefins from a catalytic cracking unit to a thermal cracking furnace with prime olefins recovered in high purity.

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Heretofore the art has not recognized that a temperature gradient or temperature staging across multiple reactors with suitable catalysts can result in significant increases in production of prime olefins without prior separation of components or removal of C_4+ materials from the feed stream and without the necessity of using steam cracking units downstream or in recycle loops.

Summary of the Invention

The present invention provides a process for improving the conversion of a hydrocarbon feedstock to light olefins comprising the step of contacting a hydrocarbon feedstock with a cracking catalyst in a reactor operated at a positive temperature gradient. In an alternate embodiment the invention provides a process for producing ethylene and propylene in a catalytic cracking process wherein a hydrocarbon feedstock is contacted with a cracking catalyst, the improvement which comprises providing a first catalyst contact zone at a first temperature and providing a second catalyst contact zone at a second temperature downstream from the first catalyst contact zone and maintaining the second catalyst contact zone at a higher temperature than the first catalyst contact zone and passing the cracked hydrocarbon feedstock from the first catalyst contact zone to the second catalyst contact zone. In either embodiment, the downstream catalyst may be the same or a different catalyst to produce the desired product mix. The second embodiment may comprise a plurality of reactor vessels so long as at least one down stream vessel is operated at a higher temperature than an upstream reactor, and both provide catalytic cracking zones.

Detailed Description of the Invention

Definitions

"Light naphtha" means a hydrocarbon distillate fraction that is predominantly C_5 to C_7 hydrocarbons.

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"Virgin naphtha" means a hydrocarbon distillate fraction obtained from crude oil or natural gas without additional conversion processing.

"Cat naphtha" means a hydrocarbon distillate fraction obtained by catalytic cracking of a heavier hydrocarbon fraction.

5 "BTX" means a mixture containing benzene, toluene, and xylenes.

"Light olefins" or "prime olefins" means ethylene, propylene or mixtures thereof.

"Improve conversion" means producing an increase in production that is a greater light olefin yield within the precision of the measurement system
10 over cracking the same feedstock with the same catalyst(s) at a constant temperature.

"Hydrocarbon feedstock" means a hydrocarbon stream comprising one or more hydrocarbons to be broken into fragments by thermal, chemical or catalytic action, the fragments forming light olefins.

15 "Positive temperature gradient" means a temperature change from a lower temperature at a first location to a higher temperature at a second location, the second location being downstream from the first location.

Reaction Conditions and Catalysts

Substantial amounts of ethylene and propylene are produced by
20 cracking hydrocarbon feedstocks such as light cat naphtha (LCN) or light virgin naphtha (LVN) over catalysts particularly zeolite containing catalysts which contain ZSM-5. The present invention provides a method for enhancing ethylene and propylene yields which comprises contacting a feed stream with a catalyst in a reactor bed operated with a positive temperature
25 gradient. Preferably the feed stream is LCN or LVN, but any catalyst crackable hydrocarbon stream may be used.

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Any cracking catalyst operable to selectively produce prime olefins may be improved by use of the reactor temperature gradient method. Suitable zeolites for use as the cracking catalyst are typically the acid form of any of the naturally occurring or synthetic crystalline zeolites, especially those
5 having a silica-alumina ratio within the range of about 2.0:1 to 2000:1. In general, any catalyst capable of cracking hydrocarbons to light olefins, having an improved conversion by the use of a temperature gradient is suitable for use in the process. By employing the simple bench test described below one skilled in the art can quickly determine whether a catalyst displays improved
10 conversion by temperature staging.

Examples of zeolites useful in the claimed process include gallium silicate zeolites such as those described in U.S. Patent No. 5,096,686, zeolite beta, zeolite rho, ZK5, titanosilicate, ferrosilicate; borosilicate zeolite; zeolites designated by the Linde Division of Union Carbide by the letters of X, Y, A, L
15 (these zeolites are described in U.S. Pat. Nos. 2,882,244; 3,130,007; 3,882,243; and 3,216,789, respectively); naturally occurring crystalline zeolites such as phillipsite, ferrierite, mazzite, heulandite, faujasite, chabazite, erionite, mordenite, offretite, gmelinite, analcite, etc., ZSM-5 as described in U.S. Pat. No. 3,702,886.

20 Particularly suitable catalysts are found among the medium and small pore zeolites. Such medium pore zeolites are considered to have a Constraint Index from about 1 to about 12. The method by which Constraint Index is determined is described fully in U.S. Pat. No. 4,016,218. Zeolites which conform to the specified values of Constraint Index for medium pore
25 zeolites include ZSM-5, ZSM-11, ZSM-5/ZSM-11 intermediate, ZSM-12, ZSM-21, ZSM-22, ZSM-23, ZSM-35, ZSM-38, ZSM-48, ZSM-50, MCM-22 and zeolite- β which are described, for example, in U.S. Pat. Nos. 3,702,886 and Re. No. 29,949, 3,709,979, 3,832,449, 4,046,859, 4,556,447, 4,076,842, 4,016,245, 4,229,424, 4,397,827, 4,954,325, 3,308,069, Re. 28,341 and EP

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127,399 to which reference is made for details of these catalysts. These zeolites may be produced with differing silica to alumina molar ratios ranging from 12:1 upwards. They have been, in fact, produced from reaction mixtures from which alumina is intentionally excluded, so as to produce materials
5 having extremely high silica to alumina ratios which, in theory at least may extend up to infinity. Preferred medium pore zeolites include ZSM-5, ZSM-11, ZSM-12, ZSM-22, ZSM-35 and MCM-22. Particularly preferred is ZSM-5. Small pore zeolites, include such crystalline aluminosilicate zeolites as erionite, chabazite, phillipsite, and such synthetic counterparts thereof as
10 zeolites A and ZK5, as described in U.S. Pat. Nos. 2,882,243 and 3,247,195, respectively.

Preferably the zeolite catalyst is selected from the group consisting of faujasite, chabazite, erionite, mordenite, offretite, gmelinite, analcite, phillipsite, ZSM-5, ZSM-11, ZSM-5/ZSM-11 intermediate, ZSM-12, ZSM-21,
15 ZSM-22, ZSM-23, ZSM-35, ZSM-38, ZSM-48, ZSM-50, MCM-22, gallium silicate zeolite, zeolite- β , zeolite-rho, ZK5, and titanosilicate, and zeolites having a silica to alumina molar ratio within the range of about 2.0:1 to 2,000:1 ferrosilicate; borosilicate zeolite such as those described in Belgian Pat. No. 859656. (4584091) and zeolites designated by the Linde Division of
20 Union Carbide by the letters of X, Y, A, L. An especially favored zeolite is ZSM-5. Preparation of suitable zeolite containing catalysts may be prepared as described in the preceding references or purchased from commercial suppliers well known to those skilled in the art.

The cracking procedure can be carried out with any conventional
25 equipment, which can be a fixed bed, moving bed, fluidized bed, such as a riser or dense fluid bed system or stationary fluid bed system, and with typical hydrocarbon feed streams. Preferably the catalyst is contacted at a temperature within the range of 500°C to 750°C; more preferably in the range of 550°C to 725°C; most preferably in the range of 600°C to 700°C. The

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reactor temperature gradient preferably will be in the range of 10° to 150°C, more preferably in the range of 50°C to 100°C; most preferably in the range of about 60°C to 80°C. The gradient may be uniform across a portion of the catalyst bed, where each downstream portion is at a slightly higher temperature than the adjacent upstream portion. Alternatively the gradient may be non-uniform, wherein the temperature of a downstream zone is higher than the temperature of an upstream zone. The process is preferably carried out at a weight hourly space velocity (WHSV) in the range of about 0.1 Hr⁻¹ WHSV to about 100 Hr⁻¹ WHSV, more preferably in the range of about 1.0 Hr⁻¹ WHSV to about 50 Hr⁻¹ WHSV, most preferably in the range of about 1.0 Hr⁻¹ WHSV to about 30 Hr⁻¹ WHSV.

Examples of hydrocarbon streams which may be used to obtain high yields of light olefins include ethane, propane, butane, naphthas, gasoils, Fischer-Tropsch liquids, and streams containing olefins or diolefins such as butenes, butadiene, steam cracked naphtha, cat cracked naphtha and coker naphtha and kerosene. A preferred feedstock is light cat naphtha (LCN) or light virgin naphtha (LVN).

An alternative embodiment to a positive temperature gradient within a single reaction vessel is the use of a plurality of reactors in series with at least one down stream reactors maintained at a higher temperature than the upstream reactor. In this alternative embodiment, one may use several reactors to approximate a uniform gradient, or may make large temperature steps between olefin production reactors. The catalyst in each reactor may be the same or different depending on the preferred product mix to be obtained. By choice of catalyst and magnitude of the temperature gradient selection between ethylene and propylene can be improved.

Example 1

A series of runs in a small bench reactor was conducted on a light cat naphtha. A control run was conducted at 650°C, 1.9 Hr⁻¹ WHSV over a fixed bed of 2.4 g ZCAT40, a ZSM-5 zeolite catalyst commercially available from Intercat, Inc. of Sea Girt, New Jersey. Prior to the cracking tests, ZCAT40 was steamed with 100% steam, at 704°C and one atmosphere for 16 hours to age the catalyst. In the test runs, steam to hydrocarbon weight ratio of 0.85 was used while reactor pressure was controlled at 6 psig. The effluent stream was analyzed by on-line gas chromatography. A 60 meter column packed with fused silica in a dual FID Hewlett-Packard Model 5880A GAS Chromatograph was used for the analysis. Test runs were conducted with the same feedstock at 1.9 Hr⁻¹ WHSV and 2.5 Hr⁻¹ WHSV over two fixed beds the first stage at 610°C and the second at 680°C.

The data for key product yields are illustrated in Table 1. The 65°C positive temperature gradient results in an increase to 32.0 Wt. % yield for ethylene compared to an average about 26.9 Wt. % at a uniform 650°C. The propylene yield in this run is slightly lower, about 21.7 Wt. % compared to 23.2 Wt. % at the uniform temperature. The run at 2.5 Hr⁻¹ WHSV and slightly less catalyst demonstrates that selectivity for propylene is a function of temperature and residence time (other factors being held constant). In the 2.5 Hr⁻¹ WHSV run, ethylene yield dropped to 28.3% while propylene rose to 30.9% with a small penalty in conversion reflecting the shorter residence time. These data show the advantage of the invention over the uniform temperature reactions of the prior art.

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Table 1 EFFECT OF TEMPERATURE GRADIENT ON KEY PRODUCT YIELDS			
WHSV Hr ⁻¹	1.9	1.9	2.5
Temperature Profile	650-650	608-680	615-680
Conversion, Wt. %	95.9	98.4	91.4
KEY PRODUCTS Wt %			
Ethylene	26.9	32.0	28.3
Propylene	23.2	21.7	30.9
Butylenes	7.0	4.7	8.8
Aromatics	21.1	21.8	11.9
Light Saturates	17.8	18.2	11.5
Methane	6.9	6.8	4.0
Ethylene + Propylene	50.1	53.7	59.2

Example 2

An additional series of runs in a small bench reactor as described for example 1 were conducted on the hexane model compound. The conditions were as described in Example 1 except the weight hourly space velocity was 12 hr.⁻¹ Reactor pressure was 6 psig while steam to hydrocarbon ratio was maintained at 0.33.

As can be seen from Table 2, there are significant light olefin yield benefits for staging of catalyst bed reaction temperature. When the first half of the bed was operated at 610°C and the second half at 680°C, the ethylene yield was 28.9 wt. % while propylene yield was 31.9 wt. %. These yields compare favorably to the yields obtained when the bed was operated isothermally, which ranged from 15.6 to 26.4 wt. % in ethylene and 21.1 to 23.5 wt. % in propylene.

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Table 2				
Temperature, °C	610	650	680	Staged 610→680
Conversion, wt. %	93.1	96.9	97.8	96.8
Key Product Yields, wt. %				
Ethylene	15.6	27.7	26.4	28.9
Propylene	21.1	27.4	23.5	31.9
Butenes	10.3	8.6	6.8	9.6
Aromatics	22.6	19.8	23.1	14.9
Light Saturates	23.5	13.4	18.0	11.5
Methane	2.0	4.5	8.2	2.8
Ethylene + Propylene	36.7	45.1	49.9	60.8

The preceding examples are presented to illustrate the invention and not as limitations. There are many variations on the invention that will be apparent to those skilled in the art. The invention is defined and limited by

5 the claims set out below.

**CLAIMS**

We claim:

1. A process for improving the conversion of a hydrocarbon to light olefins comprising:
5 contacting a hydrocarbon feedstock with a cracking catalyst in a reactor operated at a positive temperature gradient.

2. In a process for producing ethylene and propylene in a catalytic cracking process wherein a hydrocarbon feedstock is contacted with a
10 cracking catalyst, the improvement which comprises providing a first catalyst contact zone at a first temperature and providing a second catalyst contact zone at a second temperature downstream from the first catalyst contact zone and maintaining the second catalyst contact zone at a higher temperature than the first catalyst contact zone and
15 passing cracked hydrocarbon feedstock from the first catalyst contact zone to the second catalyst contact zone.

3. In a process for producing ethylene and propylene in a catalytic cracking process wherein a hydrocarbon feedstock is contacted with a
20 cracking catalyst, the improvement which comprises providing a first catalyst contact zone at a first temperature and providing a second catalyst contact zone at a second temperature downstream from the first catalyst contact zone and maintaining the second catalyst contact zone at a higher temperature than the first catalyst contact zone and
25 passing cracked hydrocarbon feedstock from the first catalyst contact zone to the second catalyst contact zone wherein the first catalyst contact zone is at a temperature within the range of about 500°C to about 750°C, the second catalyst contact zone is at a temperature in



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the range of 10°C to 150°C higher than the temperature of the first catalyst contact zone and the feedstock flows at a weight hourly space velocity in the range of about 0.1 Hr⁻¹ WHSV to about 100 Hr⁻¹ WHSV.

- 5 4. The process of claim 2 or 3 wherein the first catalyst contact zone is at a temperature within the range of about 500°C to about 750°C, the second catalyst contact zone is at a temperature in the range of 10°C to 150°C higher than the temperature of the first catalyst contact zone and the feedstock flows at a weight hourly space velocity in the range of about 0.1 Hr⁻¹ WHSV to about 100 Hr⁻¹ WHSV.
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5. The process of claim 2 or 3 wherein the catalyst is contacted at a first catalyst contact zone temperature within the range of 600°C to 700°C and the feedstock flows at a weight hourly space velocity in the range of 1.0 Hr⁻¹ WHSV to 30 Hr⁻¹ WHSV.
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6. The process of claim 2 or 3 wherein the temperature increase between the first catalyst contact zone and the second catalyst contact zone forms a uniform gradient.
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7. The process of claim 2 or 3 wherein the temperature increase between the first catalyst contact zone and the second catalyst contact zone forms a uniform gradient.
- 25 8. The process of any of the preceding claims wherein the cracking catalyst comprises a zeolite having a silica to alumina ratio within the range of about 2.0:1 to 2,000:1.



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9. The process of any of the preceding claims wherein the zeolite is selected from the group consisting of phillipsite, heulandite, mazzite, ferrierite, faujasite, chabazite, erionite, mordenite, offretite, gmelinite, analcite, ZSM-5, ZSM-11, ZSM-5/ZSM-11 intermediate, ZSM-12, ZSM-18, ZSM-21, ZSM-22, ZSM-23, ZSM-35, ZSM-38, ZSM-48, ZSM-50, MCM-22, gallium silicate zeolite, zeolite β , zeolite rho, ZK5, titanosilicate, ferrosilicate, borosilicate, zeolites designated by the Linde Division of Union Carbide by the letters of X, Y, A, L.
10. The process of claims 1 through 7 wherein the catalyst comprises ZSM-5.
11. The process of claims 1 through 7 wherein the catalyst comprises ZCAT40.
12. The process of any of the preceding claims wherein the feedstock is selected from the group consisting of ethane, propane, butane, naphthas, gasoils, Fischer-Tropsch liquids, butenes, butadiene, steam cracked naphtha, cat cracked naphtha, coker naphtha, and kerosene.
13. The process of any of the preceding claims wherein the catalyst is contacted in a reactor having a catalyst contact entry zone and a catalyst contact exit zone and the catalyst contact entry zone temperature is within the range of 500°C to 750°C and the catalyst contact exit zone is maintained at a temperature in the range of 10° to 150° higher than the catalyst contact entry zone temperature and the



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feedstock flows at a weight hourly space velocity in the range of 0.1 Hr⁻¹ WHSV to 100 Hr⁻¹ WHSV.

- 5 14. The process of any of the preceding claims wherein the catalyst is contacted at an entry temperature within the range of 550°C to 725°C.
15. The process of any of the preceding claims wherein the feedstock flow is in the range of 1.0 Hr⁻¹ WHSV to 50 Hr⁻¹ WHSV.
- 10 16. The process of any of the preceding claims wherein the catalyst is contacted at an entry temperature within the range in the range of 600°C to 700°C.
- 15 17. The process of any of the preceding claims wherein the feedstock flow is in the range of 1.0 Hr⁻¹ WHSV to 30 Hr⁻¹ WHSV.
18. The process of any of the preceding claims wherein the temperature increase forms a uniform gradient.