

PROCESS FOR CONVERTING RESIDUAL HYDROCARBON OILS

The present invention relates to a process for converting residual hydrocarbon oils. More specifically, the present invention is concerned with a process for hydrocracking residual hydrocarbon oils.

The increasing demand for distillate products together with the restricted availability of light feedstocks and high availability of relatively heavy feedstocks provide a strong incentive for developing residue conversion processes in which high conversion levels can be attained in a cost effective manner. Current commercial residue hydroconversion units are usually operated at low or medium conversion levels due to the requirement that the effluent has to be a stable liquid. It will be appreciated that this requirement has to be met in order to enable further processing of the effluent. Operating residue hydroconversion units at high conversion levels will give rise to an unstable total liquid effluent. Unless appropriate measures are taken, this will readily cause plugging in downstream piping and equipment due to deposition of asphaltenes. Yet another problem is that high conversion conditions involve higher operating temperatures to limit reactor volume, in any event above 375 °C, whilst residue hydroconversion catalysts usually comprise an alumina carrier. As is well known in the art, alumina-based conversion catalysts will rapidly coke at the high temperatures required for cost effective high conversion operations. This problem could be solved by applying a silica-based catalyst, as silica is far more resistant to higher temperatures than alumina. However, using a silica-based catalyst will not give the desired high conversion level into distillates.

It would, therefore, be desired if a residue conversion process could be provided, which can be operated at high conversion levels thereby producing a stable bottom effluent and a relatively high amount of distillates. In order to be able to produce distillates at relatively high yields from residual hydrocarbon oils hydrocracking of these residual oils inevitably will have to occur.

Hydrocracking processes are well known in the art. They generally involve contacting the hydrocarbon oil feedstock with hydrogen in the presence of a suitable hydrocracking catalyst, whereby the feedstock is converted into products having a lower average molecular weight and lower boiling point. Hydrocracking catalysts usually comprise one or more hydrogenating components, a carrier and a binder. The catalyst comprises acidic sites to promote the cracking of the heavy hydrocarbon molecules and one or more hydrogenating components to promote the supply of hydrogen to the cracked molecules. The acidic sites of a hydrocracking catalyst are usually provided by trivalent aluminium ions occupying tetravalent positions in the framework of the carrier material. Materials most commonly applied as carriers, therefore, are acidic materials like amorphous silica-alumina and faujasite type aluminosilicates, in particular zeolite Y. In EP-A-0,247,678; EP-A-0,355,929 and EP-A-0,366,027 examples of zeolite Y-based hydrocracking catalysts and hydrocracking processes are disclosed.

Hydrocracking processes are particularly known to be suitable for converting flashed distillates having an 80% by weight boiling point between about 250 and 520 °C, into lower boiling distillates. Examples of such feedstocks typically are light gasoil, heavy gasoil and vacuum gasoil. For instance, the hydrocracking processes disclosed in the aforementioned patent specifications

EP-A-0,247,678; EP-A-0,355,929 and EP-A-0,366,027 are particularly suitable for converting the more heavy gasoils like vacuum gasoil into lower boiling components as is evidently demonstrated by the working examples contained in these patent specifications. Depending on the feedstock used, useful distillate products are middle distillates (substantially boiling between 165 and 370 °C: the "kero range") and naphtha (substantially boiling below 165 °C).

It would, however, be advantageous if heavier oils and in particular residual hydrocarbon oils could be converted into lower boiling material by hydrocracking, whereby distillates of good quality boiling in the naphtha and kero range are obtained at relatively high yields. It will be appreciated that such hydrocracking process would be very attractive from an economical perspective, as residual oils can be converted into more valuable products in a single process.

In US-4,446,008 a process for hydrocracking heavy oils is disclosed, wherein heavy oils are contacted with a hydrocracking catalyst comprising a carrier consisting of from 20 to 80% by weight of a specific iron-containing aluminosilicate obtained by treating steam-treated crystalline aluminosilicate with an aqueous solution of an iron salt, and of 80 to 20% by weight of an inorganic oxide which is required to obtain the necessary mechanical strength and pore size distribution. Atmospheric and vacuum residues are listed among the heavy oils which may be applied as feedstock to the hydrocracking process. The fact that an iron-containing aluminosilicate is used, however, implies that additional steps are required in order to obtain the catalyst. The present invention aims to provide a process wherein such additional steps can be dispensed with, i.e. a process wherein the catalyst used comprises an aluminosilicate

which has not been treated to incorporate any Group VIII metals such as iron. The present invention even aims to provide a process wherein commercially available aluminosilicate-based catalysts can be used.

In US-5,354,452 a process for converting residual hydrocarbon oils is disclosed, wherein the residual hydrocarbon oil is contacted, in the presence of hydrogen, with a catalyst comprising a zeolite Y which has been modified to have a large number of secondary pores, a decreased unit cell size of below 24.19 Å and a decreased acid site density. This very specific, modified zeolite Y is obtained by hydrothermal and acid treatment of ultra-stable zeolite Y or superultra-stable zeolite Y. Again, additional steps are required to obtain the catalyst, so that the same comments as made with respect to US-4,446,008 also apply for US-5,354,452.

It has been found that all the aforementioned aims can be realised by using a catalyst comprising a modified zeolite Y, which has not been subjected to any of the treatments required according to the prior art discussed hereinbefore, and by applying medium to high conversion operating conditions.

Accordingly, the present invention relates to a process for hydrocracking residual hydrocarbon oils, which process comprises contacting a residual hydrocarbon oil in the presence of hydrogen with a hydrocracking catalyst comprising a modified zeolite Y having a unit cell size in the range of from 24.20 to 24.65 Å under operating conditions whereby at least 20% by weight, and preferably at least 40% by weight, of the hydrocarbons having a boiling point of 520 °C or higher present in the residual hydrocarbon oil is converted into hydrocarbons having a boiling point below 520 °C.

The expression "residual hydrocarbon oil" as used in this connection refers to hydrocarbon oils containing at

least 35% by weight of hydrocarbons having a boiling point of 520 °C or higher and having a Conradson Carbon Residue (CCR) content of at least 5% by weight. The CCR content is a well known parameter indicating the quantity of heavy hydrocarbonaceous material present in an oil. It can be determined according to ASTM D-189. Accordingly, both atmospheric residues and vacuum residues obtained as the bottom fractions of atmospheric and vacuum distillation of a crude oil, respectively, as well as their demetallized equivalents may very well be used. Atmospheric residues usually contain between 35 and 70% by weight of hydrocarbons having a boiling point of 520 °C or higher (520 °C+ hydrocarbons), whilst vacuum residues usually contain more than 70% by weight of such 520 °C+ hydrocarbons. CCR content of atmospheric and vacuum residues should normally be between 5 and 30% by weight, suitably between 8 and 25% by weight, whereby the CCR content of vacuum residues is usually higher than the CCR content of atmospheric residues. For the purpose of the present invention atmospheric residues containing between 45 and 70% by weight of 520 °C+ hydrocarbons and vacuum residues containing between 70 and 95% by weight of 520 °C+ hydrocarbons are particularly suitable. Although the zeolitic catalyst used has been found to have a relatively large uptake capacity of nickel and vanadium without unacceptable loss in activity or selectivity occurring, it may be advantageous to demetallise the residual hydrocarbon oil feed prior to subjecting it to hydrocracking. Particularly, when a vacuum residue is used as the feed, a preceding demetallisation treatment is preferred. In general, demetallisation of the residual oil feed prior to hydrocracking has been found advantageous, if the nickel plus vanadium content in said feed exceeds 100 ppm. For an optimum catalyst life it has been found advantageous

to demetallise the residual hydrocarbon oil when the nickel plus vanadium content in said oil exceeds 50 ppm.

Beside straight-run atmospheric and vacuum residues other suitable residual oil feeds may be used as well. For instance, the bottom fraction of a flashing operation, wherein the effluent of a hydrocarbon conversion operation is separated into one or more distillate fractions and a bottom fraction, could be used. Such hydrocarbon conversion operation may be thermal conversion, catalytic cracking or even hydrocracking. The latter case includes the embodiment wherein at least part of a hydrocracker bottom fraction is recycled and is once more subjected to hydrocracking together with the fresh residual oil feed.

The hydrocracking catalyst used in the process according to the present invention should comprise a modified zeolite Y having a unit cell size in the range of from 24.20 to 24.65 Å, and preferably in the range of from 24.30 to 24.60 Å (as determined by ASTM-D-3492). In general, zeolite Y is characterised by the faujasite X-ray diffraction pattern, whereby for the purpose of the present invention preference is given to zeolite Y having a silica to alumina molar ratio of from 4 to 60, more preferably 10 to 55. The modified zeolite Y used in accordance with the present invention is well known in the art and includes those modified zeolites Y typically denoted in the art as ultrastable zeolite Y (USY), very ultrastable (or superultrastable) zeolite Y (VUSY), extra very ultrastable zeolite Y (XVUSY) and mixtures of two or more of such zeolites. The USY and VUSY have been found to be particularly suitable. Methods for the manufacture of the aforementioned modified zeolites Y are well known in the art. In contrast to what is taught in the prior art, it has now been found that hydrocracking catalysts comprising such modified zeolite Y exhibit an excellent

performance without the necessity of subjecting the modified zeolite Y to any additional treatments, such as hydrothermal treatments, acid treatments or any treatments for incorporating iron.

In addition to the modified zeolite Y, the hydrocracking catalyst may suitably comprise a binder material. Preferably, the conventional binder materials, i.e. refractory inorganic oxides such as silica, alumina, silica-alumina, zirconia, boria, titania and mixtures of two or more of these, are used. Of these, alumina is preferred. If a binder is used, the mutual weight ratio of modified zeolite Y to binder is suitably in the range of from 90/10 to 20/80, preferably from 85/15 to 40/60.

The hydrocracking catalyst also suitably comprises a hydrogenation component, which suitably comprises at least one Group VIB metal component and/or at least one Group VIII metal component. Preferably, the catalyst comprises one Group VIB metal component and one Group VIII metal component. Preferred Group VIB metals are tungsten and molybdenum, whilst preferred Group VIII metals are nickel and cobalt with nickel having preference over cobalt. Both Group VIB and Group VIII metal components may consist of the metal in elemental form, as a sulphide, as an oxide or as a combination of two or more of these. The hydrogenation component can be combined with the modified zeolite Y by methods known in the art, such as impregnation and co-mulling. The Group VIII metal component is suitable present in an amount of from 0.1 to 40% by weight, preferably 0.5 to 10% by weight, and the Group VIB metal component is suitably present in an amount ranging from 2 to 40% by weight, preferably 5 to 20% by weight, said weight percentages being calculated as element based on total weight of catalyst.

It has been found advantageous for the yield of naphtha and middle distillates to use a hydrocracking catalyst of which the ratio of pore volume (PV, in ml) to total volume (V_{tot} , in ml) of the catalyst particles in the range of from 0.30 to 0.75, preferably from 0.35 to 0.60. The yield of naphtha and middle distillates has also been found to be positively effected by using a hydrocracking catalyst of which the ratio total volume V_{tot} (in mm^3) to external surface (S , in mm^2) of the catalyst particles is in the range of from 0.05 to 0.50, preferably from 0.15 to 0.40.

The hydrocracking catalyst is usually presulphided before being contacted with the feed in order to increase its tolerance versus heteroatoms. Suitable presulphiding method are known in the art.

Operating conditions of the hydrocracking process should be such that at least 20% by weight of the hydrocarbons having a boiling point of 520 °C or higher present in the residual hydrocarbon oil is converted into hydrocarbons having a boiling point below 520 °C, i.e. a 520 °C+ conversion of at least 20% by weight. Preferably, the hydrocracking process is operated under such conditions that a 520 °C+ conversion of at least 40% by weight is attained. This level of conversion is especially suitable, if the residual hydrocarbon oil is a vacuum residue or a demetallized vacuum residue. It has been found particularly advantageous to operate the hydrocracking process according to the present invention under such operating conditions that a 520 °C+ conversion of at least 70% by weight is attained, i.e. under high conversion conditions. Particularly, if the residual hydrocarbon oil feed is an atmospheric residue, operating the process under such high conversion conditions has been found very attractive. The process of the present invention, accordingly, is most suitably operated under

medium to high conversion conditions. In practice, this implies that the operating conditions suitably involve a temperature in the range of from 350 to 500 °C, preferably 380 to 470 °C, a hydrogen partial pressure of up to 300 bar, preferably in the range of from 100 to 250 bar, a weight hourly space velocity (WHSV) in the range of from 0.1 to 10 kg feed per kg of catalyst per hour (kg/kg/h), preferably from 0.2 to 5 kg/kg/h, and a gas/feed ratio in the range of from 100 to 5,000 Nl/kg, preferably from 250 to 2,000 Nl/kg.

The hydrocracked effluent obtained is suitably fractionated to yield a bottom fraction and at least one distillate fraction. Fractionation may be conveniently achieved by conventional techniques, such as vacuum flashing or distillation under atmospheric or reduced pressure.

The process according to the present invention is most suitably carried out in a fixed bed mode, i.e. the feed is passed over at least one fixed bed of hydrocracking catalyst. If more than one fixed bed is used, these beds can be arranged in series, in parallel or in a combination thereof and the process can be operated with all beds simultaneously in use or with one or more beds being bypassed so as to allow catalyst replacement during operation. The process according to the present invention can also be carried out in a slurry mode, whereby the feed is contacted with the catalyst particles in the reactor, after which they are passed together (as a slurry) through the reactor. Separation of product and catalyst particles takes place afterwards.

A major advantage is that it has been found that the zeolitic catalysts used unexpectedly show an excellent uptake capacity of nickel and vanadium present in the residual hydrocarbon oil without excessive deactivation of the catalyst occurring, whilst their tolerance versus

coke precursors has also been found to be excellent. It will be appreciated that poisoning and resulting rapid deactivation of catalysts by nickel and vanadium as well as fouling of the catalyst by coke formation are generally recognised problems in catalytic residue hydroconversion. Yet another advantage of the process according to the present invention is that, as compared with the conventional alumina-based catalysts, the presently used zeolite-based catalysts cause an increased in-situ flashed distillate conversion, so that a shift in the product slate towards lighter distillates has been observed. Thus, the yield of lighter distillates boiling below 370 °C is higher at the same 520 °C+ conversion level, or, in other words, the zeolite-based catalysts cause an increased 370 °C+ conversion at equal 520 °C+ conversion.

When implemented in a refinery, the process according to the present invention can be carried out in various modes, depending on the refinery lay-out. One option is the so called "once-through" mode, whereby the residual oil feed is passed once through the hydrocracker without any recycle of effluent streams. Another option is the mode with flashed distillate (FD) recycle. In this FD recycle mode, the FD fraction formed (i.e. that fraction of which 80% by weight or more of the hydrocarbons present has a boiling point between 370 and 520 °C) is recycled and is again subjected to the hydrocracking operation together with the fresh residual oil feed. In this way the yield of middle distillates (kero to gasoil) and naphtha can be maximised at minimum FD yield. This mode of operation is, for instance, attractive in a refinery lay-out wherein no or hardly any FD conversion or upgrading operations are available. Yet another option is the residue recycle mode, wherein the hydrocracker bottom fraction is recycled and again subjected to the

hydrocracking operation together with the fresh residual oil feed. It will be clear that any combination of two or more of the aforementioned modes of operation is also possible. Whichever mode is chosen is also determined by the existing situation and of course by economic considerations.

The hydrocracking process according to the present invention can also be very well integrated with other unit operations. One such unit operation is demetallisation. As has already been mentioned above, the residual hydrocarbon oil feed may be demetallized prior to being subjected to hydrocracking, which is particularly useful if the residual oil has a nickel plus vanadium content of 100 ppm or higher. Demetallisation of the residual oil can be achieved by any demetallisation method known in the art. Usually, such method involves passing the feed to be treated in an upward, downward or radial direction through one or more vertically disposed reactors containing a fixed or moving bed of hydrodemetallisation catalyst particles at an elevated temperature and pressure in the presence of hydrogen. Well known demetallisation operations are the bunker flow operation, the fixed bed operation, the fixed bed swing operation and the movable bed operation. Suitable catalysts usually consist of oxidic carriers such as alumina, silica or silica-alumina, on which one or more metals of Group VIB and/or VIII of the Periodic Table of Elements may be deposited either in elemental form or as a metal compound. Such hydrodemetallisation catalysts are commercially available from many catalyst suppliers. Particularly suitable catalysts are those having as the active agent one of the combinations nickel-molybdenum (NiMo) or cobalt-molybdenum (CoMo), optionally promoted with phosphorus (P), on an alumina carrier. For residue applications, catalysts comprising molybdenum on a silica

carrier or nickel and vanadium on a silica carrier are also very useful. Hydrodemetallisation is usually carried out at a hydrogen partial pressure of 20-250 bar, a temperature of 300-470 °C, preferably 310-440 °C, and a space velocity of 0.1-10 l/l.hr, preferably 0.2-7 l/l.hr.

The hydrocracking process according to the present invention can also be very well integrated with a hydrodesulphurisation operation either prior to or after the hydrocracking takes place. The present invention, accordingly, also includes those embodiments of the hydrocracking process, wherein the residual hydrocarbon oil, the hydrocracked effluent or one or more of the distillate fractions obtained from the hydrocracked effluent is subjected to hydrodesulphurisation.

Hydrodesulphurisation of the residual hydrocarbon oil prior to hydrocracking has the advantage that all products obtained after hydrocracking have low sulphur contents, which is desired from an environmental point of view. A drawback of such line-up may be that the entire volume of residual hydrocarbon oil feed has to be treated which requires the use of larger and hence more expensive equipment. Hydrodesulphurisation prior to hydrocracking is also beneficial when the residual hydrocarbon oil has first been demetallised. In this case demetallisation must take place prior to hydrodesulphurisation. Hydrodesulphurisation after hydrocracking is also a suitable option. In this case part or all of effluent can be subjected to hydrodesulphurisation. If the entire hydrocracker effluent is hydrodesulphurised similar advantages and potential drawbacks apply as for hydrodesulphurisation prior to hydrocracking: low product sulphur contents, but relatively large reactor volumes necessary. Smaller hydrodesulphurisation units can be used if hydrodesulphurisation takes place after fractionation of the hydrocracking effluent. In such

line-up, namely, a more selective desulphurisation of one or more fractions can take place. In practice, the most feasible lay-out will be hydrodesulphurisation of the naphtha fraction and/or the middle distillate fraction recovered from the hydrocracking operation. Hydrodesulphurisation can be achieved by methods known in the art and generally involves contacting a hydrocarbon oil feed with a suitable hydrodesulphurisation catalyst in the presence of hydrogen at elevated temperature and pressure. For residue applications the Mo-containing catalysts as described in EP-A-0,224,944 are very useful. For middle distillates and naphtha applications the well known NiMo/alumina and CoMo/alumina catalysts as well as the noble metal-based catalysts, optionally promoted with P, may suitably be applied.

The naphtha fraction obtained after fractionation of the cracked effluent is a very suitable feedstock for a catalytic reforming process for the production of gasoline blending components. Catalytic reforming processes are well known in the art. In general, the catalytic reforming results in the boiling range of the reformer feed not being significantly changed, whereas the chemical composition of the feed is significantly changed by the conversion of paraffinic hydrocarbons into aromatic hydrocarbons with hydrogen being formed. As is generally recognised, the aromatics have a positive effect on the octane number of gasoline and therefore the products from the catalytic reformer are suitably used as gasoline blending components. Catalytic reforming processes usually involve passing a naphtha type feedstock over a suitable reforming catalyst under reforming conditions, recovering the hydrogen formed and separating the product into two or more reformates useful as motor gasoline blending components. Accordingly, integration of the hydrocracking process according to the

present invention with a catalytic reformer by applying at least part of the naphtha fraction obtained from the hydrocracked effluent as a feed for the catalytic reformer is a very attractive option. Especially, when the hydrocracking catalyst used and the conditions applied are such that the production of naphtha is promoted, the integration with a catalytic reformer is very beneficial.

The bottom fraction obtained after fractionation of the hydrocracked effluent also offers various opportunities for effective integration with other unit operations. One very feasible option also falling within the scope of the present invention is the integration of the present hydrocracking process with a thermal conversion operation, whereby at least part of the bottom fraction recovered from the hydrocracked effluent operation is used as at least part of the feed to the thermal conversion operation. The thermal conversion operation can be any thermal conversion operation known in the art, of which visbreaking and the more severe delayed coking are preferred for the purpose of the present invention.

Visbreaking is a well known process. It is a continuous thermal conversion process wherein the conditions are relatively mild (low severity), so that the 520 °C+ conversion level is kept below 30% by weight. A very suitable visbreaking process is the process disclosed in European Patent Application No. 0,007,656. In this process the hydrocarbon oil feed is first preheated, suitably to a temperature in the range of 400 to 500°C, after which the hot feed is caused to flow upwards through a soaking vessel, suitably a soaking vessel having internals. Preferably, the internals are horizontal perforated plates, installed inside the soaker in a number of from 1 to 20. The residence time in the

soaker is in the range of from 5 to 60 minutes, preferably from 10 to 40 minutes. However, other visbreaking processes, such as those using soaking vessels without any internals or those employing only a conversion furnace, may also be applied in the process according to the present invention.

Delayed coking is a well known semi-continuous thermal conversion process, which involves more severe conditions than visbreaking. A delayed coking process generally involves preheating the hydrocarbon oil feed, usually to temperatures between 400 and 550 °C, and introducing the hot feed into at least one coke drum where conversion takes place and the coke formed during conversion gradually fills the coke drum. Preheating suitably takes place by passing the fresh feed through the bottom part of the separation column used for fractionating the cracked effluent and subsequently through a furnace. Cycle time in the coke drums can be in the range of from 10 to 30 hours. Usually two or more coke drums are arranged in a parallel mode, so that when one coke drum is full with coke, this coke drum can be bypassed and another drum can be put on-line. The coke is then removed from the full drum, for instance by hydraulic cleaning, and the coke drum is again ready for operation. The vaporous cracked effluent leaves the coker drum at the top for fractionation.

Beside the aforementioned options, the hydrocracker bottom stream can also suitably be applied as (part of) the feed to a partial oxidation process (gasification) resulting in a clean gas which can be applied as clean fuel gas in the refinery, for cogeneration of power and steam, for hydrogen manufacture and/or for hydrocarbon synthesis processes.

It will be understood that combinations of two or more of the aforementioned integrated processes may also be applied.

The invention is further illustrated by the following examples without restricting the scope of the present invention to these particular embodiments.

Example 1

A demetallised atmospheric residue having a composition as indicated in Table I, having a nickel plus vanadium content of 50 ppm and having a CCR content of 13% by weight, was contacted with a commercial hydrocracking catalyst (NiW on a support comprising 80% by weight of a modified zeolite Y having a unit cell size of 24.32 Å and 20% by weight of alumina binder; $V_{tot}/S = 0.30$ mm; $PV/V_{tot} = 0.50$) under such operating conditions that a 520 °C+ conversion of 80% by weight occurred. These operating conditions involved an operating temperature ranging from 410 to 430 °C, a hydrogen partial pressure of 150 bar, an average WHSV of 1.3 kg/kg/h and a gas/feed ratio of 1500 Nl/kg.

Total operation time was 4300 hours, whereby the average deactivation of the hydrocracking catalyst was 2 °C per 1000 hours of operation, which is very attractive from a commercial viewpoint.

The composition of the product is indicated in Table I.

As can be seen from Table I the 520 °C+ conversion was 80% by weight and the 370 °C+ conversion 75.8% by weight, whereby high naphtha yield (37% by weight) and middle distillate yield (total of 34% by weight) was realised.

TABLE I Composition of feed and product

Component	Feed (% wt)	Product (% wt)
C1-C4	0	7
C5-165 °C	0	37
165-250 °C	1	20
250-370 °C	8	14
370-520 °C	35	11
520 °C+	56	11

Example 2

A demetallised vacuum residue having a composition as indicated in Table II, having a nickel plus vanadium content of 58 ppm and having a CCR content of 16% by weight, was contacted with a commercial hydrocracking catalyst (NiW on a support comprising 80% by weight of a modified zeolite Y having a unit cell size of 24.56 Å and 20% by weight of alumina binder; $V_{tot}/S = 0.35$ mm; $PV/V_{tot} = 0.45$) under such operating conditions that a 520 °C+ conversion of 47% by weight occurred. These operating conditions involved an operating temperature ranging from 410 to 415 °C, a hydrogen partial pressure of 130 bar, an average WHSV of 0.7 kg/kg/h and a gas/feed ratio of 1000 Nl/kg.

The composition of the product is indicated in Table II.

TABLE II Composition of feed and product

Component	Feed (% wt)	Product (% wt)
C1-C4	0	7
C5-165 °C	0	23
165-250 °C	0	9
250-370 °C	3	6
370-520 °C	18	13
520 °C+	79	42

As can be seen from Table II the 520 °C+ conversion was 47% by weight and the 370 °C+ conversion 43.3% by weight, whereby high naphtha yield (23% by weight) and acceptable middle distillate yield (total of 15% by weight) was realised.

Example 3

A straight run atmospheric residue having a composition as indicated in Table III, having a nickel plus vanadium content of 100 ppm and having a CCR content of 12% by weight, was contacted with a commercial hydrocracking catalyst (NiW on a support comprising 80% by weight of a modified zeolite Y having a unit cell size of 24.32 Å and 20 % by weight of alumina binder; $V_{tot}/S = 0.30$ mm; $PV/V_{tot} = 0.50$) under such operating conditions that a 520 °C+ conversion of 53% by weight occurred. These operating conditions involved operating temperatures ranging from 410 to 430 °C, a hydrogen partial pressure of 150 bar, an average WHSV of 2.0 kg/kg/h and a gas/feed ratio of 1500 Nl/kg.

The composition of the product is indicated in Table III. As can be seen from Table III the 520 °C+ conversion was 53% by weight and the 370 °C+ conversion 49% by weight, whereby high naphtha yield (14% by weight) and middle distillate yield (total of 31% by weight) were realised.

TABLE III Composition of feed and product

Component	Feed (% wt)	Product (% w)
C1 - C4	0	5
C5 - 165 °C	0	14
165 °C - 250 °C	0	16
250 °C - 370 °C	2	15
370 °C - 520 °C	35	20
520 °C+	63	30



C L A I M S

1. Process for hydrocracking residual hydrocarbon oils, which process comprises contacting a residual hydrocarbon oil in the presence of hydrogen with a hydrocracking catalyst comprising a modified zeolite Y having a unit cell size in the range of from 24.20 to 24.65 Å under operating conditions whereby at least 20% by weight, and preferably at least 40% by weight, of the hydrocarbons having a boiling point of 520 °C or higher present in the residual hydrocarbon oil is converted into hydrocarbons having a boiling point below 520 °C.
2. Process according to claim 1, wherein the zeolite Y is ultra-stable zeolite Y or very ultra-stable zeolite Y.
3. Process according to claim 1 or 2, wherein the hydrocracking catalyst comprises at least one Group VIB metal component and at least one Group VIII metal component.
4. Process according to claim 3, wherein the Group VIB metal is tungsten or molybdenum and the Group VIII metal is nickel.
5. Process according to any one of the preceding claims, wherein the hydrocracking catalyst particles have a ratio of pore volume (PV, in ml) to total volume (V_{tot}, in ml) in the range of from 0.30 to 0.75.
6. Process according to any one of the preceding claims, wherein the hydrocracking catalyst particles have a ratio of total volume V_{tot} (in mm³) to external surface (S, in mm²) in the range of from 0.05 to 0.50.
7. Process according to any one of the preceding claims, wherein the operating conditions involve a temperature in the range of from 350 to 500 °C and a hydrogen partial pressure up to 300 bar.



8. Process according to any one of the preceding claims, wherein the conditions applied are such that at least 70% by weight of the hydrocarbons having a boiling point of 520 °C or higher present in the residual hydrocarbon oil is converted into hydrocarbons having a boiling point below 520 °C.
9. Process according to any one of the preceding claims, wherein the residual hydrocarbon oil is a vacuum residue.
10. Process according to any one of claims 1 to 8, wherein the residual hydrocarbon oil is an atmospheric residue.
11. Process according to any one of the preceding claims, wherein the process is operated in the once-through mode.
12. Process according to any one of claims 1 to 10, wherein at least part of the bottom fraction and/or at least part of the flashed distillate fraction obtained from the hydrocracked effluent is recycled and again subjected to the hydrocracking treatment together with the fresh residual oil feed.
13. Process according to any one of the preceding claims, wherein the residual hydrocarbon oil feed is first subjected to a demetallisation treatment.
14. Process according to any one of the preceding claims, wherein the residual hydrocarbon oil, the hydrocracked effluent or one or more of the distillate fractions obtained from the hydrocracked effluent is subjected to hydrodesulphurisation.
15. Process according to any one of the preceding claims, wherein the naphtha fraction obtained from the hydrocracked effluent is at least partly subjected to a catalytic reforming treatment.
16. Process according to any one of the preceding claims, wherein at least part of the bottom fraction obtained from the hydrocracked effluent is used as at least part of the feed to a thermal conversion unit.



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17. Process according to claim 16, wherein the thermal conversion unit is a visbreaking unit.

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Process for hydrocracking residual hydrocarbon oils, which process comprises contacting a residual hydrocarbon oil in the presence of hydrogen with a hydrocracking catalyst comprising a modified zeolite Y having a unit cell size in the range of from 24.20 to 24.65 Å under operating conditions whereby at least 20% by weight of the hydrocarbons having a boiling point of 520 °C or higher present in the residual hydrocarbon oil is converted into hydrocarbons having a boiling point below 520 °C.