PROCESS FOR SELECTIVELY PRODUCING C3? OLEFINs IN A FLUID CATALYTIC CRACKING PROCESS

VERFAHREN ZUR SELEKTIVEN PRODUKTION VON C3-OLEFINEN IN EINEM FLÜSSIG-KATALYTISCHEN KRACKING-PROZESS

PROCEDE RELATIF A LA PRODUCTION SELECTIVE D’OLEFINES C 3? DANS UN PROCESSUS DE CRAQUAGE CATALYTIQUE FLUIDE
Description

FIELD OF THE INVENTION

[0001] The present invention relates to a process for selectively producing C3 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 10 to 50 wt.% of a crystalline zeolite having an average pore diameter less than 0.7 nanometers at reaction conditions which include temperatures ranging from 500 to 650°C and a hydrocarbon partial pressure from 69 to 276 kPa (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 C3's is recovered and a stream rich in C4 and/or C5 olefins is recycled to the stripping zone.

BACKGROUND OF THE INVENTION

[0002] 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.

[0003] 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.

[0004] US-A-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.

[0005] Also, US-A-5,026,936 to Arco teaches a process for the preparation of propylene from C4 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, US-A-5,026,935; 5,171,921 and 5,043,522.

[0006] US-A-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, US-A-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.

[0007] The above-mentioned US-A-5 043 522 teaches a process for the conversion of saturated paraffin hydrocarbons having 4 or more carbon atoms to olefins having fewer carbon atoms. The feedstock is a mixture of 40 to 95 wt % paraffin hydrocarbons and 5 to 60 wt % olefins, which is contacted with a solid zeolitic catalyst such as ZSM-5 at conditions effective to form propylene.

[0008] Larry H. Hsing and Roy E. Pratt: "Cracking of FC and Coker Naphthas by ZSM-5 Catalyst and Equilibrium FC Catalyst" Preprints, vol. 39, no. 3, July 1994 (1994-07), pages 388-392, American Chemical Society, Washington, DC. US ISSN: 0569-3799 discusses the upgrading of naphtha streams to meet reformulated gasoline requirements. The paper demonstrates that Fluid Cracked Naphtha and Coker Naptha may be upgraded by ZSM-5 cracking to generate additional olefins. The cracked products have increased octane numbers.

[0009] US-A-3 974 062 discloses a process for the catalytic cracking of a full-boiling range oil mixed with a low molecular weight carbon-hydrogen fragment contributor comprising methanol optionally in admixture with C2-C3 olefins. The feed is contacted with a crystalline zeolite cracking catalyst under conversion conditions comprising a temperature of 427-760°C (800-1400°F) and a residence time of 0.5 to 12 seconds.

[0010] 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 343°+C (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,
SUMMARY OF THE INVENTION

[0011] 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 contains from 5 to 35 wt.% paraffins and from 15 to 70 wt.% olefins and 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 0.7 nm and the reaction zone is operated at a temperature from 500° to 650°C, a hydrocarbon partial pressure of 69 to 276 kPa (10 to 40 psia), a hydrocarbon residence time of 1 to 10 seconds, and a catalyst to feed ratio of 3 to 12, thereby producing a reaction product wherein no more than 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.

DETAILED DESCRIPTION OF THE INVENTION

[0016] Feedstreams which are suitable for producing the relatively high C\(_{3}\), C\(_{3}\), and C\(_{4}\) olefin yields are those streams boiling in the naphtha range and containing from 5 wt.% to 35 wt.% preferably from 10 wt.% to 30 wt.%, and more preferably from 10 to 25 wt.% paraffins, and from 15 wt.%, preferably from 20 wt.% to 70 wt.% olefins. The feed may also contain naphthenes and aromatics. Naphtha boiling range streams are typically those having a boiling range from 18.3°C (65°F) to 221°C (430°F), preferably from 18.3°C (65°F) to 149°C (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.

[0017] 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 500°C to 650°C, preferably from 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 performed 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 650°C to 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 C₂ to C₄ olefin, particularly propylene, selectivity with relatively high conversion of C₅+ 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 0.7 nanometers (nm), said crystalline zeolite comprising from 10 wt.% to 50 wt.% of the total fluidized catalyst composition. It 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 75:1, preferably less than 50:1, and more preferably less than 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).

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. The medium pore size zeolites generally have a pore size from about 0.5 nm (5Å) to about 0.7 nm (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 US-A-3,702,886 and 3,770,614, ZSM-11 is described in US-A-3,709,979; ZSM-12 in US-A-3,832,449; ZSM-21 and ZSM-38 in US-A-3,948,758; ZSM-23 in US-A-4,076,842; and ZSM-35 in US-A-4,016,245. Other suitable medium pore size zeolites include the silicoaluminophosphates (SAPO), such as SAPO-4 and SAPO-11 which is described in US-A-4,440,871; chromosilicates; gallium silicates; iron silicates; aluminum phosphates (ALPO), such as ALPO-11 described in US-A-4,310,440; titanium aluminosilicates (TASO), such as TASO-45 described in EP-A-229,295; boron silicates, described in US-A-4,254,297; titanium alumino phosphates (TAPO), such as TAPO-11 described in US-A-4,500,651; and iron aluminosilicates. In one embodiment of the present invention the Si/Al ratio of said zeolites is greater than 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 US-A-4,229,424. The crystalline 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, diasporie, 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.

Process conditions include temperatures from 500°C to 650°C, preferably from 500°C to 600°C; hydrocarbon partial pressures from 69 to 276 kPa (10 to 40 psia), preferably from 138 to 241 kPa (20 to 35 psia); and a catalyst to naphtha (wt/wt) ratio from 3 to 12, preferably from 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 50 wt.% of the hydrocarbon feed. The naphtha residence time in the reaction zone is from 1 to 10 seconds. The above conditions will be such that at least 60 wt.% of the C₅+ olefins in the naphtha stream are converted to C₄+ products and less than 20 wt.% of the paraffins are converted to C₅+ products, and that propylene comprises at least 90 mol %, preferably greater than 95 mol % of the total C₃ reaction products with the weight ratio of propylene/total C₃ products greater than 3.5. It is also preferred that ethylene comprises at least 90 mol % of the C₂ products, with the weight ratio of propylene:ethylene being greater than 4, and that the "full range" C₅+ 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 aromatic 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 examples of the present invention 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 815°C (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

<table>
<thead>
<tr>
<th>Example</th>
<th>Feed Olefins, wt%</th>
<th>Temp. °C</th>
<th>Cat/Oil</th>
<th>Oil Res. (kPa)</th>
<th>Oil Res. Time, sec</th>
<th>Cat Res. Time, sec</th>
<th>Wt.% C₃⁺</th>
<th>Wt.% C₂⁺</th>
<th>Propylene Purity %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>38.6</td>
<td>566</td>
<td>4.2</td>
<td>248 (36)</td>
<td>0.5</td>
<td>4.3</td>
<td>11.4</td>
<td>0.5</td>
<td>93.8</td>
</tr>
<tr>
<td>2</td>
<td>38.6</td>
<td>569</td>
<td>8.4</td>
<td>221 (32)</td>
<td>0.6</td>
<td>4.7</td>
<td>12.8</td>
<td>0.8</td>
<td>94.1</td>
</tr>
<tr>
<td>3</td>
<td>22.2</td>
<td>510</td>
<td>8.8</td>
<td>124 (18)</td>
<td>1.2</td>
<td>8.6</td>
<td>8.2</td>
<td>1.1</td>
<td>88.2</td>
</tr>
<tr>
<td>4</td>
<td>22.2</td>
<td>511</td>
<td>9.3</td>
<td>262 (38)</td>
<td>1.2</td>
<td>5.6</td>
<td>6.3</td>
<td>1.9</td>
<td>76.8</td>
</tr>
<tr>
<td>5</td>
<td>38.6</td>
<td>632</td>
<td>16.6</td>
<td>138 (20)</td>
<td>1.7</td>
<td>9.8</td>
<td>16.7</td>
<td>1.0</td>
<td>94.4</td>
</tr>
<tr>
<td>6</td>
<td>38.6</td>
<td>630</td>
<td>16.6</td>
<td>90 (13)</td>
<td>1.3</td>
<td>7.5</td>
<td>16.8</td>
<td>0.6</td>
<td>96.6</td>
</tr>
<tr>
<td>7</td>
<td>22.2</td>
<td>571</td>
<td>5.3</td>
<td>186 (27)</td>
<td>0.4</td>
<td>0.3</td>
<td>6.0</td>
<td>0.2</td>
<td>96.8</td>
</tr>
<tr>
<td>8</td>
<td>22.2</td>
<td>586</td>
<td>5.1</td>
<td>186 (27)</td>
<td>0.3</td>
<td>0.3</td>
<td>7.3</td>
<td>0.2</td>
<td>97.3</td>
</tr>
<tr>
<td>9</td>
<td>22.2</td>
<td>511</td>
<td>9.3</td>
<td>262 (38)</td>
<td>1.2</td>
<td>3.6</td>
<td>6.3</td>
<td>1.9</td>
<td>76.8</td>
</tr>
<tr>
<td>10</td>
<td>22.2</td>
<td>607</td>
<td>9.2</td>
<td>255 (37)</td>
<td>1.2</td>
<td>6.0</td>
<td>10.4</td>
<td>2.2</td>
<td>82.5</td>
</tr>
<tr>
<td>11</td>
<td>22.2</td>
<td>576</td>
<td>18.0</td>
<td>221 (32)</td>
<td>1.0</td>
<td>9.0</td>
<td>9.6</td>
<td>4.0</td>
<td>70.6</td>
</tr>
<tr>
<td>12</td>
<td>22.2</td>
<td>574</td>
<td>18.3</td>
<td>221 (32)</td>
<td>1.0</td>
<td>2.4</td>
<td>10.1</td>
<td>1.9</td>
<td>84.2</td>
</tr>
<tr>
<td>13</td>
<td>38.6</td>
<td>606</td>
<td>8.5</td>
<td>152 (22)</td>
<td>1.0</td>
<td>7.4</td>
<td>15.0</td>
<td>0.7</td>
<td>95.5</td>
</tr>
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**Table 1 Continued**

<table>
<thead>
<tr>
<th>Example</th>
<th>Wt.% C₃⁺</th>
<th>Wt.% C₂⁺</th>
<th>Ratio of C₃⁺ to C₂⁺</th>
<th>Ratio of C₂⁺ to C₃⁺</th>
<th>Wt.% C₄⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.35</td>
<td>2.73</td>
<td>4.9</td>
<td>4.2</td>
<td>11.4</td>
</tr>
<tr>
<td>2</td>
<td>3.02</td>
<td>3.58</td>
<td>4.2</td>
<td>3.6</td>
<td>12.8</td>
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<td>3</td>
<td>2.32</td>
<td>2.53</td>
<td>3.5</td>
<td>3.2</td>
<td>8.2</td>
</tr>
<tr>
<td>4</td>
<td>2.16</td>
<td>2.46</td>
<td>2.9</td>
<td>2.6</td>
<td>6.3</td>
</tr>
<tr>
<td>5</td>
<td>6.97</td>
<td>9.95</td>
<td>2.4</td>
<td>1.7</td>
<td>16.7</td>
</tr>
<tr>
<td>6</td>
<td>6.21</td>
<td>8.71</td>
<td>2.7</td>
<td>1.9</td>
<td>16.8</td>
</tr>
<tr>
<td>7</td>
<td>1.03</td>
<td>1.64</td>
<td>5.8</td>
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</tr>
<tr>
<td>8</td>
<td>1.48</td>
<td>2.02</td>
<td>4.9</td>
<td>3.6</td>
<td>7.3</td>
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<tr>
<td>9</td>
<td>2.16</td>
<td>2.46</td>
<td>2.9</td>
<td>2.6</td>
<td>6.3</td>
</tr>
<tr>
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<td>5.21</td>
<td>6.74</td>
<td>2.0</td>
<td>1.5</td>
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<td>4.99</td>
<td>6.67</td>
<td>1.9</td>
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<tr>
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<td>4.43</td>
<td>5.76</td>
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<td>1.6</td>
<td>10.1</td>
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<td>4.45</td>
<td>5.76</td>
<td>3.3</td>
<td>2.6</td>
<td>15.0</td>
</tr>
</tbody>
</table>

C₃⁺ = CH₄ + C₂H₄ + C₂H₆

The above examples (1,2,7 and 8) show that C₃⁺/C₂⁺ > 4 and C₃⁺/C₂⁺ > 3.5 can be achieved by selection of
suitable reactor conditions.

**Examples 14 - 17**

[0027] 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**

<table>
<thead>
<tr>
<th>Example</th>
<th>Steam Co-feed</th>
<th>Temp. C</th>
<th>Cat/Oil</th>
<th>Oil Res. Time. sec.</th>
<th>Cat Res. Time. sec.</th>
<th>Wt% Propylene</th>
<th>Wt% Propane</th>
<th>Propylene Purity, %</th>
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</thead>
<tbody>
<tr>
<td>14</td>
<td>No</td>
<td>630</td>
<td>8.7</td>
<td>124 (18)</td>
<td>0.8</td>
<td>11.7</td>
<td>0.3</td>
<td>97.5%</td>
</tr>
<tr>
<td>15</td>
<td>Yes</td>
<td>631</td>
<td>8.8</td>
<td>152 (22)</td>
<td>1.2</td>
<td>13.9</td>
<td>0.6</td>
<td>95.9%</td>
</tr>
<tr>
<td>16</td>
<td>No</td>
<td>631</td>
<td>8.7</td>
<td>124 (18)</td>
<td>0.8</td>
<td>13.6</td>
<td>0.4</td>
<td>97.1%</td>
</tr>
<tr>
<td>17</td>
<td>Yes</td>
<td>632</td>
<td>8.4</td>
<td>152 (22)</td>
<td>1.1</td>
<td>14.6</td>
<td>0.8</td>
<td>94.8%</td>
</tr>
</tbody>
</table>

**Examples 18-21**

[0028] ZCAT-40 was used to crack cat cracker naphtha as described for the above examples. The coked catalyst was then used to crack a C4 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**

<table>
<thead>
<tr>
<th>WHSV, Hr-1</th>
<th>35</th>
<th>18</th>
<th>12</th>
<th>6</th>
</tr>
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<tbody>
<tr>
<td>Temperature °C</td>
<td>575</td>
<td>575</td>
<td>575</td>
<td>575</td>
</tr>
<tr>
<td>Butylene Conversion wt.%</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Product Yields, wt.%</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ethylene</td>
<td>2.4</td>
<td>4.7</td>
<td>5.9</td>
<td>8.8</td>
</tr>
<tr>
<td>Propylene</td>
<td>20.5</td>
<td>27.1</td>
<td>28.8</td>
<td>27.4</td>
</tr>
<tr>
<td>Butylenes</td>
<td>39.7</td>
<td>29.0</td>
<td>25.5</td>
<td>19.2</td>
</tr>
<tr>
<td>C1-C4 Light Saturates</td>
<td>18.2</td>
<td>19.2</td>
<td>19.8</td>
<td>22.0</td>
</tr>
<tr>
<td>C5- Products</td>
<td>19.3</td>
<td>20.0</td>
<td>20.0</td>
<td>22.6</td>
</tr>
</tbody>
</table>

**Claims**

1. A process for selectively producing C3 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 a naphtha stream containing from 5 to 35 wt.% paraffins and from 15 to 70 wt.% olefins in the reaction zone containing a fluidized bed of catalyst comprised of a crystalline zeolite having an average pore
diameter of less than 0.7 nm and wherein the reaction zone is operated at a temperature from 500° to 650°C, a hydrocarbon partial pressure of 69 to 276 kPa (10 to 40 psia) a hydrocarbon residence time of 1 to 10 seconds, and a catalyst to feed ratio of 3 to 12, thereby producing a reaction product wherein no more than 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 C₃ fraction, a C₄ fraction rich in olefins, and optionally a C₅ fraction rich in olefins; and

f) passing the C₄ 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 any preceding claim wherein the naphtha feedstock contains from 10 to 30 wt.% paraffins and 20 to 70 wt.% olefins.

5. The process of any preceding claim wherein the reaction temperature is from 525°C to 600°C.

6. The process of any preceding claim wherein at least 60 wt.% of the C₅ + olefins in the feedstock is converted to C₄⁺ products and less than 20 wt.% of the paraffins are converted to C₄⁺ products.

7. The process of any preceding claim wherein propylene comprises at least 90 mol. % of the total C₃ products.

8. The process of claim 7 wherein the weight ratio of propylene to total C₂-products is greater than 3.5.

9. The process of any preceding claim wherein a C₅ fraction rich in olefins is also produced and is recycled to the reaction zone, the stripping zone, or both.

10. The process according to any preceding claim further comprising co-feeding an olefinic stream which is not a catalytically or thermally cracked naphtha with the naphtha stream.

11. The process according to any preceding claim further comprising pre-coking the catalyst before contacting the naphtha stream with the catalyst.

12. The process according to any preceding claim wherein the naphtha stream further comprises single ring aromatics.
b) Leiten des Katalysators durch eine Strippzone, in der flüchtige Materialien unter Verwendung eines Strippmediums gestrippt werden;

c) Leiten des gestrippten Katalysators aus der Strippzone in eine Katalysatorregenerierungszone, in der jegliche Koksablagerungen in Gegenwart eines sauerstoffhaltigen Gases abgebrannt werden;

d) Rückführen des regenerierten Katalysators in die Reaktionszone, wo er in Kontakt mit frischem Einsatzmaterial kommt;

e) Fraktionieren des Dampfproduktstroms, um eine C₃-Fraktion, eine an Olefinen reiche C₄-Fraktion und gegebenenfalls eine an Olefinen reiche C₅-Fraktion zu erzeugen; und

f) Leiten der C₄-Fraktion in die Reaktionszone oder die Strippzone oder beides.

2. Verfahren nach Anspruch 1, bei dem der kristalline Zeolith ausgewählt ist aus der ZSM-Reihe.


5. Verfahren nach einem der vorhergehenden Ansprüche, bei dem die Reaktionstemperatur 525 bis 600° beträgt.


9. Verfahren nach einem der vorhergehenden Ansprüche, bei dem auch eine an Olefinen reiche C₅-Fraktion hergestellt wird und in die Reaktionszone, die Strippzone oder beide zurückgeführt wird.

10. Verfahren nach einem der vorhergehenden Ansprüche, bei dem außerdem ein olefinischer Strom, der nicht ein katalytisch oder thermisch gecracktes Naphtha ist, zusammen mit dem Naphthastrom eingespeist wird.


Revendications

1. Procédé pour la production sélective d'oléfines en C₃ à partir d'un courant de naphta d'alimentation dans une unité de traitement constituée d'une zone réactionnelle, d'une zone d'entraînement, d'une zone de régénération de catalyseur et d'une zone de fractionnement, procédé qui comprend les étapes consistant :

   a) à faire réagir le courant de naphta contenant 5 à 35 % en poids de paraffines et 5 à 70 % en poids d'oléfines dans la zone réactionnelle contenant un lit fluidisé de catalyseur constitué d'une zéolite cristalline ayant un diamètre moyen des pores inférieur à 0,7 nm, la zone réactionnelle étant soumise à un fonctionnement à une température comprise dans l'intervalle de 500 à 650°C, une pression partielle d'hydrocarbure comprise dans l'intervalle de 69 à 276 kPaa (10 à 40 psia), un temps de séjour d'hydrocarbure de 1 à 10 secondes et un rapport du catalyseur à la charge d'alimentation de 3 à 12, ce qui donne un produit de réaction dans lequel
une proportion non supérieure à 20 % en poids des paraffines est convertie en oléfines.
b) à faire passer le catalyseur à travers une zone d'entraînement dans laquelle les substances volatiles sont
entraînées au moyen d'un milieu d'entraînement ;
c) à faire passer le catalyseur ayant subi l'entraînement de la zone d'entraînement à une zone de régénération
de catalyseur dans laquelle tous les dépôts de coke sont brûlés en présence d'un gaz contenant de l'oxygène ;
d) à recycler le catalyseur régénéré à la zone réactionnelle où il entre en contact avec de la charge d'alimen-
tation fraîche ;
e) à fractionner le courant de produits sous forme de vapeur pour produire une fraction en C₃, une fraction en
C₄ riche en oléfines, et, facultativement, une fraction en C₅ riche en oléfines ; et
f) à faire passer la fraction en C₄ à la zone réactionnelle ou à la zone d'entraînement, ou bien à ces deux zones.

2. Procédé suivant la revendication 1, dans lequel la zéolite cristalline est choisie dans la série des ZSM.

3. Procédé suivant la revendication 2, dans lequel la zéolite cristalline est la ZSM-5.

4. Procédé suivant l'une quelconque des revendications précédentes, dans lequel la charge de naphta d'alimentation
contient 10 à 30 % en poids de paraffines et 20 à 70 % en poids d'oléfines.

5. Procédé suivant l'une quelconque des revendications précédentes, dans lequel la température réactionnelle est
comprise dans l'intervalle de 525°C à 600°C.

6. Procédé suivant l'une quelconque des revendications précédentes, dans lequel une proportion d'au moins 60 %
en poids des oléfines en C₅+ dans le courant d'alimentation est convertie en produits en C₄- et une proportion
inférieure à 20 % en poids des paraffines est convertie en produits en C₄-.

7. Procédé suivant l'une quelconque des revendications précédentes, dans lequel le propylène représente au moins
90 % en moles des produits totaux en C₃.

8. Procédé suivant la revendication 7, dans lequel le rapport pondéral du propylène au produits totaux en C₂ est
supérieur à 3,5.

9. Procédé suivant l'une quelconque des revendications précédentes, dans lequel une fraction en C₅ riche en oléfines
est également produite et recyclée à la zone réactionnelle, à la zone d'entraînement ou à ces deux zones.

10. Procédé suivant l'une quelconque des revendications précédentes, comprenant en outre la co-introduction d'un
courant oléfinique, qui n'est pas un naphta de craquage catalytique ou thermique avec le courant de naphta.

11. Procédé suivant l'une quelconque des revendications précédentes, comprenant en outre la prékokéfaction du
catalyseur avant la mise en contact du courant de naphta avec le catalyseur.

12. Procédé suivant l'une quelconque des revendications précédentes, dans lequel le courant de naphta comprend
en outre des composés aromatiques monocycliques.