

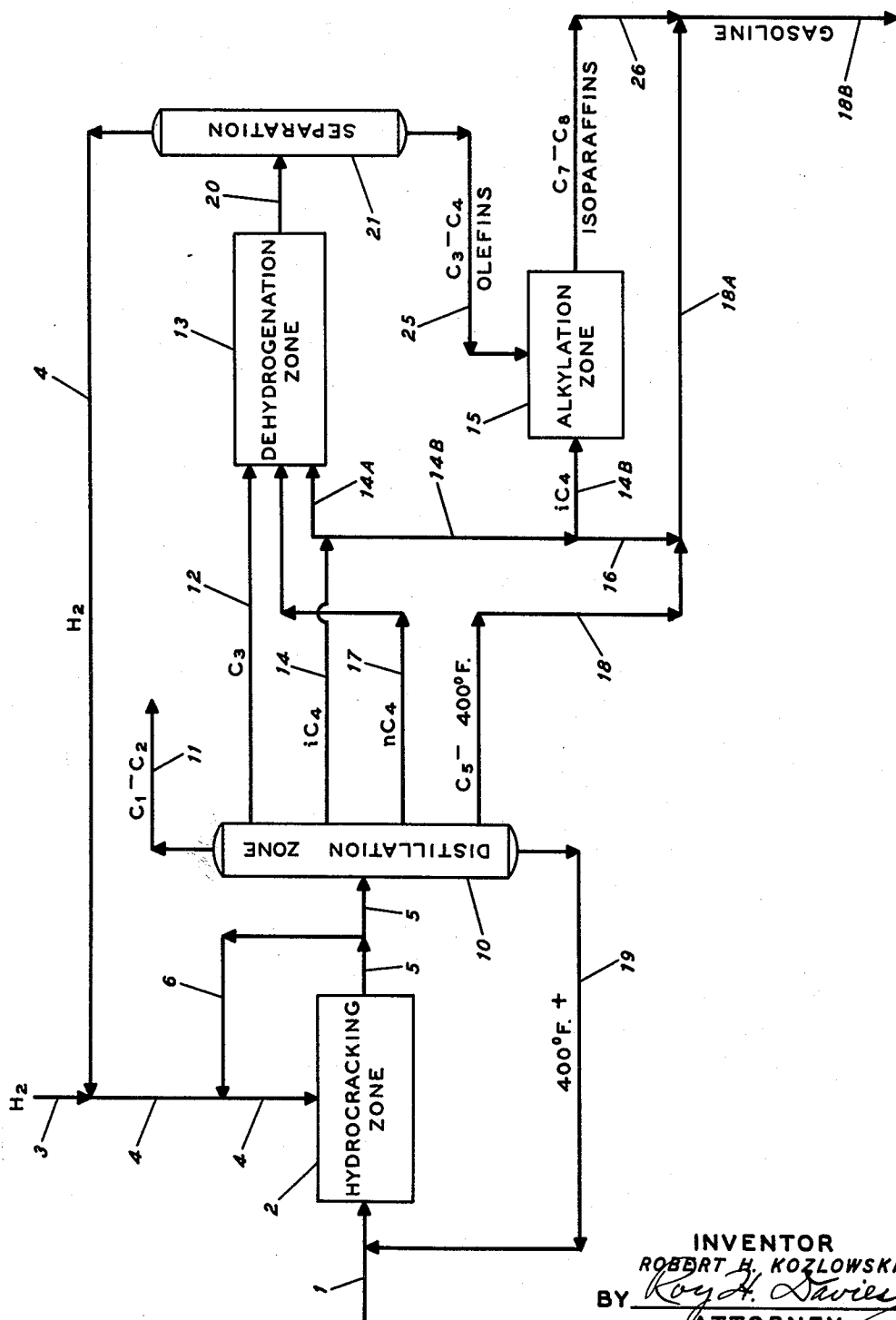
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**3,172,834**

PROCESS FOR MANUFACTURING GASOLINE BY BLENDING THE  
HYDROCRACKED GASOLINE WITH THE DEHYDROGENATED  
AND ALKYLATED PRODUCTS OBTAINED FROM  
THE HYDROCRACKING STAGE  
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**PROCESS FOR MANUFACTURING GASOLINE BY BLENDING THE HYDROCRACKED GASOLINE WITH THE DEHYDROGENATED AND ALKYLATED PRODUCTS OBTAINED FROM THE HYDROCRACKING STAGE****Robert H. Kozlowski, Berkeley, Calif., assignor to California Research Corporation, San Francisco, Calif., a corporation of Delaware**

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4 Claims. (Cl. 208—58)

This invention relates to a hydrocarbon conversion process, and particularly to a process for the catalytic conversion of petroleum distillates to produce gasoline.

It is known that hydrocracking processes are useful in gasoline manufacture, both alone and in combination with other processing steps. However, there has been a need for a combination process including a hydrocracking step that would operate to minimize the production of fuel gas and use excess isobutane in a manner that would maximize the production of C<sub>5</sub>+ gasoline from the combined process, and it is an object of the present invention to accomplish these results.

The invention will be more clearly understood, and further objects and advantages thereof will be apparent, from the following description when read in connection with the accompanying drawing. The drawing is a diagrammatic illustration of an embodiment of process units and flow paths suitable for carrying out the process of the invention.

In accordance with the present invention, there is provided a process for producing gasoline in high yields which comprises hydrocracking a petroleum distillate to produce gasoline and light normally gaseous paraffinic hydrocarbons, converting said paraffinic hydrocarbons to olefins by dehydrogenation, alkylating said olefins to produce isoparaffins, and combining said isoparaffins with said gasoline to produce the final gasoline product.

Further in accordance with the present invention, there is provided, in a process for producing gasoline by the cracking of a petroleum distillate in a hydrocracking zone, the improvement which comprises separating in a fractionating zone the effluent from said hydrocracking zone into a gasoline stream, a fraction containing isobutane, a fraction containing methane and ethane, a fraction containing propane, and a fraction containing normal butane, dehydrogenating said propane and normal butane to produce olefins, alkylating said olefins with said isobutane to produce C<sub>7</sub> to C<sub>8</sub> isoparaffins, and combining said isoparaffins with said gasoline to produce a final gasoline product.

Still further in accordance with the present invention, there is provided, in a process for producing gasoline by the cracking of a petroleum distillate in a hydrocracking zone at 500° to 900° F., 500 to 3000 p.s.i.g., and an LHSV of 0.1 to 3.0, in the presence of hydrogen and a catalyst comprising a hydrogenating-dehydrogenating component selected from Groups VI and VIII of the Periodic Table disposed on an active cracking support, the improvement which comprises separating in a fractionating zone the effluent from said hydrocracking zone into a gasoline fraction, an isobutane fraction, a normally gaseous fraction containing methane and ethane, a normally gaseous fraction containing propane, a normal butane fraction, and a bottoms fraction boiling above the gasoline boiling range, dehydrogenating said propane and normal butane in a dehydrogenation zone in the presence of a chromia-alumina dehydrogenation catalyst to produce olefins, alkylating said olefins with said isobutane at low temperature in an alkylation zone containing a catalyst selected from

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the group consisting of sulfuric acid, aluminum chloride and hydrofluoric acid to produce C<sub>7</sub> to C<sub>8</sub> isoparaffins, and combining said isoparaffins with said gasoline to produce a final gasoline product.

The feed stocks employed in the process of the present invention may be hydrocarbon distillates boiling within the range of from about 300° to 1050° F., and preferably from 400° to 850° F.

While the invention can be practiced with utility with hydrocarbon feeds to the hydrocracking zone which contain relatively large quantities of nitrogen, the operation becomes much more economical with stocks containing less than 200 parts per million (p.p.m.), preferably less than 100 p.p.m., and much more preferably less than 10 p.p.m. of total nitrogen. A reduction in feed nitrogen level generally permits the hydrocracking reaction to be conducted at lower temperatures than with feeds containing relatively large amounts of nitrogen compounds. Therefore, in the case of feeds which are not inherently low in nitrogen, acceptable levels can be reached by hydrofining the feed prior to passing it into the hydrocracking zone. Where hydrofining of the feed is required, this may be accomplished in a conventional manner, for example at temperatures of from about 400° to 900° F., preferably from about 500° to 800° F., pressures of at least 300 p.s.i.g., liquid hourly space velocities (LHSV) of from about 0.3 to 5.0, along with at least 500 s.c.f. of hydrogen per barrel of feed with a sulfur-resistant hydrogenation catalyst, for example a molybdenum sulfide catalyst promoted by a minor amount of nickel sulfide supported on activated alumina.

Referring now to the drawing, there shown is an exemplary overall process flow diagram suitable for carrying out the process of the present invention.

The hydrocarbon distillate feed is passed through line 1 into hydrocracking zone 2, which is operated at pressures of at least 500 p.s.i.g., preferably about from 800 to 3000 p.s.i.g., and temperatures about from 400° to 900° F., preferably 500° to 800° F. The operating temperature during the on-stream period preferably is maintained at as low a value as possible consistent with maintaining adequate per-pass conversions as catalyst fouling progresses.

The catalyst in hydrocracking zone 2 may be a conventional acidic hydrocracking catalyst. The cracking component may comprise any one or more of such acidic materials as silica-alumina, silica-magnesia, silica-alumina-zirconia composites, alumina-boria, fluorided composites and the like, as well as various acid-treated clays and similar materials. Preferred catalysts will comprise silica-alumina supports having a silica content in the range of from about 30 to 99 percent by weight. The hydrogenating-dehydrogenating components of the catalyst can be selected from any one or more of the various Groups VI and VIII metals, as well as the oxides, sulfides and selenides thereof, alone or together with promoters or stabilizers that may have, by themselves, small catalytic effect, representative materials being the oxides, sulfides and selenides of molybdenum, tungsten, vanadium, chromium and the like, as well as of metals such as iron, nickel, cobalt, platinum and palladium. If desired, more than one hydrogenating-dehydrogenating component can be present, and good results have been obtained with catalysts containing composites of two or more of the oxides of molybdenum, cobalt, nickel, chromium, copper, silver and zinc, and with mixtures of said oxides with fluorides. The amount of the hydrogenating-dehydrogenating component present can be varied within relatively wide limits of from about 0.5 to 30% based on the weight of the entire catalyst.

Exemplary acidic-type catalysts having satisfactory char-

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acteristics as aforesaid include those containing (a) about 1 to 12% molybdenum oxide, (b) a mixture of from 1 to 12% molybdenum oxide and from 0.1 to 10% cobalt oxide or nickel oxide, (c) mixtures of from about 0.5 to 10% each of cobalt oxide and chromium oxide, (d) 0.1 to 10% nickel, nickel oxide or nickel sulfide, (e) 0.1 to 10% cobalt, cobalt oxide or cobalt sulfide, (f) mixtures of from 0.1 to 10% each of nickel and cobalt, as metal, oxide or sulfide (g) 0.1 to 5% platinum or palladium.

Hydrocracking zone 2 is supplied with fresh hydrogen as necessary through line 3 and, if desired, with recycle hydrogen through line 4 from zone 21 as hereinafter discussed. Hydrogen not consumed in zone 2 is recycled thereto through line 6.

From hydrocracking zone 2, an effluent is passed through line 5 to distillation zone 10 where it is separated into various fractions.

A  $C_1$ - $C_2$  fraction is withdrawn from the system through line 11; if desired, this minor amount of gaseous material formed in the hydrocracking reaction in zone 2 can be returned to a hydrogen producing plant for conversion to additional hydrogen. A  $C_3$  fraction is passed through line 12 to dehydrogenation zone 13. An  $iC_4$  fraction is withdrawn from zone 10 through line 14 and at least a portion thereof is passed through line 14B to alkylation zone 15. If desired, a portion of this withdrawn fraction may be passed through line 16 for blending with the gasoline stream flowing in line 18. If desired, another portion of this withdrawn fraction may be passed through line 14A to dehydrogenation zone 13 to be converted to additional olefinic material; such a procedure will be especially useful where an excess of isobutane is produced in zone 2. An  $nC_4$  fraction is passed through line 17 to dehydrogenation zone 13. A  $C_5$  to 400° F. fraction is withdrawn through line 18 for use as a high quality gasoline, and a 400° F.+ bottoms fraction is recycled through line 19 to hydrocracking zone 2.

Dehydrogenation zone 13 is a conventional dehydrogenation zone employing any one of a wide variety of known dehydrogenation catalysts, of which the commercially available chromia on alumina catalyst, containing about 20 weight percent  $Cr_2O_3$  is a typical and suitable embodiment. Operating conditions may include temperatures from about 950° to 1200° F., preferably 1000° to 1100° F., relatively low pressures, generally atmospheric or subatmospheric, and 0.5 to 2.1 volumes of charge per volume of catalyst per hour. Propylene and butylenes are produced in dehydrogenation zone 13.

From dehydrogenation zone 13, an effluent is passed through line 20 to separation zone 21, from which the hydrogen produced in dehydrogenation zone 13 is recycled through line 4, and from which  $C_3$  and  $C_4$  olefins are passed through line 25 to alkylation zone 15.

In alkylation zone 15, the  $C_3$  and  $C_4$  olefins entering through line 25 are alkylated with the isobutane entering through line 14B, in the presence of a conventional alkylation catalyst at conventional alkylation conditions. The conventional alkylation catalyst may be, for example, sulfuric acid, aluminum chloride or hydrofluoric acid. With a sulfuric acid catalyst, the operating temperature in alkylation zone 15 may be from about 40° to 55° F. using make-up acid of approximately 99% concentration. With propylene present, the temperature should be kept at least as high as 50° F. When hydrofluoric acid catalyst is used, the temperature can be from about 40° to about 100° F.; with this catalyst, temperature effects are not so marked as with sulfuric acid and, because of internal catalyst regeneration, acid consumption is not such a problem as it is with sulfuric acid. With either catalyst, the reaction rates will be lower with lower operating temperatures and with either catalyst a pressure will be used that is sufficient to maintain a liquid phase at the operating temperature. A higher pressure will be required with hydrofluoric acid. Generally, it is desirable to have an isobutane concentration of about

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from 55 to 75% in the reaction mix; with a higher isobutane concentration, the product will have a higher octane number.

From alkylation zone 15 the  $C_7$  to  $C_8$  isoparaffins produced in the alkylation reaction are passed through line 26 to meet the gasoline stream flowing in line 18A and thereby to provide in line 18B a resultant mixture of primarily  $C_5$ + gasoline.

From the foregoing, it may be seen that, with the process of the present invention, the total product produced by the process can be substantially all high quality  $C_5$ + gasoline, with no byproduct fuel gas and no excess isobutane over that needed for gasoline blending.

The following table indicates results obtainable with the process of the present invention, with three different specific feeds, A, B and C. Feed A is a mixture of 50 volume percent straight run California gas oil and 50 volume percent coker distillate from a straight run California gas oil. Feed B is a mixture of 85 volume percent Mid-Continent light catalytic cycle oil and 15 volume percent Mid-Continent light straight run gas oil. Feed C is a California heavy cracked naphtha. The aforesaid feeds have the following characteristics:

Table

|                                   | A       | B       | C       |
|-----------------------------------|---------|---------|---------|
| Gravity, ° API.....               | 27.8    | 27.6    | 36.7    |
| Aniline point, ° F.....           | 126     | 120     | -----   |
| ASTM distillation range, ° F..... | 410-700 | 425-676 | 372-450 |

The aforesaid feeds are separately processed in accordance with the present invention, using the flow arrangement and process units shown in the drawing, using a nickel sulfide on silica-alumina hydrocracking catalyst, a chromia-alumina dehydrogenation catalyst, a sulfuric acid alkylation catalyst, and using process conditions hereinabove recited. The volume percent of products, based on fresh hydrocarbon feed to the hydrocracking zone, in the various lines in the drawing, is as follows, assuming conventional yields for the individual conventional process zones, and assuming extinction recycle to the hydrocracking zone of material boiling above the initial boiling point of the feed (i.e., material unconverted in the hydrocracking zone).

| Line on Drawing | Product       | Volume Percent Product |                       |                       |
|-----------------|---------------|------------------------|-----------------------|-----------------------|
|                 |               | Example 1<br>(Feed A)  | Example 2<br>(Feed B) | Example 3<br>(Feed C) |
| 12.....         | $C_3$         | 5.1                    | 5.1                   | 6.3                   |
| 17.....         | $nC_4$ =      | 4.4                    | 6.3                   | 5.8                   |
| 25.....         | $C_3$         | 3.4                    | 3.5                   | 4.2                   |
| 25.....         | $nC_4$ =      | 2.9                    | 4.2                   | 4.1                   |
| 14B.....        | $iC_4$        | 7.7                    | 8.4                   | 10.2                  |
| 26.....         | $C_7$ - $C_8$ | 111.2                  | 113.7                 | 114.8                 |
| 14.....         | $iC_4$        | 11.9                   | 11.0                  | 14.0                  |
| 14A.....        | $iC_4$        | 0.0                    | 0.0                   | 0.0                   |
| 16.....         | $iC_4$        | 4.2                    | 2.6                   | 3.8                   |
| 18.....         | $C_5$ +       | 104.3                  | 104.9                 | 94.0                  |
| 18B.....        | $C_5$ +       | 115.5                  | 118.6                 | 108.8                 |

- 1 Octane No. F-1 Clear, 92; F-1+3, 104.  
 2 Octane No. F-1 Clear, 93; F-1+3, 105.  
 3 Octane No. F-1 Clear, 92; F-1+3, 104.  
 4 Octane No. F-1 Clear, 69; F-1+3, 86.  
 5 Octane No. F-1 Clear, 73; F-1+3, 88.  
 6 Octane No. F-1 Clear, 84; F-1+3, 98.  
 7 Octane No. F-1 Clear, 71; F-1+3, 88.  
 8 Octane No. F-1 Clear, 76; F-1+3, 90.  
 9 Octane No. F-1 Clear, 86; F-1+3, 100.

From a comparison of the above volume percent product, and octane number thereof, in line 18 (corresponding with prior art results without using the process of the present invention), with the above volume percent product, and octane number thereof, in line 18B (results using the process of the present invention), it may be seen that the process of the present invention results in a higher yield of gasoline having a higher octane number.

The aforesaid volume percent product in lines 14A and

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16 assume that all excess isobutane is passed through line 16. If no excess isobutane is passed through line 16, and instead one-half of said excess is passed through line 14A and one-half through line 14B, the volume percent alkylate produced from said excess increases the amount of product in line 26, and various other quantities will be different, as follows:

| Line On Drawing | Product                        | Volume Percent Product |                       |                       |
|-----------------|--------------------------------|------------------------|-----------------------|-----------------------|
|                 |                                | Example 1<br>(Feed A)  | Example 2<br>(Feed B) | Example 3<br>(Feed C) |
| 14B-----        | iC <sub>4</sub>                | 9.8                    | 9.7                   | 12.1                  |
| 26-----         | C <sub>7</sub> -C <sub>8</sub> | 13.9                   | 15.4                  | 17.2                  |
| 14A-----        | iC <sub>4</sub>                | 2.1                    | 1.3                   | 1.9                   |
| 16-----         | iC <sub>4</sub>                | 0.4                    | 0.2                   | 0.3                   |
| 18B-----        | C <sub>8</sub> +               | 118.2                  | 120.3                 | 111.2                 |

All variations and all modes of operation of the present invention that are within the spirit of the invention are intended to be covered by the following claims.

I claim:

1. In a process for producing gasoline by the cracking of a petroleum distillate in the presence of hydrogen in a hydrocracking zone, the improvement which comprises separating in a fractionating zone the effluent from said hydrocracking zone into a gasoline stream, a fraction containing isobutane, a fraction containing methane and ethane, a fraction containing propane, and a fraction containing normal butane, dehydrogenating said propane and normal butane to produce olefins, alkylating said olefins with said isobutane to produce C<sub>7</sub> to C<sub>8</sub> isoparaffins, and combining said isoparaffins with said gasoline to produce a final gasoline product.

2. In a process for producing gasoline by the cracking of a petroleum distillate in a hydrocracking zone at 500°

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to 900° F., 500 to 3000 p.s.i.g., and an LHSV of 0.1 to 3.0, in the presence of hydrogen and a catalyst comprising a hydrogenating-dehydrogenating component selected from Groups VI and VIII of the Periodic Table and comprising an active cracking support, the improvement which comprises separating in a fractionating zone the effluent from said hydrocracking zone into a gasoline fraction, an isobutane fraction, a normally gaseous fraction containing methane and ethane, a normally gaseous fraction containing propane, a normal butane fraction, and a bottoms fraction boiling above the gasoline boiling range, dehydrogenating said propane and normal butane in a dehydrogenation zone in the presence of a chromia-alumina dehydrogenation catalyst to produce olefins, alkylating said olefins with said isobutane at low temperature in an alkylation zone containing a catalyst selected from the group consisting of sulfuric acid, aluminum chloride and hydrofluoric acid to produce C<sub>7</sub> to C<sub>8</sub> isoparaffins, and combining said isoparaffins with said gasoline to produce a final gasoline product.

3. A process as in claim 2, wherein a portion of said isobutane is passed to said dehydrogenation zone for dehydrogenation to olefinic material.

4. A process as in claim 2, wherein the hydrogen produced in said dehydrogenation zone is returned to said hydrocracking zone.

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