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(54) **VACUUM GAS OIL CONVERSION PROCESS**

VERFAHREN ZUR VAKUUMGASÖLUMWANDLUNG

PROCÉDÉ DE CONVERSION DE GAZOLE SOUS VIDE

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Description

FIELD OF THE INVENTION

[0001] The present invention relates to a process for the selective conversion of a heavy hydrocarbon oil in a two-step process. The first is thermal conversion and the second is catalytic cracking of products from the thermal conversion. The present invention results in a process for increasing the distillate production from the heavy oil feed in the catalytic cracking unit. The product distribution from the process can be varied by changing the conditions in the thermal and catalytic cracking steps as well as by changing the catalyst in the cracking step.

BACKGROUND

[0002] The upgrading of atmospheric and vacuum residual oils (resids) to lighter, more valuable products has been accomplished by thermal cracking processes such as visbreaking and coking. In visbreaking, a vacuum resid or other heavy feed is sent to a visbreaker where it is thermally cracked under relatively mild conditions controlled to produce the desired products and minimize coke formation. The products from the visbreaker have reduced viscosity and pour points, and include naphtha, visbreaker gas oils and visbreaker residues. The residues or bottoms from the visbreaker are heavy oils such as heavy fuel oils. The conversion in visbreakers is a function of the asphaltene and Conradson Carbon Residue (or "CCR") content of the feed. Generally, lower levels of asphaltene and CCR content in the hydrocarbon feed are favorable to visbreaking. Higher values of asphaltene and CCR content lead to increased coking and lower yields of light liquid products.

[0003] Petroleum coking operates under more severe conditions than visbreaking. Residual feeds are converted to liquid hydrocarbon products of lower boiling point (atmospheric) than that of the feed while carbon is rejected in the form of relatively large amounts of petroleum coke. Some coking processes, such as delayed coking, are batch processes where the coke accumulates and is subsequently removed from a large drum while in fluid coking, for example, the Flexicoking® process of Exxon-Mobil Research and Engineering Co., the heavy oil feed is continuously subjected to thermal cracking conditions in a fluidized bed. Lower boiling products are formed by the thermal decomposition of the feed at elevated reaction temperatures, typically from about 480 to 590°C (about 895 to 1095°F), using heat supplied by combustion of a portion of the fluidized coke particles in a heater vessel. In the FLEXICOKING® process, the excess coke is converted to fuel gas in a gasifier by reaction with air and steam to produce a clean fuel gas that can be used in boilers and furnaces. Approximately 97% of the coke generated in the cracking reactor is consumed in the process, with a small amount of product coke recovered from the fines system.

[0004] The fluid catalytic cracking (FCC) process has become the workhorse of the refinery for gasoline production while hydrocracking, the other major catalytic cracking process remains the source for road diesel, jet fuel and other distillates. Current industry projects worldwide market growth for diesel relative to gasoline. In response to this changing market demand, decreasing naphtha yield while increasing both FCC distillate yield and quality presents the potential for rebalancing the product slate to match projections while retaining use of existing refinery equipment. In order to be economically attractive, this must be accomplished with no (or minimal) loss in bottoms conversion or coke selectivity. Keeping the bottoms and coke yields at today's levels ensures no increase in fuel oil production and ensures that FCC regenerator air limits are not exceeded.

[0005] Currently, in many refineries, only a limited amount of distillate material from the FCC (LCO) normally goes into the diesel pool. FCC distillate has a very high aromatics content with a low cetane index (<30 cetane index) as a result of the removal of alkyl side chains besides having DBT (dibenzothiophene) molecules in it that are difficult to hydrotreat. As a result FCC distillate gets blended into fuel oil (downgraded). There is accordingly a need in the industry for improved processes for treating high boiling range hydrocarbon feeds such as vacuum gas oils in order to increase the production of distillate boiling range products from such feeds, especially of road diesel fuel if the relevant product specifications can be met. To this end, integrated thermal/catalytic treatment processes for heavy oil feeds have been proposed, including those described in U.S.2010/0018895 and U.S.2010/0018896. The process described in U.S. 2010/0018895 includes two basic steps: the first is of thermal conversion and the second is catalytic cracking of the higher boiling products of the thermal conversion with an optional hydrotreatment of the thermally cracked bottoms fraction to reduce the proportion of heteroatoms sent to the FCCU. The variant of this process described in U.S. 2010/0018896 uses a divided wall fractionator to separate the bottoms fractions obtained from the thermal and catalytic cracking steps.

[0006] U.S. 4,039,429 describes a process for converting heavy feeds into light distillate fractions involving thermal and catalytic cracking.

[0007] During the thermal cracking step it is desirable but not essential for the feed to be kept in the liquid phase during the thermal treatment in order to control the residence time and hence, the severity of the cracking and the conversion. With the temperatures encountered during this step, relatively high pressures are necessary, to be provided by robust feed pumps. These may be provided by the feed system for existing visbreakers but if other furnaces are used, for example, furnaces converted from FCC preheat operation, upgraded equipment may be necessary. If the bottoms hydrotreatment option described in U.S. 2010/0018895 is utilized with a gas oil feed, high pressure pumps may be available and incor-

porated into the integrated unit but depending on the nature of the feed, additional problems may arise. If the gas oil contains significant amounts of lighter ends, e.g. naphtha (boiling below 200°C) and distillate (boiling below 350°C), routing such feeds to either the thermal or catalytic cracking steps may result in overcracking and reactor upsets as these units are not typically designed for operations with such feeds. There is therefore a need for developing a fully integrated thermal/catalytic cracking process for use with heavy oil feeds.

SUMMARY OF PREFERRED EMBODIMENTS OF THE INVENTION

[0008] We have now devised an integrated thermal/catalytic cracking process which incorporates hydrotreatment of the thermally cracked bottoms fraction before passing to the catalytic cracking step. According to the present invention, the process comprises:

- separating a heavy hydrocarbon, preferably a gas oil, feed to form a light fraction boiling below about 345°C (650°F) and a heavy fraction boiling above about 345°C (650°F);
- thermally cracking the heavy fraction in a thermal conversion zone to produce a thermally cracked product;
- combining the light fraction with the thermally cracked heavy fraction;
- hydrotreating the combined light and heavy fractions;
- separating the hydrotreated product in a fractionator into a hydrotreated bottoms fraction and a hydrotreated light fraction;
- catalytically cracking at least a portion of the hydrotreated bottoms fraction; and
- fractionating the catalytically cracked product to separate a naphtha fraction, a distillate fraction and a bottoms fraction.

[0009] Since the lightest portion (C₄-) of the combined light and heavy fractions from the thermal cracking step will not normally require hydrotreatment, it may be bypassed around the hydrotreatment step in order to increase the capacity of the hydrotreater. This configuration with the hydrotreatment of the thermally cracked heavy VGO (345°C+, 650°F+) fraction increases the yield of high quality distillate (45+ Cetane Index) relative to the base case of sending the VGO fraction directly to the FCCU, while at the same time reducing the amount of naphtha. The quantity of distillate produced and reduction in the quantity of naphtha will be refinery specific

since they depend on the sizes and capabilities of the available equipment.

[0010] The term "naphtha" or "naphtha fraction" is used here to mean a hydrocarbon fraction in which at least 90 wt % of the fraction boils in the range of about 15°C to about 210°C (59°F to 430°F) as measured by ASTM D 86. The term "distillate" or "distillate fraction" is used here to mean a hydrocarbon fraction in which at least 90 wt % of the distillate fraction boils in the range of about 200°C to about 345°C (392°F to 650°F) as measured by ASTM D 86. In the C₄-fraction, referred to here, at least 90 wt % of the fraction boils at temperatures below 0°C (32°F) as measured by ASTM D 86.

FIGURES

[0011] The single FIGURE of the accompanying drawings illustrates a simplified process schematic of an embodiment of the integrated thermal cracking/hydrotreatment/catalytic cracking processes herein.

DETAILED DESCRIPTION

Process Configuration

[0012] The Figure shows a very much simplified configuration for one version of the process in which the light ends by-pass the thermal cracking step with the lightest (C₄-) fractions also routed around the hydrotreater. The heavy feed is introduced through line 10 and enters separator 11 which splits out the 345°C- (650°F-) fraction and routes it through line 12 around visbreaker furnace 13 and visbreaker (coil or drum) 14 to combine with the visbroken product in line 16. Depending upon the severity regime in the furnace (temperature, retention time), it may be possible to omit the coil or drum while still achieving a sufficient degree of cracking. If the severity of the thermal cracking step is relatively high, (nominally above 100 equivalent seconds @875°F/470°C), the combined fractions pass to optional hot separator 20 in which the C₄- light ends are split out to pass through line 21 around the gas oil hydrotreater 22 before being recombined with the hydrotreated product fraction in line 23 which takes the combined fractions to the hydrotreater fractionator 25 in which a separation between the naphtha, middle distillate and bottoms (345°C+, 650°F+) fractions is made. The bottoms fraction from fractionator 25 is sent to the FCCU 26 for cracking in the absence of added hydrogen and in the presence of a fluid catalytic cracking catalyst while the hydrotreated middle distillate is sent to the recovery section as an additional contribution for potential use in the refinery diesel pool.

[0013] From the FCCU 26, the catalytically cracked products pass by way of line 27 to the FCC main column and product recovery section where they and, optionally, the lower boiling fraction from the hydrotreater fractionator, are separated into products including naphtha, distillate and bottoms. The C₄- fraction is taken off the top

of the fractionator and sent for further processing as desired. Some, or all, of the naphtha product stream may be optionally recycled back to the FCC reactor in the catalytic cracking step and the bottoms from the fractionator may also be recycled back to the FCC reactor in the catalytic cracking step for further processing.

Heavy Oil Feed

[0014] The feedstock to the present conversion process is typically a heavy oil feed having a Conradson Carbon Residue (CCR, ASTM D4530) content of from 0 to 6 wt %, based on the total feed, and is most preferably a vacuum gas oil (VGO). The vacuum gas oil (VGO) will normally be a hydrocarbon fraction in which at least 90 wt % boils in the range of about 290° to about 565°C. (about 550° to 1050°F) as measured by ASTM D 2887 (unless otherwise noted, all boiling point temperatures are referenced at atmospheric pressure). It is preferred that the heavy oil feed be suitable as a feed to the FCC unit. The bulk of this fraction will boil above about 345°C (about 650°F) with up to about 25 wt % of material boiling in the 290-345°C (550-650°F) may be present. The portion boiling below about 345°C (650°F) is initially removed in order to reduce cracking of the desired distillate to naphtha in the thermal conversion step. While VGOs are typically low in CCR content and low in metal content, feeds having >1 wt % CCR may include a resid component, typically not more than 10 wt % boiling above about 565°C (1050°F) with the permissible amount depending upon the quality of the resid component: if no significant quantities of heavy metals is present and if the CCR is low, it may be possible to process higher resid content feedstocks. The feedstock to the thermal conversion zone may be heated to the necessary reaction temperature by an independent furnace or by the feed furnace to the FCC unit itself.

[0015] In preferred embodiments herein, the heavy oil feed comprises a gas oil feed having a boiling point above 290°C. In other preferred embodiments, the gas oil feed comprises a vacuum gas oil in which at least 75 wt % of the gas oil feed boils in the range of 345° to 565°C (ASTM D 2887). In yet other preferred embodiments, the gas oil feed comprises a vacuum gas oil in which at least 90 wt % of the gas oil feed boils in the range of 345° to 565°C (ASTM D 2887).

Thermal Conversion

[0016] The heavy oil feed is first thermally converted in a thermal conversion zone. When the hydrocarbon feed contains a substantial amount of VGO and little or no resid, the thermal conversion zone can be operated at more severe conditions because VGO fractions tend to be low in CCR and metals; this tends to limit the production of excessive coke, gas make, toluene insolubles, or reactor wall deposits as compared to a typical vacuum resid feed that is thermally cracked.

[0017] The conditions used for the thermal cracking step may be determined empirically and are generally expressed as a severity which is dependent upon both the temperature and residence time of the hydrocarbon feed in the thermal conversion zone. Severity has been described as equivalent reaction time (ERT) in U.S. Pat. Nos. 4,892,644 and 4,933,067 to which reference is made herein for a description of the ERT calculation. As described in U.S. 4,892,644, ERT is expressed as a time in seconds of residence time at a fixed temperature of 427°C, and is calculated using first order kinetics. The ERT range in the U.S. 4,892,644 patent is from 250 to 1500 ERT seconds at 427°C, more preferably at 500 to 800 ERT seconds. As noted there, raising the temperature causes the operation to become more severe: raising the temperature from 427°C to 456°C leads to a five-fold increase in severity.

[0018] In the present process, a similar methodology is used to determine severities which are expressed in equivalent seconds at 470°C. In the present process, severities are in the range of 25-450 equivalent seconds at 470°C (875°C). At a cracking severity of about 50 eq. seconds (470°F/875°C), an increase of 3 to 5 wt % in distillate production relative to the base case (no hydrotreating) without adverse effect on the operation of the VGO hydrotreater with a distillate of 45-50 Cetane Number. Because the present feeds are normally low in CCR, the present process can operate at severities higher than those described for visbreaking of a vacuum resid. These low CCR hydrocarbon feeds have a lower tendency to form wall deposits and coke, and minimize the yield of poor quality naphthas that are produced in the thermal conversion.

Thermal Conversion Products

[0019] The products from thermal conversion are conducted next to the hydrotreating step to remove heteroatoms and improve crackability in the FCCU. Optionally, the hot separator following the visbreaker and ahead of the hydrotreater is used to route the gas fraction (C₄-) around the hydrotreater section since there is no advantage as well as an increase in hydrotreater throughput to be gained by doing so. The separation may be accomplished using conventional separators such as a hot separator, a flash tower or a distillation tower. In the separator, the thermally cracked products can be separated into a bottoms fraction and a lower boiling fraction comprised of a naphtha and/or a distillate, depending on the conditions used in the thermal cracking step. This fraction will have boiling points commensurate with these products and can be sent to a fractionator for further separation into desired products, for example, visbreaker naphtha etc. This lower boiling fraction may also contain a thermally cracked C₄- fraction which may be separately isolated and sent to the hydrotreater product fractionator with or without the naphtha and/or distillate fraction.

[0020] The thermally cracked bottoms fraction con-

tains higher boiling material, e.g., fractions having a boiling point in excess of about 345°C (650°F). The thermally cracked bottoms fraction is sent to a FCC unit for catalytic cracking and may be combined with other FCC feeds prior to the FCC unit.

[0021] A portion or all of the thermally cracked fraction is hydrotreated in a gas oil hydrotreater prior to being sent to the FCC unit. The gas oil hydrotreater is one adapted to operate with feeds boiling in the 345-565°C (650-1050°F) range without significant amounts of lower and higher boiling materials although some higher boiling residual ends may be present if they can be accommodated for treatment in the FCCU, as noted above. In the present process, the feed to the VGO hydrotreater will also contain the thermally cracked distillate fraction which undergoes a limited degree of desulfurization in the hydrotreater; the limited degree of desulfurization which does take place is not disadvantageous since the thermally cracked distillate has a relatively low content of dibenzothiophenes as compared to FCC light cycle oil so that the extent of desulfurization required to meet current road diesel specifications is itself limited. The thermally cracked fraction, with or without the light (C₄-) ends, is contacted with hydrogen and a hydrotreating catalyst to remove at least a portion of the sulfur and/or nitrogen contaminants to produce a hydrotreated product fraction which may be recombined with the by-passed light ends before being sent to the hydrotreater fractionator. After hydrotreating, at least a portion of the hydrotreated bottoms fraction is sent to an FCC unit for further processing. In the present invention, the hydrotreated naphtha and middle distillate fractions will not benefit from being cracked in the FCC step and will, in any event, load up the unit, they are preferably removed at this stage of the present processes and sent to product recovery for use as blend components in the refinery gasoline pool, heating oil, distillate, e.g. diesel, since the aromatic and heteroatom content has been reduced in the hydrotreater.

[0022] The hydrotreating step herein is preferably carried out at a minimum temperature of about 280°C, more usually from 300°C with maximum temperatures in this step of about 380° or 400°C. Pressures preferably range from a minimum of about 1,500 or 3,000 kPag to a maximum of about 20,000 or, more usually, about 14,000 kPag. Space velocity in the hydrotreating zone is preferably from about 0.1 to about 10 LHSV, more commonly from about 0.1 to about 5 LHSV. Hydrogen treat gas rates of from about 100 to about 2,000 m³/m³ (562 to 11,200 scf/B), more preferably 200 to 1000 m³/m³ (1125 to 5620 scf/B) may be utilized in the hydrotreating zone. Optimally, it is recommended that the feed to the hydrotreater should not contain material that boils higher than about 650°C (about 1200°F) with the Simdist 99 wt % (ASTM D7096-10) point not greater than that same value. Higher boiling feeds will increase the costs associated with implementing this technology. In preferred embodiments herein, the recommended operating conditions for the hydrotreater should be 6,000 to 10,000 kPag (about

870-1450 psig) hydrogen pressure, Liquid Hourly Space velocity of 0.2-0.8 hr⁻¹ and temperature range of 355 to 455°C (670 to 850°F).

[0023] Hydrotreating catalysts suitable for use herein are those containing at least one Group 6 (based on the IUPAC Periodic Table having Groups 1-18) metal and at least one Groups 8-10 metal, including mixtures thereof. Preferred metals include Ni, W, Mo, Co and mixtures thereof. These metals or mixtures of metals are typically present as oxides or sulfides on refractory metal oxide supports. The mixture of metals may also be present as bulk metal catalysts wherein the amount of metal is 30 wt % or greater, based on the catalyst. Suitable metal oxide supports include oxides such as silica, alumina, silica-alumina or titania, preferably alumina. Preferred aluminas are porous aluminas such as gamma or eta. The acidity of metal oxide supports can be controlled by adding promoters and/or dopants, or by controlling the nature of the metal oxide support, e.g., by controlling the amount of silica incorporated into a silica-alumina support. The amount of metals for supported hydrotreating catalysts, either individually or in mixtures, ranges from 0.5 to 35 wt %, based on the catalyst. In the case of preferred mixtures of Group 6 and Groups 8-10 metals, the Group 8-10 metals are present in amounts of from 0.5 to 5 wt %, based on the catalyst and the Group 6 metals are present in amounts of from 5 to 30 wt % based on the catalyst. Nonlimiting examples of suitable commercially available hydrotreating catalysts include RT-721, KF-840, KF-848, and Sentinel™. Preferred catalysts are low acidity, high metals content catalysts including KF-848 and RT-721.

FCC Process

[0024] The conventional FCC process includes a riser reactor and a regenerator wherein petroleum feed is injected into the reaction zone in the riser containing a bed of fluidized cracking catalyst particles which typically contain zeolites. Gases that may be inert gases, hydrocarbon vapors, steam or some combination thereof are normally employed as lift gases to assist in fluidizing the hot catalyst particles.

[0025] Catalyst particles that have contacted feed produce product vapors and catalyst particles containing strippable hydrocarbons as well as coke. The catalyst exits the reaction zone as spent catalyst particles and is separated from the reactor's effluent in a separation zone. The separation zone for separating spent catalyst particles from reactor effluent may employ separation devices such as cyclones. Spent catalyst particles are stripped of hydrocarbons using a stripping agent such as steam. The stripped catalyst particles are then sent to a regeneration zone in which any remaining hydrocarbons are stripped and coke is removed. In the regeneration zone, coked catalyst particles are contacted with an oxidizing medium, usually air, and coke is oxidized (burned) at temperatures preferably in the range of about 650 to

760°C (1202 to 1400°F). The regenerated catalyst particles are then passed back to the riser reactor.

[0026] FCC catalysts may be amorphous, e.g., silica-alumina, crystalline, e.g., molecular sieves including zeolites, or mixtures thereof. A preferred catalyst particle comprises (a) an amorphous, porous solid acid matrix, such as alumina, silica-alumina, silica-magnesia, silica-zirconia, silica-thoria, silica-beryllia, silica-titania, silica-alumina-rare earth and the like; and (b) a zeolite such as a faujasite. The matrix can comprise ternary compositions, such as silica-alumina-thoria, silica-alumina-zirconia, magnesia and silica-magnesia-zirconia. The matrix may also be in the form of a cogel. Silica-alumina is particularly preferred for the matrix, and can contain about 10 to 40 wt % alumina. As discussed, promoters can be added. The catalyst zeolite component includes zeolites which are iso-structural to zeolite Y. These include the ion-exchanged forms such as the rare-earth hydrogen and ultrastable (USY) form. The zeolite may range in crystallite size from about 0.1 to 10 microns, preferably from about 0.3 to 3 microns. The amount of zeolite component in the catalyst particle will generally range from about 1 to about 60 wt %, preferably from about 5 to about 60 wt %, and more preferably from about 10 to about 50 wt %, based on the total weight of the catalyst. The catalyst particle size will typically range from about 10 to 300 microns in diameter, with an average particle diameter of about 60 microns. The surface area of the matrix material after artificial deactivation in steam will typically be ≤ 350 m²/g, more typically about 50 to 200 m²/g, and most typically from about 50 to 100 m²/g. While the surface area of the catalysts will be dependent on such things as type and amount of zeolite and matrix components used, it will usually be less than about 500 m²/g, more typically from about 50 to 300 m²/g, and most typically from about 100 to 250 m²/g.

[0027] The cracking catalyst may also include an additive catalyst in the form of a medium pore zeolite having a Constraint Index (defined in U.S. Pat. No. 4,016,218) of about 1 to about 12. Suitable medium pore zeolites include ZSM-5, ZSM-11, ZSM-12, ZSM-22, ZSM-23, ZSM-35, ZSM-48, ZSM-57, SH-3 and MCM-22, either alone or in combination. Preferably, the medium pore zeolite is ZSM-5.

[0028] In the process embodiments herein, FCC process conditions in the reaction zone include temperatures from about 482 to about 740°C (900 to 1364°F); hydrocarbon partial pressures from about 70 to 300 kPa (about 15 to about 43 psia, preferably from about 150 to 250 kPa (22 to about 36 psia); and a catalyst to feed (wt/wt) ratio from about 3 to about 10, where the catalyst weight is total weight of the catalyst composite. The total pressure in the reaction zone is preferably from about atmospheric to about 450 kPa (50 psi). Though not required, it is preferred that steam be concurrently introduced with the feedstock into the reaction zone, with the steam comprising up to about 50 wt %, preferably from about 0.5 to about 5 wt % of the primary feed. Also, it is

preferred that vapor residence time in the reaction zone be less than about 20 seconds, preferably from about 0.1 to about 20 seconds, and more preferably from about 1 to about 5 seconds. Preferred conditions are short contact time conditions which include riser outlet temperatures from 482-621°C (900-1150°F), total pressures from about 100 to 450 kPa (0 to about 50 psi) and riser reactor residence times from 1 to 5 seconds.

[0029] Different feeds may require different cracking conditions. In the present process, if it is desired to make the maximum amount of distillate from the hydrocarbon feed, then the thermal cracker will be run at maximum temperature consistent with avoiding excess coke or coke precursor make.

[0030] Additionally or alternatively, the present invention can be described according to one or more of the following embodiments.

[0031]

Embodiment 1. A thermal and catalytic process for converting a heavy petroleum oil feed into lower boiling products, comprising:

- separating a heavy hydrocarbon feed to form a light fraction boiling below about 345°C (650°F) and a heavy fraction boiling above about 345°C (650°F);
- thermally cracking the heavy fraction in a thermal conversion zone to produce a thermally cracked product;
- combining the light fraction with the thermally cracked heavy fraction;
- hydrotreating the combined light and heavy fractions;
- separating the hydrotreated product in a fractionator into a hydrotreated bottoms fraction and a hydrotreated light fraction;
- catalytically cracking at least a portion of the hydrotreated bottoms fraction; and
- fractionating the catalytically cracked product to separate a naphtha fraction, a distillate fraction and a bottoms fraction.

Embodiment 2. The process according to embodiment 1, wherein the heavy hydrocarbon feed comprises a gas oil feed having a boiling point above 290°C.

Embodiment 3. The process according to embodiment 2, wherein the gas oil feed has a Conradson Carbon Residue (CCR) content greater than 1 wt %.

Embodiment 4. The process according to any of embodiments 2-3, wherein the gas oil feed comprises a vacuum gas oil in which at least 75 wt % of the gas oil feed boils in the range of 345° to 565°C (ASTM D 2887).

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Embodiment 5. The process according to any of embodiments 2-4, wherein the gas oil feed comprises a vacuum gas oil in which at least 90 wt % of the gas oil feed boils in the range of 345° to 565°C (ASTM D 2887).

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Embodiment 6. The process according to any of embodiments 2-5, wherein the gas oil feed comprises up to 10 wt % of a resid boiling above 565°C.

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Embodiment 7. The process according to any prior embodiment, the C₄- fraction of the combined hydrotreated light and heavy fractions is by-passed around the hydrotreating step.

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Embodiment 8. The process according to any prior embodiment, wherein the severity of the thermal cracking step is from 25 to 450 equivalent seconds at 470°C.

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Embodiment 9. The process according to any prior embodiment, wherein the hydrotreating step includes the following conditions: 6,000 to 10,000 kPag (about 870-1450 psig) hydrogen pressure, liquid hourly space velocity (LHSV) of 0.2-0.8 hr⁻¹ and a temperature of from 355 to 455°C (670 to 850°F).

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Embodiment 10. The process according to any prior embodiment, wherein the hydrotreating step includes a hydrotreating catalyst containing at least one Group 6 metal and at least one Group 8-10 metal on a metal oxide support.

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Embodiment 11. The process according to embodiment 10, wherein the metal oxide support is selected from silica, alumina, silica-alumina, and titania.

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Embodiment 12. The process according to any prior embodiment, wherein the catalytic cracking step includes the following conditions: temperatures from about 482 to about 740°C (900 to 1364°F); hydrocarbon partial pressures from about 70 to 300 kPaa (about 15 to about 43 psia); a catalyst to feed (wt/wt) ratio from about 3 to about 1, and a riser reactor residence time from 1 to 5 seconds.

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Embodiment 13. The process according to any prior embodiment, wherein the catalytic cracking step includes a cracking catalyst containing an amorphous, porous solid acid matrix selected from alumina, silica-alumina, silica-magnesia, silica-zirconia, silica-thoria, silica-beryllia, silica-titania, and silica-alumi-

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na-rare earth; and a zeolite.

Embodiment 14. The process according to any prior embodiment, wherein the distillate fraction has a Cetane Number of at least 45.

Embodiment 15. The process according to any prior embodiment, wherein at least a portion of the naphtha fraction is recycled back to the catalytic cracking step.

Embodiment 16. The process according to any prior embodiment, wherein at least a portion of the bottoms fraction is recycled back to the catalytic cracking step.

Claims

1. 1. A thermal and catalytic process for converting a heavy petroleum oil feed into lower boiling products, comprising:
 - separating a heavy hydrocarbon feed to form a light fraction boiling below 345°C (650°F) and a heavy fraction boiling above 345°C (650°F);
 - thermally cracking the heavy fraction in a thermal conversion zone to produce a thermally cracked product;
 - combining the light fraction with the thermally cracked heavy fraction;
 - hydrotreating the combined light and heavy fractions;
 - separating the hydrotreated product in a fractionator into a hydrotreated bottoms fraction and a hydrotreated light fraction;
 - catalytically cracking at least a portion of the hydrotreated bottoms fraction; and
 - fractionating the catalytically cracked product to separate a naphtha fraction, a distillate fraction and a bottoms fraction.
2. The process according to claim 1, wherein the heavy hydrocarbon feed comprises a gas oil feed having a boiling point above 290°C.
3. The process according to claim 2, wherein the gas oil feed has a Conradson Carbon Residue (CCR) content greater than 1 wt %.
4. The process according to any one of claims 2-3, wherein the gas oil feed comprises a vacuum gas oil in which at least 75 wt %, preferably at least 90 wt%, of the gas oil feed boils in the range of 345° to 565°C (ASTM D 2887).
5. The process according to any one of claims 2-4, wherein the gas oil feed comprises up to 10 wt % of

a resid boiling above 565°C.

6. The process according to any prior claim, wherein the C₄- fraction of the combined hydrotreated light and heavy fractions is by-passed around the hydrotreating step. 5
7. The process according to any prior claim, wherein the severity of the thermal cracking step is from 25 to 450 equivalent seconds at 470°C. 10
8. The process according to any prior claim, wherein the hydrotreating step includes the following conditions: 6,000 to 10,000 kPag (870-1450 psig) hydrogen pressure, liquid hourly space velocity (LHSV) of 0.2-0.8 hr⁻¹ and a temperature of from 355 to 455°C (670 to 850°F). 15
9. The process according to any prior claim, wherein the hydrotreating step includes a hydrotreating catalyst containing at least one Group 6 metal and at least one Group 8-10 metal on a metal oxide support. 20
10. The process according to claim 9, wherein the metal oxide support is selected from silica, alumina, silica-alumina, and titania. 25
11. The process according to any prior claim, wherein the catalytic cracking step includes the following conditions: temperatures from 482 to 740°C (900 to 1364°F); hydrocarbon partial pressures from 70 to 300 kPaa (15 to 43 psia); a catalyst to feed (wt/wt) ratio from 3 to 1, and a riser reactor residence time from 1 to 5 seconds. 30
12. The process according to any prior claim, wherein the catalytic cracking step includes a cracking catalyst containing an amorphous, porous solid acid matrix selected from alumina, silica-alumina, silica-magnesia, silica-zirconia, silica-thoria, silica-beryllia, silica-titania, and silica-alumina-rare earth; and a zeolite. 35
13. The process according to any prior claim, wherein the distillate fraction has a Cetane Number of at least 45. 45
14. The process according to any prior claim, wherein at least a portion of the naphtha fraction is recycled back to the catalytic cracking step. 50
15. The process according to any prior claim, wherein at least a portion of the bottoms fraction is recycled back to the catalytic cracking step. 55

Patentansprüche

1. Thermisches und katalytisches Verfahren zur Umwandlung eines schweren Erdöleinsatzmaterials in niedriger siedende Produkte, bei dem
 - ein schweres Kohlenwasserstoffeinsatzmaterial getrennt wird, um eine leichte Fraktion, die unterhalb von 345°C (650°F) siedet, und eine schwere Fraktion, die oberhalb von 345°C (650°F) siedet, zu bilden,
 - die schwere Fraktion in einer thermischen Umwandlungszone thermisch gecrackt wird, um ein thermisch gecracktes Produkt herzustellen,
 - die leichte Fraktion mit der thermisch gecrackten schweren Fraktion kombiniert wird,
 - die kombinierten leichten und schweren Fraktionen wasserstoffbehandelt werden,
 - das wasserstoffbehandelte Produkt in einem Fraktionierer in eine wasserstoffbehandelte Bodenfraktion und eine wasserstoffbehandelte leichte Fraktion getrennt wird,
 - mindestens ein Teil der wasserstoffbehandelten Bodenfraktion katalytisch gecrackt wird und
 - das katalytisch gecrackte Produkt fraktioniert wird, um eine Naphthafraktion, eine Destillatfraktion und eine Bodenfraktion zu bilden.
2. Verfahren nach Anspruch 1, wobei das schwere Kohlenwasserstoffeinsatzmaterial ein Gasöleinsatzmaterial mit einem Siedepunkt oberhalb von 290°C umfasst.
3. Verfahren nach Anspruch 2, wobei das Gasöleinsatzmaterial einen Koksrückstand nach Conradson (CCR) von mehr als 1 Gew.-% aufweist.
4. Verfahren nach einem der Ansprüche 2-3, wobei das Gasöleinsatzmaterial ein Vakuumgasöl umfasst, in dem mindestens 75 Gew.-%, bevorzugt mindestens 90 Gew.-%, des Gasöleinsatzmaterials im Bereich von 345°C bis 565°C siedet (ASTM D 2887).
5. Verfahren nach einem der Ansprüche 2-4, wobei das Gasöleinsatzmaterial bis zu 10 Gew.-% eines Rückstandes umfasst, der oberhalb von 565°C siedet.
6. Verfahren nach einem der vorhergehenden Ansprüche, wobei die C₄-Fraktion der kombinierten wasserstoffbehandelten leichten und schweren Fraktionen an dem Wasserstoffbehandlungsschritt vorbeigeleitet wird.
7. Verfahren nach einem der vorhergehenden Ansprüche, wobei die Strenge des thermischen Crackschrittes 25 bis 450 äquivalente Sekunden bei 470°C entspricht.

8. Verfahren nach einem der vorhergehenden Ansprüche, wobei der Wasserstoffbehandlungsschritt die folgenden Bedingungen aufweist: 6000 bis 10000 kPa Überdruck (870-1450 psi Überdruck) Wasserstoffdruck, stündliche Flüssigkeitsraumgeschwindigkeit (LHSV) von 0,2-0,8 h⁻¹ und eine Temperatur von 355 bis 455 °C (670 bis 850 °F). 5
9. Verfahren nach einem der vorhergehenden Ansprüche, wobei der Wasserstoffbehandlungsschritt einen Wasserstoffbehandlungskatalysator beinhaltet, der mindestens ein Metall der Gruppe 6 und mindestens ein Metall der Gruppe 8-10 auf einem Metalloxidträger enthält. 10
10. Verfahren nach Anspruch 9, wobei der Metalloxidträger aus Siliziumdioxid, Aluminiumdioxid, Siliziumdioxid-Aluminiumdioxid und Titandioxid ausgewählt ist. 15
11. Verfahren nach einem der vorhergehenden Ansprüche, wobei der katalytische Crackschritt die folgenden Bedingungen aufweist: Temperaturen von 482 bis 740 °C (900 bis 1364 °F), Kohlenwasserstoffpartialdrücke von 7 0 bis 300 kPa (absolut) (15 bis 43 psi (absolut)), ein Katalysator-zu-Einsatzmaterial-Verhältnis (Gew./Gew.) von 3:1 und eine Steigrohrreaktor-Verweilzeit von 1 bis 5 Sekunden. 20
12. Verfahren nach einem der vorhergehenden Ansprüche, wobei der katalytische Crackschritt einen Crackkatalysator beinhaltet, der eine amorphe, poröse, saure Feststoffmatrix beinhaltet, die aus Aluminiumdioxid, Siliziumdioxid-Aluminiumdioxid, Siliziumdioxid-Magnesiumoxid, Siliziumdioxid-Zirkoniumdioxid, Siliziumdioxid-Thoriumdioxid, Siliziumdioxid-Berylliumoxid, Siliziumdioxid-Titandioxid, Siliziumdioxid-Aluminiumdioxid-Seltenerdmetalle und Zeoliten ausgewählt ist. 25
13. Verfahren nach einem der vorhergehenden Ansprüche, wobei die Destillatfraktion eine Cetanzahl von mindestens 45 aufweist. 30
14. Verfahren nach einem der vorhergehenden Ansprüche, wobei mindestens ein Teil der Naphthafraktion zu dem katalytischen Crackschritt zurückgeführt wird. 35
15. Verfahren nach einem der vorhergehenden Ansprüche, wobei mindestens ein Teil der Bodenfraktion zu dem katalytischen Crackschritt zurückgeführt wird. 40

Revendications

1. Procédé thermique et catalytique de conversion d'une charge d'huile lourde en produits à point

d'ébullition inférieur, comprenant :

- la séparation d'une charge d'hydrocarbures lourds pour former une fraction légère à point d'ébullition inférieur à 345 °C (650 °F) et une fraction lourde à point d'ébullition supérieur à 345 °C (650 °F) ;
- le craquage thermique de la fraction lourde dans une zone de conversion thermique pour générer un produit craqué thermiquement ;
- la combinaison de la fraction légère avec la fraction lourde craquée thermiquement ;
- l'hydrotraitement des fractions légère et lourde combinées ;
- la séparation du produit hydrotraité dans une colonne de fractionnement en une fraction de queue hydrotraitée et une fraction légère hydrotraitée ;
- le craquage catalytique d'au moins une partie de la fraction de queue hydrotraitée ; et
- le fractionnement du produit craqué catalytiquement pour séparer une fraction de naphta, une fraction de distillat et une fraction de queue.

2. Procédé selon la revendication 1, dans lequel la charge d'hydrocarbures lourds comprend une charge de gazole ayant un point d'ébullition supérieur à 290 °C. 25
3. Procédé selon la revendication 2, dans lequel la charge de gazole a une teneur en résidu Conradson (CCR) supérieure à 1 % en poids. 30
4. Procédé selon l'une quelconque des revendications 2 et 3, dans lequel la charge de gazole comprend un gazole sous vide dans lequel au moins 75 % en poids, de préférence au moins 90 % en poids de la charge de gazole a un point d'ébullition dans l'intervalle de 345° à 565 °C (ASTM D 2887). 35
5. Procédé selon l'une quelconque des revendications 2 à 4, dans lequel la charge de gazole comprend jusqu'à 10 % en poids d'un résidu à point d'ébullition supérieur à 565 °C. 40
6. Procédé selon une quelconque revendication précédente, dans lequel la fraction en C₄- des fractions légère et lourde hydrotraitées combinées est écartée de l'étape d'hydrotraitement. 45
7. Procédé selon une quelconque revendication précédente, dans lequel la sévérité de l'étape de craquage thermique est de 25 à 450 secondes équivalentes à 470 °C. 50
8. Procédé selon une quelconque revendication précédente, dans lequel l'étape d'hydrotraitement comporte les conditions suivantes : pression d'hydrogène 55

ne de 6000 à 10 000 kPag (870-1450 psig), vitesse spatiale horaire de liquide (LHSV) de 0,2-0,8 h⁻¹ et température de 355 à 455 °C (670 à 850 °F).

9. Procédé selon une quelconque revendication précédente, dans lequel l'étape d'hydrotraitement comporte un catalyseur d'hydrotraitement contenant au moins un métal du groupe 6 et au moins un métal des groupes 8-10 sur un support d'oxyde métallique. 5
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10. Procédé selon la revendication 9, dans lequel le support d'oxyde métallique est choisi parmi la silice, l'alumine, la silice-alumine, et le dioxyde de titane.
11. Procédé selon une quelconque revendication précédente, dans lequel l'étape de craquage catalytique comporte les conditions suivantes : températures de 482 à 740 °C (900 à 1364 °F) ; pressions partielles d'hydrocarbures de 70 à 300 kPaa (15 à 43 psia) ; rapport entre catalyseur et charge (m/m) de 3 à 1 ; et temps de résidence dans le réacteur à colonne montante de 1 à 5 secondes. 15
20
12. Procédé selon une quelconque revendication précédente, dans lequel l'étape de craquage catalytique comporte un catalyseur de craquage contenant une matrice acide solide amorphe, poreuse choisie parmi l'alumine, la silice-alumine, la silice-magnésie, la silice-zircone, la silice-oxyde de thorium, la silice-oxyde de béryllium, la silice-dioxyde de titane, et la silice-alumine-terre rare ; et une zéolithe. 25
30
13. Procédé selon une quelconque revendication précédente, dans lequel la fraction de distillat a un indice de cétane d'au moins 45. 35
14. Procédé selon une quelconque revendication précédente, dans lequel au moins une partie de la fraction de naphta est recyclée vers l'étape de craquage catalytique. 40
15. Procédé selon une quelconque revendication précédente, dans lequel au moins une partie de la fraction de queue est recyclée vers l'étape de craquage catalytique. 45

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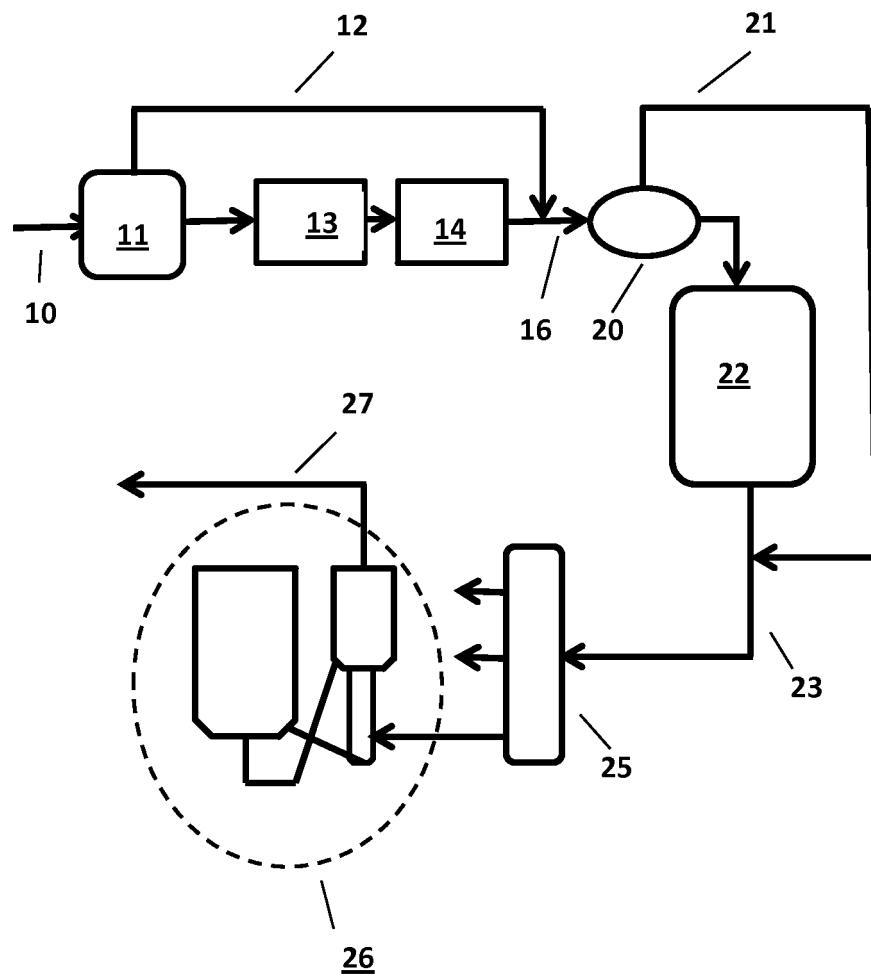


FIGURE 1

REFERENCES CITED IN THE DESCRIPTION

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