PROCESS FOR REFINING PETROLEUM FRACTIONS

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Filed Dec. 9, 1963, Ser. No. 328,856

7 Claims. (Cl. 208—68)

This invention relates to the refining of petroleum feedstocks. More particularly, this invention relates to a process comprising a combination of mutually interrelated and interdependent steps for the refining of mid-boiling petroleum fractions. Specifically, this invention in one of its applications includes provision for a cascade refining sequence which permits the selective processing of various types of hydrocarbons contained in the mid-boiling fraction of petroleum and without the use of conventional intermediate separation processes.

Because of the increased demand for petroleum products and because of the almost negligible supplies of paraffin-base crude, the petroleum industry today processes a large portion of naphthenic, aromatic, or mixed-base crude petroleum. Hence, it is found that the mid-boiling fraction, that is, fractions boiling between 400 and 1100° F., which result from the processing of the mixed-base crude petroleum, contain a mixture of hydrocarbons which is comprised predominantly of such naphthenes and aromatics, as well as paraffins. The disposal of such hydrocarbon types in the past was facilitated by their extensive use as feedstocks in various processes, the particular type or types of hydrocarbon employed being dictated by the feedstock required by each process. For example, naphthenic type gas oils and aromatics are the desired feeds for catalytic cracking processes, straight chain paraffins are the desired feeds for steam cracking processes and aromatics are the desired feeds for hydrocracking processes. Thus, in many cases it has been found desirable to separate the hydrocarbon types in order to secure the desired fraction for each process. Examples of the separation reactions involved include phenol extraction for the removal of aromatics from catalytic cracking feed and dewaxing and deoiling so as to obtain straight chain paraffins for steam cracking feed.

While the foregoing scheme offered a feasible method of disposing of the hydrocarbon types referred to, albeit an expensive one, because of steadily increasing demand for gasoline type distillates there has been a steady impetus to devise methods by which such mid-boiling hydrocarbon-containing oils could be economically upgraded to more valuable products. One solution to this problem of satisfying increasing demand for distillates is, of course, utilization of one or more of the basic refinery cracking processes, for example, either thermal or catalytic cracking. However, it is found that the thermal cracking per se of such mid-boiling hydrocarbons is of only marginal value since the gasoline produced therefrom is usually of inferior quality and the cracked residue which represents a sizable proportion of the yield is high in contamination and further is relatively heavier. Catalytic cracking with recycle of the catalytic cycle oil substantially to extinction, on the other hand, is virtually impossible from a practical viewpoint because of the excessive formation of coke on the surface of the catalyst.

It is an object of the present invention, therefore, to provide a process for converting crude petroleum feedstocks almost entirely to more valuable lower boiling hydrocarbons, principally in the motor gasoline boiling range, in an economical and efficacious manner. It is also an object of the invention to provide a process whereby heretofore relatively unsuitable mid-boiling fractions (400–1100° F.) of petroleum are upgraded without employing conventional intermediate separation process. It is a particular object of this invention to provide a processing sequence which will produce from the original feedstock a maximum quantity of motor gasoline plus other usable products, for example, petroleum coke and coke binder oil. These and other objects, as well as other aspects and advantages, of the invention will be apparent from the description of the invention and the drawings wherein.

The figure is a schematic flow diagram illustrating a preferred method for practicing the process in a continuous manner.

Broadly, the process of this invention involves a sequence of refinery steps which comprises in critical sequence: a once-through or one-pass catalytic cracking, steam cracking the resulting catalytic cycle oil, followed by hydrocracking the steam-cracked aromatic fractions, which sequence permits selective processing of mid-boiling hydrocarbon fractions to the most desirable utilization without conventional intermediate separation processes such as aromatic extraction or dewaxing. Thus, refractive aromatics which boil between 450–900° F. are utilized in conversions by hydrocracking to motor gasoline and in thermal operations to petroleum coke and/or coke binder oil.

More specifically, the processing sequence, which as before stated reduces or eliminates the need for conventional separation processes, involves processing and mid-boiling fractions of crude in the following manner:

(1) Mid-boiling fractions, i.e. gas oil (500–1050° F.) from crude petroleum, is introduced to a one-pass catalytic cracking in which the naphthenes and isoparaffins contained therein are largely converted to lighter boiling products including gasoline and heating oils. Trace impurities such as nitrogen, sulfur, and metals are reduced in this step prior to the subsequent steam-cracking step.

(2) The mid-boiling fraction (390–750° F.) from step (1) is sent to steam cracking at temperatures of about 1100° F. to 1500° F. in which the linear chain paraffins are substantially converted to olefins and diolefins for further utilization as basic chemical raw materials.

(3) The unconverted feed from step (2) contains the remaining hydrocarbon type fraction, that is, mid-boiling aromatics (400–750° F.), which fraction is hydrocracked to valuable products such as motor gasoline, distillates or jet fuels.

(4) The higher boiling aromatics and condensation products (650 or 750° F. or above) from step (2) are recovered as a steam-cracked tar material. This material is processed in a coking unit which produces high quality coke which is suitably used for electrodes, or optionally the material may be selectively converted by additional thermal operation at temperatures, for example of 750–950° F. to produce highly favorable binder oils for coke electrodes. The distillate produced from coking this material is highly aromatic in nature and is hydrocracked.
The charge stock for the process of this invention can be any petroleum crude oil which ordinarily would be used for the preparation of petroleum products. The process is particularly valuable for the preparation of such products from "naphthenic base" crude oils such as those obtained from south Louisiana fields.

The actual practice of this invention may be understood more readily by reference to the figure of the drawing. In the figure, a topped crude oil from an atmospheric tower, not shown, in which, for example, a furnace oil and lighter fractions have been removed, is delivered through line 11 to vacuum tower 1. In accordance with the invention, the topped crude oil introduced into the vacuum tower is heated to a temperature of about 600° F. and preferably a boiling range of 650 to 1150° F. Vacuum tower 1 is operated at a flash temperature, corrected to atmospheric pressure above about 900° F., and may range up to a corrected temperature of about 1200° F. A distillate gas oil, that is, a heavy virgin gas oil, suitable for use as a catalytic cracking charge stock is discharged through line 12 from the top of vacuum tower 1 and a bottoms fraction containing virgin heavy residual oils is delivered via line 14 from the bottom of the vacuum tower 1. Ordinarily steam is injected through a line into the bottom of the vacuum tower to aid in the stripping of volatile components from the bottoms fraction, i.e., low asphaltene or asphalt which are removed from the bottom of tower 1. Thus, in accordance with the invention, the vacuum distillation effected in tower 1 may be defined as one adapted to remove a distillate, i.e., the heavy gas oil fraction having a boiling range of 500 to 1050° F.

The heavy virgin gas oil removed from the top of tower 1 via line 12 is introduced into catalytic cracking zone 2. The operation conducted in zone 2 may constitute any desired type of once-through catalytic cracking operation. Hence, the catalytic cracking may constitute the fixed bed type of cracking, moving bed type of cracking, or fluidized catalytic cracking. In each of these types of operation any of these various well known cracking catalysts may be employed. Generally, such catalysts are the metal oxide types and preferably include silica-alumina, silica-magnesia, or silica-gel promoted with metal oxides which are adsorbed thereon. Cracking conditions require maintenance of temperatures in the range of about 750 to 1050° F. and pressures ranging from atmospheric to somewhat above atmospheric pressure. The catalytic agent employed is regenerated intermittently or continuously in order to restore or maintain the activity of the catalyst. For typical operation, catalytic cracking of such feedstock results in conversion about 30 to 60% boiling in the gasoline boiling range.

The products of the once-through catalytic cracking are removed from the catalytic cracking zone 2 through line 16 for introduction to a product fractionator 3 which may constitute one or more distillation zones. Distillation zone 3 may be operated to permit removal of light portions of the catalytically cracked product through an overhead line, to permit removal of gasoline, furnace oil, and heavy oil through one or more sidestream withdrawals and heavier fractions of the catalytically cracked products, for example, light catalytic cycle oil (LCCO) and heavy catalytic cycle oil (HCCO) from lower portions of the fractionator. Thus, a light catalytic cycle oil (LCCO) fraction boiling about above 400° F. and boiling up to about 600° F. may be removed from a lower sidestream withdrawal 18. Similarly, a heavy catalytic cycle oil (HCCO) fraction boiling above about 590° F. and boiling up to about 750° F. may be removed from a lower sidestream withdrawal 20. Heavy residual fractions of the catalytically cracked products are removed from the bottom of the fractionator through line 22. Bottoms withdrawal stream 22 will include hydrocarbons boiling above about 750° F. and boiling up to about 1200° F. or higher. In the event that powdered catalyst is employed in the catalytic cracking zone 2, some catalyst will be entrained in the bottoms withdrawal. In this case the product of line 22 may be subjected to a clarification or settling operation in order to segregate the hydrocarbons from cracking catalysts, and the product of this operation is commonly called clarified oil.

As indicated above, the fractions of a catalytically cracked product boiling above about 400° F. are conventionally called cycle oil and in the process illustrated include the streams of both lines 18 and 20. While the process of this invention can be employed by using either the streams of line 18 or 20, the invention particularly employs both of these streams as combined in line 24 of the drawing and designated by the term "cycle oil." It is well known that cycle oil of the character identified constitutes low grade catalytic cracking feedstock. Cycle oil particularly includes refractory high molecular weight hydrocarbons which, if recycled to a catalytic cracking operation, cause excessive formation of gas, coke, and clarified oil during catalytic cracking. The constituents which are particularly objectionable for cracking are high molecular weight aromatic hydrocarbons and particularly those boiling above about 860° F. The aromatic hydrocarbons in the bottoms fraction may include polynuclear aromatic hydrocarbons and condensed ring aromatic hydrocarbons. The condensed ring aromatic hydrocarbons are particularly undesirable for inclusion in catalytic cracking feedstock. As will be seen, the process of this invention provides a means for upgrading the cycle oil and consequently precludes the formation and, thus, the need for removal of the said undesirable aromatic hydrocarbon types.

In accordance with the present invention, the cycle oil, that is, either the light catalytic cycle oil (LCCO) or the heavy catalytic cycle oil (HCCO) or a mixture of both, is introduced via line 24 as feed into the inlet coil of steam cracker 4 wherein it is subjected to a high temperature-low pressure cracking operation. Such steam cracking operation is effected by contacting the cycle oil feed with about 40 to 100 mole percent of steam, introduced via line 26, and for a holding time of 0.1 to 2.5 seconds, preferably 0.5 to 0.7 second. The steam cracker 4 is maintained at a coil outlet temperature of between 1100 and 1500° F. and preferably between 1300 and 1450° F. The resulting cracked cycle oil is immediately quenched in a quenching zone in the fractionator 5 to a temperature less than 800° F. and preferably to a temperature between 450 and 650° F. with a quenching medium introduced through line 28 and which comprises an oil having a boiling range between about 450 and 650° F. or which comprises a quenching medium as derived in the manner described hereinafter, for a quenching time of from about 0.01 to 0.50 minute and preferably 0.03 to 0.10 minute.

The quenched steam-cracked stream is introduced through line 30 into product fractionator 5 which may constitute one or more distillation zones. Distillation zone 5 may be operated to permit removal of products boiling at about 450° F. or less and comprising hydrogen, saturated hydrocarbons, olefins, diolefins, and the like, by continuous withdrawal through overhead line 32, to permit removal of a fraction boiling between about 540 and 650° F. through sidestream withdrawal 34; and to permit removal of a heavier residual aromatic fraction, that is, tar bottoms, of the steam-cracker products from the bottom of the fractionator 5 through line 36. Bottoms withdrawal stream 36 will include tar bottoms boiling above about 650° F. and boiling up to about 1200° F. In accordance with the invention, the fraction boiling between 450 and 650° F. and withdrawn through sidestream 34 is introduced into hydrocracking zone 6 wherein said fraction is hydrocracked, that is, catalytically
cracked in the presence of hydrogen, to lighter materials boil- ing in the gasoline range. The present invention, therefore, also provides a step for hydroprocessing a petroleum hydrocarbon fraction boiling between 450 and 650°F. by contacting said fraction with a catalyst comprising for example silica combined with alumina, zinc, cation, and the like, and which may have undergone a regeneration with a minor proportion of a dehydro- genation component such as platinum molybdenum, and with the preferred catalyst being palladium on magnesium 13Y sieve base. The hydrocracking reaction is effected in the presence of hydrogen at a hydrogen partial pressure between about 100 and about 5,000 p.s.i.g., preferably 600 to 2000 p.s.i.g., at a liquid hourly space velocity of between about 0.1 and about 10, at a temperature between about 500°F. and about 800°F. employing a molar ratio of hydrogen of hydrogen charge between about 2 and about 80.

The product from the hydrocracking step effected in zone 6 is withdrawn through line 36 and includes light ends and gasoline of high octane number and a heavy fraction boiling above about 400°F. This product is sepa- rated in separation zone 7 into a gasoline and lighter fraction boiling below about 400°F. in line 40 and the heavy fraction boiling above 400°F. which is withdrawn through line 42 and which may be subjected if desired to further process, for example, a second hydrocracking step in which all of its components can be converted to gasoline boiling range hydrocarbons (except for some unavoidable light ends formation), in the presence of a hydrocracking catalyst which can be the same or different than employed in the first hydrocracking step and under conditions which favor the net hydrogenation of aromatics to napthenes.

As diagrammatically illustrated in the drawings, the highly aromatic tar bottoms stream, as referred to above, from steam-cracked light or heavy catalytic cycle oil feed streams boiling above about 650°F. is transferred directly from the steam cracking-fractionation zone 5 via line 36 or from a suitable storage vessel, not shown, and delivered to heater 8 through said line 36. In the heater 8, the feed is heated to a temperature of about between 750 and 950°F. and preferably between 775 and 800°F. From heater 8, the heated feedstock flows through line 37 to the thermal soaking zone maintained between 750 and 950°F. and preferably between 775 and 790°F. where the feed is treated under conditions advantageous to the instant invention. Thus, the feed is delivered at superatmospheric pressure to a soaking vessel 9, which is pref- erably insulated, which is also maintained at superatmospheric pressure, i.e., pressures of from about 100 to 1000 p.s.i.g., and preferably 200 to 400 p.s.i.g. Heat soaking vessel 9 comprises a soaking drum of substantial capacity so as to retain the aromatic tar feedstock in the drum for a sufficient time to effect the desired treatment. Flow is then regulated through the soaking drum that the resi- dence time for any increment of feedstock is between 2 and 6 hours and is preferably between 5 and 6 hours. In order to accomplish one of the objects of the present invention, that is, maximized production of usable product, for example, production of a pitch which fulfills requisite specifications set forth in the art, the feedstock in the heat soaking vessel should be maintained at temperatures be- tween 750 and 950°F., preferably between 775 and 790°F. and specifically 775°F. During this heat soaking step some cracking is found to occur which results in the formation of substantial quantities of gaseous hydrocarbons. These volatile hydrocarbons are permitted to leave the soaking vessel through conduit 44, for ex- ample, by means of a self-acting pressure control or pressure, which flow of such volatiles is essentially con- tinuous inasmuch as fresh feed is continuously supplied to soaking vessel 9. It is found that as much as 3–7% C₅ and lighter hydrocarbons plus H₂ based on feed intro- duced is found in the flow of volatiles removed, the recovery of which greatly adds to the intrinsic advantage of the instant process.

The product from thermal soaker 9 comprising thermal- treated steam-cracked catalytic cycle oil is deliv- ered through line 46 into an atmospheric flash distilla- tion tower 10. Fractions boiling at 750°F. and lower are removed as distillate products from tower 10, via lines 48 and 50, and a petroleum pitch is dis- charged as a bottoms product through line 52. The flash temperature in tower 10 is controlled such that the overhead vapors range from about 725°F. to about 800°F. The maximum flash temperature in the tower is somewhat critical since it may be used to obtain the desired specific softening point in the final binder product prepared from the pitch.

In an embodiment of the present process at least a portion of the distillate fractions separated in tower 10 is recycled via lines 48 and 54 to line 28 for use as quenching medium in the quenching zone of steam cracking zone 4.

The petroleum pitch final product, which collects in the bottom of tower 10, is continuously withdrawn through line 52, as mentioned above.

It should be noted that the cascade refining sequence of the present invention permits the selective processing of various types of hydrocarbons which are contained in the mid-boiling fraction and accomplishes this result ad- vantageously without the use of conventional separation processes.

It should also be noted that various other advantages accrue by practice of the process of the present invention. Such additional advantages may be enumerated as follows:

(1) The present process requires less catalytic cracking capacity. Such reduction in capacity is based on the fact that with a given amount of steam cracking capacity, less catalytic cracking capacity is required when catalytic cycle oil is steam cracked instead of being catalytically cracked. Further, only a comparatively small amount of added furnace capacity is required for the steam cracking step in order to crack catalytic cycle oil instead of light virgin gas oil, which is the alternate feed. In addition, the facilities for handling the gas and liquid prod- ucts are found to be about the same for each of these feeds. Thus, the need for less catalytic cracking capacity can be translated into the advantage of lower investment cost.

(2) The refining sequence of this invention produces less catalytic coke, i.e., carbon on catalyst, since an increment of catalytic cycle oil is not catalytically cracked. Catalytic coke is burned from the catalyst in the regener- ator and subsequently provides energy in the catalytic cracking process. In the novel sequence of this inven- tion, the coke-forming components form a tar. The heavy fraction of this tar has a much higher value based on the feeding of this material to a coking unit and there- by reduces the need for purchased virgin residual oil. In addition, the lighter portion of the tar (400–650°F.) produced in the steam cracking step also has value as prime hydrocracker feed.

With a limited supply of low cost hydrogen (available in powerformer tail gas), the novel refining sequence permits the optimization of feeds to the Hydrocracking Unit, with aromatic gas oil being the most attractive.

(3) The advantages for the novel sequence in comparison with a conventional sequence can be expressed in terms of the cost of products produced from a given quantity of crude for each of the two sequences. It should be noted that the novel sequence produces more marketable products from a given amount of crude while maintaining motor gasoline production level con- stant and consequently permits meeting requirements of
a lower crude input. The following is a comparison of the output from 1000 barrels of crude for each sequence.

<table>
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<tr>
<th></th>
<th>Present</th>
<th>Conv.</th>
<th>Difference</th>
<th>Value (bbl/ml)</th>
<th>Net Value (50,000 bbl)</th>
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<tr>
<td>Pool Motor Gasoline</td>
<td>657</td>
<td>657</td>
<td>0</td>
<td>1.00</td>
<td>500</td>
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<td>Distillate, Bbl.</td>
<td>215</td>
<td>206</td>
<td>9</td>
<td>1.00</td>
<td>215</td>
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<td>Pool Gas, F+E</td>
<td>38</td>
<td>40</td>
<td>2</td>
<td>1.05</td>
<td>38</td>
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<tr>
<td>C6, Bbl.</td>
<td>29</td>
<td>30</td>
<td>1</td>
<td>1.08</td>
<td>29</td>
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<tr>
<td>H9, Bbl.</td>
<td>Base</td>
<td>4</td>
<td>Base 4</td>
<td>Base</td>
<td>4</td>
</tr>
<tr>
<td>Petroleum Coke, F+E</td>
<td>14</td>
<td>15</td>
<td>1</td>
<td>0.98</td>
<td>14</td>
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<tr>
<td>Octane Improvement RON, defeet</td>
<td>Base</td>
<td>10</td>
<td>Base 10</td>
<td>Base</td>
<td>10</td>
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<tr>
<td>Operating Costs, N.</td>
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<td>Base 6</td>
<td>Base</td>
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<tr>
<td>Expansion, Vol. Per 100</td>
<td>100.3</td>
<td>100.0</td>
<td>0.3</td>
<td>2.6</td>
<td>250.6</td>
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*Does not include catalytic coke which has no value in the example. Parentheses signify negative values.

From this tabulation it can be seen that approximately 2.2 bbl of input is saved by operating the sequence of this invention. Thus, a saving of about $4,400 per day is represented relative to an average size (200,000 bbl. per day) refinery.

Although the invention has been described in considerable detail in the foregoing for the purpose of illustration, it is to be understood that such detail is solely for this purpose and that variations may be made by those skilled in the art without departing from the spirit and scope of the invention except as set forth in the claims.

What is claimed is:

1. A process for upgrading the mid-boiling fractions of petroleum crude oil which comprises flashing a topped crude oil under vacuum at a flash temperature above about 900° F. (equivalent at 760 mm. Hg) to produce a heavy gas oil fraction having a boiling range of about 500 to 1050° F., catalytically cracking said heavy gas oil fraction in one-pass catalytic cracking zone at a temperature between 750 and 1050° F., distilling the catalytically cracked product to separate furnace oil and lighter fractions and a heavy residual fraction and produce a cycle oil fraction boiling within the range of about 400 to 750° F., passing said cycle oil to a steam cracker, steam cracking said cycle oil at a low pressure and at a temperature between 1100 and 1500° F. and holding time of 2 to 2.5 seconds, distilling the steam cracked product to separate hydrocarbons boiling at about 450° F. or less and to produce a side stream fraction boiling at 450 and 650° F. and a tar bottoms fraction boiling above about 650° F. and up to about 1200° F., contacting said side stream fraction with hydrogen in at least one hydrocracking stage in the presence of a hydrocracking catalyst at a temperature between 550 and 800° F. and distilling the resulting hydrocracked product to separate a residue fraction from a product gasoline fraction, passing said tar bottoms fraction resulting from the distillation of said steam-cracked product into a thermal soaking zone, subjecting said tar bottoms fraction to a temperature between 750 and 950° F. for a period of from 2 to 6 hours to convert said tar bottoms to pitch and more volatile products, passing said pitch and volatile products to a distillation zone and therein stripping the pitch of substantially all the volatile products boiling below about 750° F.

2. The process of claim 1 in which said quenching medium is the volatile products boiling below about 750° F. which have been stripped from the pitch produced in said thermal soaking zone.

3. The process of claim 1 in which said cycle oil comprises a mixture of light catalytic cycle oil boiling between 400 and 600° F. and heavy catalytic cycle oil boiling between 590 and 750° F.

4. The process of claim 1 in which said cycle oil is contacted with about 40 to 100 mole percent of steam in said steam cracking zone.

5. A process for upgrading the mid-boiling fractions of petroleum crude oil which comprises flashing a topped crude oil under vacuum at a flash temperature above about 900° F. (atmospheric pressure) to produce a heavy gas oil fraction having a boiling range of about 500 to 1050° F., catalytically cracking said heavy gas oil fraction in a one-pass catalytic cracking zone, at a temperature between 750 and 1050° F., distilling the catalytically cracked product to separate furnace oil and lighter fractions and a heavy residual fraction and produce a heavy catalytic cycle oil fraction having a boiling range of about 590 to 750° F., passing said cycle oil to a steam cracker, steam cracking said cycle oil at a low pressure and at a temperature between 1300 and 1450° F., and for a holding time of 0.5 to 0.7 second, distilling the steam-cracked product to separate hydrocarbons boiling at about 450° F. or less and to produce a side stream fraction boiling between 450 and 650° F. and a tar bottoms fraction boiling above about 650° F. and up to about 1200° F., contacting said side stream with hydrogen in at least one hydrocracking stage in the presence of a hydrocracking catalyst at a temperature between 550 and 800° F., and distilling the resulting hydrocracked product to separate a residue fraction from a product gasoline fraction, passing said tar bottoms fraction resulting from the distillation of said steam-cracked product into a thermal soaking zone, subjecting said tar bottoms fraction to a temperature between 775 and 790° F. for a period of from 5 to 6 hours to convert said tar bottoms to pitch and more volatile products, passing said pitch and volatile products to a distillation zone and therein stripping the pitch of substantially all the volatile products boiling below about 750° F.

6. The process of claim 5 in which the hydrocracking catalyst employed is palladium on magnesium 13Y seive base.

7. The process of claim 5 in which the hydrocracking reaction is carried out at a hydrogen partial pressure between 600 and 2000 p.s.i.g.

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