PCT WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ^{6} **:**
C10G 11/02, 11/04, 11/05, C07C 4/02, 4/06
A1

(11) International Publication Number: **WO 99/57225**

(43) International Publication Date: 11 November 1999 (11.11.99)

(21) International Application Number: PCT/US99/09111

(22) International Filing Date: 27 April 1999 (27.04.99)

(30) Priority Data:
09/073,083 5 May 1998 (05.05.98) US

(71) Applicant: EXXON RESEARCH AND ENGINEERING COMPANY [US/US]; 180 Park Avenue, P.O. Box 390, Florham Park, NJ 07932-0390 (US).

(72) Inventors: LADWIG, Paul, Kevin; 9 Cottonwood Drive, Randolph, NJ 07869 (US). ASPLIN, John, Ernest; 18822 Windward Lane, Houston, TX 77058 (US). STUNTZ, Gordon, Frederick; 12217 Lake Lingham Circle, Baton Rouge, LA 70816 (US). CHEN, Tan-Jen; 5615 Lofty Magnolia Court, Kingwood, TX 77345 (US).

(74) Agents: NAYLOR, Henry, E. et al.; Exxon Research and Engineering Company, P.O. Box 390, Florham Park, NJ 07932-0390 (US).

(81) Designated States: AL, AU, BA, BB, BG, BR, CA, CN, CU, CZ, EE, GE, HR, HU, ID, IL, IN, IS, JP, KP, KR, LC, LK, LR, LT, LV, MG, MK, MN, MX, NO, NZ, PL, RO, SG, SI, SK, SL, TR, TT, UA, UZ, VN, YU, ZA, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published
With international search report.

(54) Title: PROCESS FOR SELECTIVELY PRODUCING C_3 OLEFINS IN A FLUID CATALYTIC CRACKING PROCESS

(57) Abstract

A process for selectively producing olefins containing 3 carbons from a catalytically cracked or thermally cracked naphtha stream. The process involves reacting the cracked naphtha in the presence of a catalyst containing from about 10 to 50 wt.% of a crystalline zeolite having an average pore diameter less than about 0.7 nanometers, stripping the catalyst, regenerating the catalyst and fractionating the reaction products. Process conditions include temperatures ranging from about 500–650 degrees celsius and a hydrocarbon partial pressure from about 10 to 40 psia.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania
AM	Armenia
AT	Austria
AU	Australia
AZ	Azerbaijan
BA	Bosnia and Herzegovina
BB	Barbados
BE	Belgium
BF	Burkina Faso
BG	Bulgaria
BJ	Benin
BR	Brazil
BY	Belarus
CA	Canada
CF	Central African Republic
CG	Congo
CH	Switzerland
CI	Côte d'Ivoire
CM	Cameroon
CN	China
CU	Cuba
CZ	Czech Republic
DE	Germany
DK	Denmark
EE	Estonia
ES	Spain
FI	Finland
FR	France
GA	Gabon
GB	United Kingdom
GE	Georgia
GH	Ghana
GN	Guinea
GR	Greece
HU	Hungary
IE	Ireland
IL	Israel
IS	Iceland
IT	Italy
JP	Japan
KE	Kenya
KG	Kyrgyzstan
KP	Democratic People's Republic of Korea
KR	Republic of Korea
KZ	Kazakstan
LC	Saint Lucia
LI	Liechtenstein
LK	Sri Lanka
LR	Liberia
LS	Lesotho
LT	Lithuania
LU	Luxembourg
LV	Latvia
MC	Monaco
MD	Republic of Moldova
MG	Madagascar
MK	The former Yugoslav Republic of Macedonia
ML	Mali
MN	Mongolia
MR	Mauritania
MW	Malawi
MX	Mexico
NE	Niger
NL	Netherlands
NO	Norway
NZ	New Zealand
PL	Poland
PT	Portugal
RO	Romania
RU	Russian Federation
SD	Sudan
SE	Sweden
SG	Singapore
SI	Slovenia
SK	Slovakia
SN	Senegal
SZ	Swaziland
TD	Chad
TG	Togo
TJ	Tajikistan
TM	Turkmenistan
TR	Turkey
TT	Trinidad and Tobago
UA	Ukraine
UG	Uganda
US	United States of America
UZ	Uzbekistan
VN	Viet Nam
YU	Yugoslavia
ZW	Zimbabwe

PROCESS FOR SELECTIVELY PRODUCING C_3 OLEFINS IN A FLUID CATALYTIC CRACKING PROCESS

FIELD OF THE INVENTION

The present invention relates to a process for selectively producing C_3 olefins from a catalytically cracked or thermally cracked naphtha stream. The naphtha stream is introduced into a process unit comprised of a reaction zone, a stripping zone, a catalyst regeneration zone, and a fractionation zone. The naphtha feedstream is contacted in the reaction zone with a catalyst containing from about 10 to 50 wt.% of a crystalline zeolite having an average pore diameter less than about 0.7 nanometers at reaction conditions which include temperatures ranging from about 500 to 650°C and a hydrocarbon partial pressure from about 10 to 40 psia. Vapor products are collected overhead and the catalyst particles are passed through the stripping zone on the way to the catalyst regeneration zone. Volatiles are stripped with steam in the stripping zone and the catalyst particles are sent to the catalyst regeneration zone where coke is burned from the catalyst, which is then recycled to the reaction zone. Overhead products from the reaction zone are passed to a fractionation zone where a stream of C_3's is recovered and a stream rich in C_4 and/or C_5 olefins is recycled to the stripping zone.

BACKGROUND OF THE INVENTION

The need for low emissions fuels has created an increased demand for light olefins for use in alkylation, oligomerization, MTBE and ETBE synthesis processes. In addition, a low cost supply of light olefins, particularly propylene, continues to be in demand to serve as feedstock for polyolefin, particularly polypropylene production.

Fixed bed processes for light paraffin dehydrogenation have recently attracted renewed interest for increasing olefin production. However, these types of processes typically require relatively large capital investments as well as high operating costs. It is therefore advantageous to increase olefin yield using processes, which require relatively small capital investment. It would be particularly advantageous to increase olefin yield in catalytic cracking processes.

U.S. Patent No. 4,830,728 discloses a fluid catalytic cracking (FCC) unit that is operated to maximize olefin production. The FCC unit has two separate risers into which a different feed stream is introduced. The operation of the risers is designed so that a suitable catalyst will act to convert a heavy gas oil in one riser and another suitable catalyst will act to crack a lighter olefin/naphtha feed in the other riser. Conditions within the heavy gas oil riser can be modified to maximize either gasoline or olefin production. The primary means of maximizing production of the desired product is by using a specified catalyst.

Also, U.S. Pat. No. 5,026,936 to Arco teaches a process for the preparation of propylene from C_4 or higher feeds by a combination of cracking and metathesis wherein the higher hydrocarbon is cracked to form ethylene and propylene and at least a portion of the ethylene is metathesized to propylene. See also, U.S. Pat. Nos. 5,026,935; 5,171,921 and 5,043,522.

U.S. Patent No. 5,069,776 teaches a process for the conversion of a hydrocarbonaceous feedstock by contacting the feedstock with a moving bed of a zeolitic catalyst comprising a zeolite with a pore diameter of 0.3 to 0.7 nm, at a temperature above about 500°C and at a residence time less than about 10 seconds. Olefins are produced with relatively little saturated gaseous hydrocarbons being formed. Also, U.S.Patent No. 3,928,172 to Mobil teaches a process for converting hydrocarbonaceous feedstocks wherein olefins are produced by reacting said feedstock in the presence of a ZSM-5 catalyst.

A problem inherent in producing olefin products using FCC units is that the process depends on a specific catalyst balance to maximize production of light olefins while also achieving high conversion of the 650°+F feed components. In addition, even if a specific catalyst balance can be maintained to maximize overall olefin production, olefin selectivity is generally low due to undesirable side reactions, such as extensive cracking, isomerization, aromatization and hydrogen transfer reactions. Light saturated gases produced from undesirable side reactions result in increased costs to recover the desirable light olefins. Therefore, it is desirable to maximize olefin production in a process that allows a high degree of control over the selectivity of C_3 and C_4 olefins.

SUMMARY OF THE INVENTION

In accordance with the present invention there is provided a process for selectively producing C_3 olefins from a naphtha feedstream in a process unit comprised of a reaction zone, a stripping zone, a catalyst regeneration zone, and a fractionation zone. The naphtha stream is contacted in the reaction zone that contains a bed of catalyst, preferably in the fluidized state. The catalyst is comprised of a zeolite having an average pore diameter of less than about 0.7 nm and wherein the reaction zone is operated at a temperature from about 500° to 650°C, a hydrocarbon partial pressure of 10 to 40 psia, a hydrocarbon residence time of 1 to 10 seconds, and a catalyst to feed ratio of about 2 to 10, thereby producing a reaction product wherein no more than about 20 wt.% of paraffins are converted to olefins. The catalyst is passed from the reaction zone through a stripping zone where volatiles are stripped by use of steam, then passed to a catalyst regeneration zone where any coke deposits are burned in the presence of an oxygen containing gas. The regenerated catalyst is recycled to the reaction zone where it contacts fresh feed. The reaction product is sent to a fractionation zone wherein a C_3 fraction and a C_4 fraction are produced. The C_3 fraction is recovered and a C_4 and/or a C_5 fraction rich in olefins is recycled to either the stripping zone or to the reaction zone.

In another preferred embodiment of the present invention the catalyst is a ZSM-5 type catalyst.

In a preferred embodiment of the present invention a C_5 fraction rich in olefins is also recycled.

In still another preferred embodiment of the present invention the feedstock contains about 10 to 30 wt.% paraffins, and from about 20 to 70 wt.% olefins.

In yet another preferred embodiment of the present invention the reaction zone is operated at a temperature from about 525°C to about 600°C.

DETAILED DESCRIPTION OF THE INVENTION

Feedstreams which are suitable for producing the relatively high C_2, C_3, and C_4 olefin yields are those streams boiling in the naphtha range and containing from about 5 wt.% to about 35 wt.%, preferably from about 10 wt.% to about 30 wt.%, and more preferably from about 10 to 25 wt.% paraffins, and from about 15 wt.%, preferably from about 20 wt.% to about 70 wt.% olefins. The feed may also contain naphthenes and aromatics. Naphtha boiling range streams are typically those having a boiling range from about 65°F to about 430°F, preferably from about 65°F to about 300°F. The naphtha can be a thermally cracked or a catalytically cracked naphtha. Such streams can be derived from any appropriate source, for example, they can be derived from the fluid catalytic cracking (FCC) of gas oils and resids, or they can be derived from delayed or fluid coking of resids. It is preferred that the naphtha streams used in the practice of the present invention be derived from the fluid catalytic cracking of gas oils and resids. Such naphthas are typically rich in olefins and/or diolefins and relatively lean in paraffins. It is within the scope of the instant invention that other olefinic streams that are not catalytically or thermally cracked naphthas, such as an MTBE raffinate, be co-fed into said reaction zone with the primary feed. It is believed that this will increase the yield of propylene.

The process of the present invention is performed in a process unit comprised of a reaction zone, a stripping zone, a catalyst regeneration zone, and a fractionation zone. The naphtha feedstream is fed into the reaction zone where it contacts a source of hot, regenerated catalyst. The hot catalyst vaporizes and cracks the feed at a temperature from about 500°C to 650°C, preferably from about 525°C to 600°C. The cracking reaction deposits carbonaceous hydrocarbons, or coke, on the catalyst, thereby deactivating the catalyst. The cracked products are separated from the coked catalyst and sent to a fractionator. The coked catalyst is passed through the stripping zone where volatiles are stripped from the catalyst particles with steam. The stripping can be preformed under low severity conditions in order to retain adsorbed hydrocarbons for heat balance. The stripped catalyst is then passed to the regeneration zone where it is regenerated by burning coke on the catalyst in the presence of an oxygen containing gas, preferably air. Decoking restores catalyst activity and simultaneously heats the catalyst to a temperature from about 650°C to about 750°C. The hot catalyst is then recycled to the reaction zone to react with fresh naphtha feed. Flue gas formed by burning coke in the regenerator may be treated for removal of particulates and for conversion of carbon monoxide, after which the flue gas is normally discharged into the atmosphere. The cracked products from the reaction zone are sent to a fractionation zone where various products are recovered, particularly a C_3 fraction, a C_4 fraction, and optionally a C_5 fraction. The C_4 fraction and the C_5 fraction will typically be rich in olefins. One or both of these fractions can be recycled to the reactor. They can be recycled to either the main section of the reactor, or a riser section, or a stripping section. It is preferred that they be recycled to the upper part of the stripping section, or stripping zone. Recycling one or both of these fractions will convert at least a portion of these olefins to propylene.

While attempts have been made to increase light olefins yields in the FCC process unit itself, the practice of the present invention uses its own distinct process unit, as previously described, which receives naphtha from a suitable source in the refinery. The reaction zone is operated at process conditions that will maximize C_2 to C_4 olefin, particularly propylene, selectivity with relatively high conversion of C_5+ olefins. Catalysts suitable for use in the practice of the present invention are those which are comprised of a crystalline zeolite having an average pore diameter less than about 0.7 nanometers (nm), said crystalline zeolite comprising from about 10 wt.% to about 50 wt.% of the total fluidized catalyst composition. t is preferred that the crystalline zeolite be selected from the family of medium pore size (< 0.7 nm) crystalline aluminosilicates, otherwise referred to as zeolites. Of particular interest are the medium pore zeolites with a silica to alumina molar ratio of less than about 75:1, preferably less than about 50:1, and more preferably less than about 40:1. The pore diameter also sometimes referred to as effective pore diameter can be measured using standard adsorption techniques and hydrocarbonaceous compounds of known minimum kinetic diameters. See Breck, *Zeolite Molecular Sieves,* 1974 and Anderson et al., J. Catalysis 58, 114 (1979), both of which are incorporated herein by reference.

Medium pore size zeolites that can be used in the practice of the present invention are described in "Atlas of Zeolite Structure Types", eds. W. H. Meier and D.H. Olson, Butterworth-Heineman, Third Edition, 1992, which is hereby incorporated by reference. The medium pore size zeolites generally have a pore size from about 5Å, to about 7Å and include for example, MFI, MFS, MEL, MTW, EUO, MTT, HEU, FER, and TON structure type zeolites (IUPAC Commission of Zeolite Nomenclature). Non-limiting examples of such medium pore size zeolites, include ZSM-5, ZSM-12, ZSM-22, ZSM-23, ZSM-34, ZSM-35, ZSM-38, ZSM-48, ZSM-50, silicalite, and silicalite 2. The most preferred is ZSM-5, which is described in U.S. Patent Nos. 3,702,886 and 3,770,614. ZSM-11 is described in U.S. Patent No. 3,709,979; ZSM-12 in U.S. Patent No. 3,832,449; ZSM-21 and ZSM-38 in U.S. Patent No. 3,948,758; ZSM-23 in U.S. Patent No. 4,076,842; and ZSM-35 in U.S. Patent No. 4,016,245. All of the above patents are incorporated herein by reference. Other suitable medium pore size zeolites include the silicoaluminophosphates (SAPO), such as SAPO-4 and SAPO-11 which is described in U.S. Patent No. 4,440,871; chromosilicates; gallium silicates; iron silicates; aluminum phosphates (ALPO), such as ALPO-11 described in U.S. Patent No. 4,310,440; titanium aluminosilicates (TASO), such as TASO-45 described in EP-A No. 229,295; boron silicates, described in U.S. Patent No. 4,254,297; titanium aluminophosphates (TAPO), such as TAPO-11 described in U.S. Patent No. 4,500,651; and iron aluminosilicates. In one embodiment of the present invention the Si/Al ratio of said zeolites is greater than about 40.

The medium pore size zeolites can include "crystalline admixtures" which are thought to be the result of faults occurring within the crystal or crystalline area during the synthesis of the zeolites. Examples of crystalline admixtures of ZSM-5 and ZSM-11 are disclosed in U.S. Patent No. 4,229,424 which is incorporated herein by reference. The crytalline admixtures are themselves medium pore size zeolites and are not to be confused with physical admixtures of zeolites in which distinct crystals of crystallites of different zeolites are physically present in the same catalyst composite or hydrothermal reaction mixtures.

The catalysts of the present invention are held together with an inorganic oxide matrix component. The inorganic oxide matrix component binds the catalyst components together so that the catalyst product is hard enough to survive interparticle and reactor wall collisions. The inorganic oxide matrix can be made from an inorganic oxide sol or gel which is dried to "glue" the catalyst components together. Preferably, the inorganic oxide matrix is not catalytically active and will be comprised of oxides of silicon and aluminum. It is also preferred that separate alumina phases be incorporated into the inorganic oxide matrix. Species of aluminum oxyhydroxides-g-alumina, boehmite, diaspore, and transitional aluminas such as a-alumina, b-alumina, g-alumina, d-alumina, e-alumina, k-alumina, and r-alumina can be employed. Preferably, the alumina species is an aluminum trihydroxide such as gibbsite, bayerite, nordstrandite, or doyelite. The matrix material may also contain phosphorous or aluminum phosphate.

Preferred process conditions include temperatures from about 500°C to about 650°C, preferably from about 500°C to 600°C; hydrocarbon partial pressures from about 10 to 40 psia, preferably from about 20 to 35 psia; and a catalyst to naphtha (wt/wt) ratio from about 3 to 12, preferably from about 4 to 10, where catalyst weight is total weight of the catalyst composite. It is also preferred that steam be concurrently introduced with the naphtha stream into the reaction zone, with the steam comprising up to about 50 wt.% of the hydrocarbon feed. Also, it is preferred that the naphtha residence time in the reaction zone be less than about 10 seconds, for example from about 1 to 10 seconds. The above conditions will be such that at least about 60 wt.% of the C_5+ olefins in the naphtha stream are converted to C_4- products and less than about 25 wt.%, preferably less than about 20 wt.% of the paraffins are converted to C_4- products, and that propylene comprises at least about 90 mol %, preferably greater than about 95 mol % of the total C_3 reaction products with the weight ratio of propylene/total C_2- products greater than about 3.5. It is also preferred that ethylene comprises at least about 90 mol % of the C_2 products, with the weight ratio of propylene:ethylene being greater than about 4, and that the "full range" C_5+ naphtha product is enhanced in both motor and research octanes relative to the naphtha feed. It is within the scope of this invention that the catalysts be precoked prior to introduction of feed in order to further improve the selectivity to propylene. It is also within the scope of this invention that an effective amount of single ring aromatics be fed to the reaction zone to also improve the selectivity of propylene vs ethylene. The aromatics may be from an external source such as a reforming process unit or they may consist of heavy naphtha recycle product from the instant process.

The following examples are presented for illustrative purposes only and are not to be taken as limiting the present invention in any way.

Examples 1-12

The following examples illustrate the criticality of process operating conditions for maintaining chemical grade propylene purity with samples of cat naphtha cracked over ZCAT-40 (a catalyst that contains ZSM-5) which had been steamed at 1500°F for 16 hrs to simulate commercial equilibrium. Comparison of Examples 1 and 2 show that increasing Cat/Oil ratio improves propylene yield, but sacrifices propylene purity. Comparison of Examples 3 and 4 and 5 and 6 shows reducing oil partial pressure greatly improves propylene purity without compromising propylene yield. Comparison of Examples 7 and 8 and 9 and 10 shows increasing temperature improves both propylene yield and purity. Comparison of Examples 11 and 12 shows decreasing cat residence time improves propylene yield and purity. Example 13 shows an example where both high propylene yield and purity are obtained at a reactor temperature and cat/oil ratio that can be achieved using a conventional FCC reactor/regenerator design for the second stage.

TABLE 1

Example	Feed Olefins, wt%	Temp. °C	Cat/Oil	Oil psia	Oil Res. Time, sec	Cat Res. Time, sec	Wt.% $C_3^=$	Wt.% C_3^-	Propylene Purity, %
1	38.6	566	**4.2**	36	0.5	4.3	11.4	0.5	95.8%
2	38.6	569	**8.4**	32	0.6	4.7	12.8	0.8	94.1%
3	22.2	510	8.8	**18**	1.2	8.6	8.2	1.1	88.2%
4	22.2	511	9.3	**38**	1.2	5.6	6.3	1.9	76.8%
5	38.6	632	16.6	**20**	1.7	9.8	16.7	1.0	94.4%
6	38.6	630	16.6	**13**	1.3	7.5	16.8	0.6	96.6%
7	22.2	**571**	5.3	27	0.4	0.3	6.0	0.2	96.8%
8	22.2	**586**	5.1	27	0.3	0.3	7.3	0.2	97.3%
9	22.2	**511**	9.3	38	1.2	5.6	6.3	1.9	76.8%
10	22.2	**607**	9.2	37	1.2	6.0	10.4	2.2	82.5%
11	22.2	576	18.0	32	1.0	**9.0**	9.6	4.0	70.6%
12	22.2	574	18.3	32	1.0	**2.4**	10.1	1.9	84.2%
13	38.6	606	8.5	22	1.0	7.4	15.0	0.7	95.5%

Table 1 Continued

Example	Wt.% $C_2^=$	Wt.% C_2^-	Ratio of $C_3^=$ to $C_2^=$	Ratio of $C_3^=$ to C_2^-	Wt.% $C_3^=$
1	2.35	2.73	**4.9**	**4.2**	11.4
2	3.02	3.58	**4.2**	**3.6**	12.8
3	2.32	2.53	3.5	3.2	8.2
4	2.16	2.46	2.9	2.6	6.3
5	6.97	9.95	2.4	1.7	16.7
6	6.21	8.71	2.7	1.9	16.8
7	1.03	1.64	**5.8**	**3.7**	6.0
8	1.48	2.02	**4.9**	**3.6**	7.3
9	2.16	2.46	2.9	2.6	6.3
10	5.21	6.74	2.0	1.5	10.4
11	4.99	6.67	1.9	1.4	9.6
12	4.43	6.27	2.3	1.6	10.1
13	4.45	5.76	3.3	2.6	15.0

$C_2^- = CH_4 + C_2H_4 + C_2H_6$

The above examples (1,2,7 and 8) show that $C_3^=/C_2^= > 4$ and $C_3^=/C_2^- > 3.5$ can be achieved by selection of suitable reactor conditions.

Examples 14 - 17

The cracking of olefins and paraffins contained in naphtha streams (e.g., FCC naphtha, coker naphtha) over small or medium pore zeolites such as ZSM-5 can produce significant amounts of ethylene and propylene. The selectivity to ethylene or propylene and selectivity of propylene to propane varies as a function of catalyst and process operating conditions. It has been found that propylene yield can be increased by co-feeding steam along with cat naphtha to the reactor. The catalyst may be ZSM-5 or other small or medium pore zeolites. Table 2 below illustrates the increase in propylene yield when 5 wt.% steam is co-fed with an FCC naphtha containing 38.8 wt.% olefins. Although propylene yield increased, the propylene purity is diminished. Thus, other operating conditions may need to be adjusted to maintain the targeted propylene selectivity.

TABLE 2

Example	Steam Co-feed	Temp. C	Cat/Oil	Oil psia	Oil Res. Time, sec	Cat Res. Time, sec	Wt% Propylene	Wt% Propane	Propylene Purity, %
14	No	630	8.7	18	0.8	8.0	11.7	0.3	97.5%
15	Yes	631	8.8	22	1.2	6.0	13.9	0.6	95.9%
16	No	631	8.7	18	0.8	7.8	13.6	0.4	97.1%
17	Yes	632	8.4	22	1.1	6.1	14.6	0.8	94.8%

Examples 18 - 21

ZCAT-40 was used to crack cat cracker naphtha as described for the above examples. The coked catalyst was then used to crack a C_4 stream composed of 6 wt.% n-butane, 9 wt.% i-butane, 47 wt.% 1-butene, and 38 wt.% i-butene in a reactor at the temperatures and space velocities indicated in the table below. As can be seen from the results in the table below, a significant fraction of the feed stream was converted to propylene.

TABLE 3

WHSV, Hr-1	35	18	12	6
Temperature °C	575	575	575	575
Butylene Conversion wt.%				
Product Yields, wt.%				
Ethylene	2.4	4.7	5.9	8.8
Propylene	20.5	27.1	28.8	27.4
Butylenes	39.7	29.0	25.5	19.2
C_1-C_4 Light Saturates	18.2	19.2	19.8	22.0
C_5+ Products	19.3	20.0	20.0	22.6

CLAIMS:

1. A process for selectively producing C_3 olefins from a naphtha feedstream in a process unit comprised of a reaction zone, a stripping zone, a catalyst regeneration zone, and a fractionation zone, which process comprises:

a) reacting the naphtha stream in the reaction zone containing a fluidized bed of catalyst comprised of a zeolite having an average pore diameter of less than about 0.7 nm and wherein the reaction zone is operated at a temperature from about 500° to 650°C, a hydrocarbon partial pressure of 10 to 40 psia, a hydrocarbon residence time of 1 to 10 seconds, and a catalyst to feed ratio of about 2 to 10, thereby producing a reaction product wherein no more than about 20 wt.% of paraffins are converted to olefins;

b) passing the catalyst through a stripping zone where volatiles are stripped by use of a stripping medium;

c) passing the stripped catalyst from the stripping zone to a catalyst regeneration zone where any coke deposits are burned in the presence of an oxygen containing gas;

d) recycling the regenerated catalyst to the reaction zone where it contacts fresh feed;

e) fractionating the vapor product stream to produce a C_3 fraction, a C_4 fraction rich in olefins, and optionally a C_5 fraction rich in olefins; and

f) passing the C_4 fraction to the reaction zone or the stripping zone, or both.

2. The process of claim 1 wherein the crystalline zeolite is selected from the ZSM series.

3. The process of claim 2 wherein the crystalline zeolite is ZSM-5.

4. The process of claim 2 wherein the naphtha feedstock contains from about 10 to 30 wt.% paraffins and about 15 to 70 wt.% olefins.

5. The process of claim 4 wherein the reaction temperature is from about 500°C to about 600°C.

6. The process of claim 4 wherein at least about 60 wt.% of the C_5 + olefins in the feedstream is converted to C_4- products and less than about 25 wt.% of the paraffins are converted to C_4- products.

7. The process of claim 6 wherein propylene comprises at least about 90 mol. % of the total C_3 products.

8. The process of claim 7 wherein the weight ratio of propylene to total C_2- products is greater than about 3.5.

9. The process of claim 1 wherein a C_5 fraction rich is olefins is also produced and is recycled to the reaction zone, the stripping zone, or both.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US99/09111

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :C10G 11/02, 11/04, 11/05; C07C 4/02, 4/06
US CL : 208/118, 120.01, 122; 585/648, 651, 654
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. : 208/118, 120.01, 122; 585/648, 651, 654

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.
Y,P	US 5,846,403 A (SWAN ET AL.) 08 December 1998 (08/12/98), see column 2, lines 46-47 and 53-59, column 4, lines 35-46 and column 6, lines line 61.	1-9
Y	US 5,043,522 A (LEYSHON ET AL.) 27 August 1991 (27/08/91), see column 2, lines 59-69.	1-9
Y	US 5,059,735 A (NEMET-MAVRODIN) 22 October 1991 (22/10/91), see column 3, lines 31-67 and column 6, lines 7-8.	3-8
A	US 4,918,256 A (NEMET-MAVRODIN) 17 April 1990 (17/04/90), see entire document.	1-9
A	US 3,812,029 A (SNYDER, JR.) 21 May 1974 (21/05/74), see entire document.	1-9

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

*	Special categories of cited documents:
"A"	document defining the general state of the art which is not considered to be of particular relevance
"E"	earlier document published on or after the international filing date
"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)
"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
"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
"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
"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&"	document member of the same patent family

Date of the actual completion of the international search 21 MAY 1999	Date of mailing of the international search report 04 JUN 1999
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 305-3230	Authorized officer NADINE PREISCH Telephone No. (703) 308-0661

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4,251,348 A (O'REAR ET AL.) 17 February 1981 (17/02/81), see entire document.	1-9
A	US 4,282,085 A (O'REAR ET AL.) 04 August 1981 (04/08/81), see entire document.	1-9
A	US 4,324,688 A (CASTAGNOS, JR. ET AL.) 13 April 1982 (13/04/82), see entire document.	1-9
A	US 4,370,222 A (MCGOVERN ET AL.) 25 January 1983 (25/01/83), see entire document.	1-9
A	US 4,385,985 A (GROSS ET AL.) 31 May 1983 (31/05/83), see entire document.	1-9
A	US 4,863,585 A (HERBST ET AL.) 05 September 1989 (05/09/89), see entire document.	1-9
A	US 4,980,053 A (LI ET AL.) 25 December 1990 (25/12/90), see entire document.	1-9
A	US 5,055,176 A (HERBST ET AL.) 08 October 1991 (08/10/91), see entire document.	1-9
A	US 5,286,370 A (CHU ET AL.) 15 February 1994 (15/02/94), see entire document.	1-9
A	US 5,348,642 A (SERRAND ET AL.) 20 September 1994 (20/09/94), see entire document.	1-9
A	US 5,389,232 A (ADEWUYI ET AL.) 14 February 1995 (14/02/95), see entire document.	1-9
A	US 5,549,813 A (DAI ET AL.) 27 August 1996 (27/08/96), see entire document.	1-9
A	US 5,670,037 A (ZAITING ET AL.) 23 September 1997 (23/09/97), see entire document.	1-9
A, P	US 5,846,402 A (MANDAL ET AL.) 08 December 1998 (08/12/98,) see entire document.	1-9
Y	US 5,723,040 A (LETZSCH ET AL.) 03 March 1998 (03/03/98), see column 6, lines 63-69.	1-9