

Description

The invention relates to a process for the production of deasphalted oils and hydrocarbon oil distillates from asphaltenes-containing hydrocarbon mixtures.

The atmospheric distillation of crude mineral oil for the production of light hydrocarbon oil distillates, such as gasoline, kerosine and gas oil yields an asphaltenes-containing residue as a by-product. Originally these residues (which usually in addition to asphaltenes also contain a considerable percentage of sulphur and metals) were used as fuel oil. In view of the growing demand of light hydrocarbon oil distillates and the shrinking reserves of crude mineral oil, several treatments aiming at the production of light hydrocarbon oil distillates from atmospheric residues have already been proposed. For instance, a deasphalted oil may be separated from an atmospheric residue by solvent deasphalting and this deasphalted oil may be subjected to catalytic cracking in the presence or absence of hydrogen. Another option is to separate an atmospheric residue into a vacuum distillate and a vacuum residue by vacuum distillation, to separate a deasphalted oil from the vacuum residue by solvent deasphalting and to subject both the vacuum distillate and the deasphalted oil to catalytic cracking in the presence or absence of hydrogen.

Solvent deasphalting (DA), a process in which an asphaltenes-containing feedstock is converted into a product from which a deasphalted oil can be separated as the desired main product and an asphaltic bitumen as a by-product, has proven in actual practice to be a suitable treatment for the production of deasphalted oils from a variety of asphaltenes-containing hydrocarbon mixtures.

It has now been investigated whether combining the DA treatment with a pretreatment of the asphaltenes-containing feed and/or an after-treatment of the asphaltic bitumen separated in the DA treatment and using at least part of the asphaltic bitumen that has been subjected to the after-treatment as the feed for the DA, might yield better results than employing nothing but the DA. In the assessment of the results the yields of deasphalted oil and light product(s) are most important. The qualities of the deasphalted oil and the light product(s) as well as the quality of the heavy by-product are also important. In this context the quality of the deasphalted oil is taken to be its suitability for conversion into hydrocarbon oil distillates by catalytic cracking in the presence or absence of hydrogen. This suitability is greater according as the deasphalted oil has, among other things, lower asphaltenes, metal and sulphur contents. In this context the quality of the light product is taken to be its suitability for processing into a valuable light fuel. This suitability is greater according as the light product has, among other things, lower sulphur and olefins contents. In this context the quality of the heavy product is taken to be its suitability for

serving as a fuel oil component. This suitability is greater according as the heavy product has among other things, lower metal and sulphur contents and lower viscosity and density. For use as pretreatments of the feed for the DA and as aftertreatments of the asphaltic bitumen separated in the DA, the following treatments were investigated: thermal cracking (TC) in which a heavy feed is converted into a product which contains less than 20% w C₄- hydrocarbons and from which one or more distillate fractions and a heavy fraction are separated and catalytic hydro-treatment (HT) in which an asphaltenes-containing feed is converted into a product having a reduced asphaltenes content from which one or more distillate fractions and a heavy fraction are separated.

During this investigation a comparison was made between the results that can be obtained when a deasphalted oil and possibly a hydrocarbon oil distillate having a given boiling range as well as a heavy by-product are produced starting from equal quantities of an asphaltenes-containing hydrocarbon mixture by using a) DA only, b) DA in combination with TC, c) DA in combination with HT and d) DA in combination with both TC and HT, the conditions of the various treatments being similar as much as possible. In view of quantity and quality of the deasphalted oil and the hydrocarbon oil distillate to be obtained in each of the procedures and the quality of the heavy by-product, the various procedures may be arranged as follows:

35	Quantity of deasphalted oil	$d = c > b = a$
	Quality of the deasphalted oil	$d = c > b = a$
40	Quantity of hydrocarbon oil distillate	$d > c > b$
45	Quality of the hydrocarbon oil distillate	$c > d > b$
50	Quality of the heavy product	$c > d > a > b$

Taking into account the considerable difference in hydrocarbon oil distillate yields obtained according to procedures c) and d) and the no more than minor differences in quality between the hydrocarbon oil distillates and between the heavy by-products obtained according to procedures c) and d) a procedure in which a combination is used of a DA treatment, a TC treatment and a HT, is much preferred.

As regards the order in which the three treatments are carried out, a number of embodiments may be considered. Each of the embodiments may be placed in one of the two following classes.

1. The asphaltenes-containing feed is first sub-

jected to a HT or a DA treatment and the heavy fraction or asphaltic bitumen separated from the respective products obtained, is subjected to a combination of a DA treatment and a TC treatment or a combination of a TC treatment and a HT, respectively.

II. The asphaltenes-containing feed is first subjected to a TC treatment and the heavy fraction separated from the product obtained is subjected to a combination of a DA treatment and a HT.

The embodiments belonging to class I constitute the subject matter of the present patent application.

The embodiments to which the present patent application relates, may be subdivided further depending on whether the asphaltenes-containing feed is used as a feed component for the HT (class IA), or as a feed component for the DA treatment (class IB). In all the embodiments the asphaltic bitumen fraction which is separated from the product of the DA treatment is used as the feed for the TC treatment. In the embodiments belonging to class IA the heavy fraction which is separated from the product of the TC treatment is used as a feed component for the HT and the heavy fraction which is separated from the product of the HT is used as the feed for the DA treatment. In the embodiments belonging to class IB the heavy fraction which is separated from the product of the HT is used as a feed component for the DA treatment and the heavy fraction which is separated from the product of the TC treatment is used as the feed for the HT.

The present patent application therefore relates to a process for the production of deasphalted oils and hydrocarbon oil distillates from asphaltenes-containing hydrocarbon mixtures, in which an asphaltenes-containing hydrocarbon mixture (stream 1) is subjected to a combination of the following three treatments: a catalytic hydrotreatment (HT) in which an asphaltenes-containing feed is converted into a product having a reduced asphaltenes content, from which one or more distillate fractions and a heavy fraction (stream 2) are separated, a solvent deasphalting (DA) treatment in which an asphaltenes-containing feed is converted into a product from which a deasphalted oil and an asphaltic bitumen (stream 3) are separated and a thermal cracking treatment (TC) in which a feed is converted into a product which contains less than 20% w C₄-hydrocarbons and from which one or more distillate fractions and a heavy fraction (stream 4) are separated, in which stream 3 is used as the feed for the TC treatment and stream 1 is used either 1) together with stream 4 as a feed component for the HT with stream 2 being used as the feed for the DA treatment, or 2) together with stream 2 as a feed component for the DA treatment with stream 4 being used as the feed for the HT.

In the process according to the invention the feed used is an asphaltenes-containing hydrocarbon mixture. A suitable parameter for assessing the asphaltenes content of a hydrocarbon

mixture and the reduction of the asphaltenes content which occurs when an asphaltenes-containing hydrocarbon mixture is subjected to a HT, is the Ramsbottom Carbon Test value (RCT). The higher the asphaltenes content of the hydrocarbon mixture, the higher the RCT. Preferably the process is applied to hydrocarbon mixtures which boil substantially above 350°C and more than 35% w of which boils above 520°C and which have an RCT higher than 7.5% w. Examples of such hydrocarbon mixtures are residues obtained in the distillation of crude mineral oils and also heavy hydrocarbon mixtures obtained from shale and tar sands. If desired, the process may also be applied to heavy crude mineral oils, residues obtained in the distillation of products formed in the thermal cracking of hydrocarbon mixtures and asphaltic bitumen obtained in the solvent deasphalting of asphaltenes-containing hydrocarbon mixtures. The process according to the invention can very suitably be applied to residues obtained in the vacuum distillation of atmospheric distillation residues from crude mineral oils. If the feed available for the process according to the invention is an atmospheric distillation residue from a crude mineral oil, it is preferred to separate a vacuum distillate therefrom by vacuum distillation and to subject the resulting vacuum residue to the process according to the invention. The separated vacuum distillate may be subjected to thermal cracking or to catalytic cracking in the presence or absence of hydrogen to convert it into light hydrocarbon oil distillates.

The process according to the invention is a three-step process in which an asphaltenes-containing feed (stream 1) is subjected in the first step to a HT or a DA treatment and in which the heavy fraction (stream 2) and the asphaltic bitumen (stream 3) separated from the product obtained by the respective treatments are subjected in the second and the third step of the process to a combination of a DA treatment and a TC treatment and a combination of a TC treatment and a HT, respectively.

Asphaltenes-containing hydrocarbon mixtures usually include a considerable percentage of metals, particularly vanadium and nickel. When such hydrocarbon mixtures are subjected to a catalytic treatment, for instance a HT for the reduction of the asphaltenes content as in the case in the process according to the invention, these metals will be deposited on the catalyst used in the HT, thus shortening its useful life. In view of this, asphaltenes-containing hydrocarbon mixtures having a vanadium + nickel content higher than 50 parts per million by weight (ppmw) should preferably be subjected to a demetallization treatment before being contacted with the catalyst used in the HT. This demetallization may very suitably be carried out by contacting the asphaltenes-containing hydrocarbon mixture in the presence of hydrogen with a catalyst more than 80% w of which consists of silica. Both catalysts consisting entirely of silica and catalysts containing one or more metals with hydrogen-

tion activity — in particular a combination of nickel and vanadium — supported on a carrier consisting substantially of silica, are suitable for the purpose. When in the process according to the invention an asphaltene-containing feed is subjected to a catalytic demetallization treatment in the presence of hydrogen, this demetallization may be carried out in a separate reactor. Since the catalytic demetallization and the HT for the reduction of the asphaltene content can be carried out under the same conditions, the two processes may also very suitably be carried out in the same reactor, which successively contains a bed of the demetallization reactor and a bed of the catalyst used in the HT.

Suitable catalysts for carrying out the HT are those which contain at least one metal chosen from the group formed by nickel and cobalt and in addition at least one metal chosen from the group formed by molybdenum and tungsten supported on a carrier, which carrier consists more than 40% w of alumina.

Very suitable catalysts for use in the HT are those which comprise the metal combination nickel/molybdenum or cobalt/molybdenum supported on alumina as the carrier. The HT is preferably carried out at a temperature of from 300—500°C and in particular of from 350—450°C, a pressure of from 50—300 bar and in particular of from 75—200 bar, a space velocity of from 0.02—10 g.g⁻¹.h⁻¹ and in particular of from 0.1—2 g.g⁻¹.h⁻¹ and a H₂/feed ratio of from 100—5000 NI.kg⁻¹ and in particular of from 500—2000 NI.kg⁻¹. The same preference applies to the conditions which are used in a possible catalytic demetallization in the presence of hydrogen as to those given hereinbefore for the HT aiming at reduction of the asphaltene content.

The HT is preferably carried out in such a manner that it yields a product, the C₅⁺ fraction of which meets the following requirements:

- a) the RCT of the C₅⁺ fraction amounts to 20—70% of the RCT of the feed, and
- b) the difference between the percentages by weight of hydrocarbons boiling below 350°C present in the C₅⁺ fraction and in the feed is at most 40.

It should be noted that in the catalytic demetallization the reduction of the metal content is accompanied by some reduction of the RCT and some formation of C₅—350°C product. A similar phenomenon occurs in the HT in which the reduction of the RCT and the formation of C₅—350°C product are accompanied by some reduction of the metal content. The requirements mentioned hereinbefore under a) and b) bear upon the overall reduction of RCT and formation of C₅—350°C product (viz. including those occurring in a possible catalytic demetallization treatment).

The HT yields a product with a reduced asphaltene content from which one or more distillate fractions and a heavy fraction (stream 2) are separated. The distillate fractions separated from the product may be only atmospheric distillates,

but preferably a vacuum distillate should be separated from the product as well. The vacuum distillate may be converted into light hydrocarbon oil distillates in the ways mentioned hereinbefore.

In the process according to the invention instead of a HT the first step applied may be a DA treatment in which an asphaltene-containing feed is converted into a product from which a deasphalted oil and an asphaltic bitumen (stream 3) are separated. Suitable solvents for carrying out the DA treatment are paraffinic hydrocarbons having 3—6 carbon atoms per molecule, such as n-butane and mixtures thereof, such as mixtures of propane and n-butane and mixtures of n-butane and n-pentane. Suitable solvent/oil weight ratios lie in the range of from 7:1 to 1:1 and in particular of from 4:1 to 1:1. The DA treatment is preferably carried out at a pressure in the range of from 20—100 bar. When n-butane is used as the solvent, the deasphalting is preferably carried out at a pressure of from 35—45 bar and a temperature of from 100—150°C.

In the process according to the invention the second or third step used is a TC treatment in which stream 3 is converted into a product which contains less than 20% w C₄⁻ hydrocarbons and from which one or more distillate fractions and a heavy fraction (stream 4) are separated. The distillate fractions separated from the product may be only atmospheric distillates, but preferably a vacuum distillate should be separated from the product as well. This vacuum distillate may be converted into light hydrocarbon oil distillates in the manners indicated hereinbefore. The TC treatment is preferably carried out at a temperature of from 400—525°C and a space velocity of from 0.01—5 kg fresh feed per litre cracking reactor volume per minute.

As stated hereinbefore, the embodiments belonging to class I to which the present patent application relates are subdivided depending on whether stream 1 is used as a feed component for the HT (class IA) or as a feed component for the DA treatment (class IB).

The embodiment belonging to class IA is represented schematically in Figure I. The various streams, fractions and reaction zones are indicated by three digit numbers, the first of which refers to the Figure concerned. The vacuum residue (302), for instance, refers to vacuum residue 2 in the context of Figure III. According to Figure I the process is carried out in an apparatus comprising a HT zone (105), a DA zone (106) and a TC zone (107), successively. An asphaltene-containing hydrocarbon mixture (101) and a residual fraction (104) are subjected to a HT and the hydro-treated product is separated into one or more distillate fractions (108) and a residual fraction (102). Stream 102 is subjected to a DA treatment and the product is separated into a deasphalted oil (109) and an asphaltic bitumen (103). Stream 103 is subjected to TC and the cracked product is separated into one or more distillate fractions (110) and a residual fraction (104).

The embodiment belonging to class IB is repre-

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sented schematically in Figure II. According to this Figure the process is carried out in an apparatus consisting of a DA zone (205), a TC zone (206) and a HT zone (207), successively. An asphaltene-containing hydrocarbon mixture (201) and a residual fraction (202) are subjected to a DA treatment and the product is separated into a deasphalted oil (208) and an asphaltic bitumen (203). Stream 203 is subjected to a TC treatment and the cracked product is separated into one or more distillate fractions (209) and a residual fraction (204). Stream 204 is subjected to a HT and the hydrotreated product is separated one or more distillate fractions (210) and a residual fraction (202).

In the embodiments where it is the object to achieve the completest possible conversion of stream (201) into deasphalted oil and hydrocarbon oil distillates, a so-called "bleed stream" should preferably be separated from one of the heavy streams of the process. In this way the build-up of undesirable heavy components during the process can be obviated.

Two flow diagrams for the preparation of deasphalted oil and hydrocarbon oil distillates from asphaltene-containing hydrocarbon mixtures according to the invention will hereinafter be explained in more detail with the aid of Figures III and IV.

Flow diagram A (based on embodiment IA)

See Figure III

The process is carried out in an apparatus comprising successively, a HT zone composed of a unit for catalytic hydrotreatment (305), a unit for atmospheric distillation (306) and a vacuum distillation unit (307), a DA zone (308) and a TC zone composed of a thermal cracking unit (309), a second atmospheric distillation unit (310) and a second vacuum distillation unit (311). An asphaltene-containing hydrocarbon mixture (301) is mixed with a recirculation stream (312) and the mixture (313) is subjected together with hydrogen (314) to a catalytic hydrotreatment. The hydrotreated product (315) is separated by atmospheric distillation into a gas fraction (316), an atmospheric distillate (317) and an atmospheric residue (318). The atmospheric residue (318) is separated by vacuum distillation into a vacuum distillate (319) and a vacuum residue (302). The vacuum residue (302) is separated by solvent deasphalting into a deasphalted oil (320) and an asphaltic bitumen (303). The asphaltic bitumen (303) is subjected to thermal cracking and the thermally cracked product (321) is separated by atmospheric distillation into a gas fraction (322), an atmospheric distillate (323) and an atmospheric residue (324). The atmospheric residue (324) is separated by vacuum distillation into a vacuum distillate (325) and a vacuum residue (304). The vacuum residue (304) is divided into two portions (312) and (326).

Flow diagram B (based on embodiment IB)

See Figure IV.

The process is carried out in an apparatus comprising, successively, a DA zone (405), a TC zone composed of a thermal cracking unit (406), an atmospheric distillation unit (407) and a vacuum distillation unit (408) and a HT zone composed of a unit for catalytic hydrotreatment (409), a second atmospheric distillation unit (410) and a second vacuum distillation unit (411). As asphaltene-containing hydrocarbon mixture (401) is mixed with a vacuum residue (402) and the mixture (412) is separated by solvent deasphalting into a deasphalted oil (413) and an asphaltic bitumen (403). The asphaltic bitumen (403) is subjected to thermal cracking and the thermally cracked product (414) is separated by atmospheric distillation into a gas fraction (415), an atmospheric distillate (416) and an atmospheric residue (417). The atmospheric residue (417) is separated by vacuum distillation into a vacuum distillate (418) and a vacuum residue (404). The vacuum residue (404) is divided into two portions (419) and (420). Portion (420) is subjected together with hydrogen (421) to a catalytic hydro-treatment. The hydrotreated product (422) is separated by atmospheric distillation into a gas fraction (423), an atmospheric distillate (424) and an atmospheric residue (425). The atmospheric residue (425) is separated by vacuum distillation into a vacuum distillate (426) and vacuum residue (402).

The present patent application also includes apparatuses for carrying out the process according to the invention substantially corresponding with those represented schematically in Figures I-IV.

The invention is now elucidated with the aid of the following Examples.

In the process according to the invention two asphaltene-containing hydrocarbon mixtures obtained as residues in the vacuum distillation of atmospheric distillation residues from crude mineral oils were used as the starting material. The two vacuum residues both boiled substantially above 520°C and they had RCT's of 19.1 to 19.8% w, respectively. The process was carried out according to flow diagrams A and B. The conditions used in the various zones were the following.

The unit for catalytic hydrotreatment as described in both the flow diagrams consisted of two reactors, the first of which was filled with a Ni/V-SiO₂ catalyst containing 0.5 parts by weight (pbw) nickel and 2.0 pbw vanadium per 100 pbw silica and the second of which was filled with a Co/Mo/Al₂O₃ catalyst containing 4 pbw cobalt and 12 pbw molybdenum per 100 pbw alumina. The catalysts were used in a 1:4 volume ratio. The HT was carried out at a hydrogen pressure of 150 bar, a space velocity (measured over the two reactors) of 0.5 kg feed per litre catalyst per hour, a H₂/feed ratio of 1000 NI per kg and an average tempera-



ture of 410°C in the first reactor and 385°C in the second reactor.

In both the flow diagrams the DA treatment was carried out using n-butane as solvent, at a temperature of 115°C, a pressure of 40 bar and a solvent/oil weight ratio of 3:1.

In both the flow diagrams the TC treatment was carried out in a cracking coil, at a pressure of 10 bar, a space velocity of 0.4 kg fresh feed per litre cracking coil volume per minute and a temperature of 500°C (temperature measured at the outlet of the cracking coil).

Example 1

This Example was carried out according to flow diagram A as represented by Figure III.

100 pbw Vacuum residue (301) having an RCT of 19.1% w yielded the various streams in the following quantities:

102.2 pbw mixture (313) having an RCT of 19.5% w, a product (315), the C_5^- fraction of which had an RCT of 9.4% w,

20.7 pbw C_5^- —350°C atmospheric distillate (317),

75.1 pbw 350°C⁻ atmospheric residue (318),

30.1 pbw 350—520°C vacuum distillate (319),

45.0 pbw 520°C⁻ vacuum residue (302),

30.6 pbw deasphalted oil (320),

14.4 pbw asphaltic bitumen (303),

2.3 pbw C_5^- —350°C atmospheric distillate (323),

11.7 pbw 350°C⁻ atmospheric residue (324),

1.5 pbw 350—520°C vacuum distillate (325),

10.2 pbw 520°C⁻ vacuum residue (304),

2.2 pbw portion (312) and

8.0 pbw portion (326):

Example 2

This Example was carried out according to flow diagram B as represented by Figure IV.

100 pbw Vacuum residue (401) having an RCT of 19.8% w yielded the various streams in the following quantities:

117.6 pbw mixture (412),

71.7 pbw deasphalted oil (413),

45.9 pbw asphaltic bitumen (403),

5.9 pbw C_5^- —350°C atmospheric distillate (416),

39.1 pbw 350°C⁻ atmospheric residue (417),

4.7 pbw 350—520°C vacuum distillate (418),

34.4 pbw 520°C⁻ vacuum residue (404),

5.0 pbw portion (419),

29.4 pbw portion (420) having an RCT of 41.2% w, a product (422), the C_5^- fraction of which had an RCT of 18.5% w,

4.1 pbw C_5^- —350°C atmosphere distillate (424),

23.8 pbw 350°C⁻ atmospheric residue (425),

6.2 pbw 350—520°C vacuum distillate (426) and

17.6 pbw 520°C⁻ vacuum residue (402).

Claims

1. A process for the production of deasphalted oils and hydrocarbon oil distillates from asphaltene-containing hydrocarbon mixtures, characterized in that an asphaltene-containing hydrocarbon mixture (1) is subjected to a combination of the following three treatments:

a catalytic hydrotreatment (HT) in which an asphaltene-containing feed is converted into a product having a reduced asphaltene content from which one or more distillate fractions and a heavy fraction (stream 2) are separated,

a solvent deasphalting (DA) treatment in which an asphaltene-containing feed is converted into a product from which a deasphalted oil and an asphaltic bitumen (stream 3) are separated and

a thermal cracking (TC) treatment in which a feed is converted into a product which contains less than 20% w C_4^- hydrocarbons and from which one or more distillate fractions and a heavy fraction (stream 4) are separated, that stream 3 is used as the feed for the TC treatment and that stream 1 is used either

1) together with stream 4 as a feed component for the HT with stream 2 being used as the feed for the DA treatment, or

2) together with stream 2 as a feed component for the DA treatment, with stream 4 being used as the feed for the HT.

2. A process as claimed in claim 1, characterized in that a hydrocarbon mixture which boils substantially above 350°C and more than 35% w of which boils above 520°C and which has an RCT of more than 7.5% w, such as a residue obtained in the vacuum distillation of an atmospheric distillation residue from the crude mineral oil is used as stream 1.

3. A process as claimed in claim 1 or 2, characterized in that one or more vacuum distillates are separated from one or more of streams 1, 2 and 4.

4. A process as claimed in any one of claims 1—3, characterized in that the catalyst used in the HT aiming at the reduction of the asphaltene content of the feed, is a catalyst containing at least one metal chosen from the group formed by nickel and cobalt and in addition at least one metal chosen from the group formed by molybdenum and tungsten supported on a carrier, which carrier consists more than 40% w of alumina.

5. A process as claimed in any one of claims 1—4, characterized in that the HT is carried out at a temperature of from 350—450°C, a pressure of from 75—200 bar, a space velocity of from 0.1—2 g.g⁻¹.h⁻¹ and a H₂/feed ratio of from 500—2000 NI.kg⁻¹.

6. A process as claimed in any one of claims 1—5, characterized in that the HT is carried out in such a way that it yields a product, the C_5^- fraction of which meets the following requirements:

a) the RCT of the C_5^- fraction is 20—70% of the RCT of the feed and

(b) the difference between the weight per-



ture of 410°C in the first reactor and 385°C in the second reactor.

In both the flow diagrams the DA treatment was carried out using n-butane as solvent, at a temperature of 115°C, a pressure of 40 bar and a solvent/oil weight ratio of 3:1.

In both the flow diagrams the TC treatment was carried out in a cracking coil, at a pressure of 10 bar, a space velocity of 0.4 kg fresh feed per litre cracking coil volume per minute and a temperature of 500°C (temperature measured at the outlet of the cracking coil).

Example 1

This Example was carried out according to flow diagram A as represented by Figure III.

100 pbw Vacuum residue (301) having an RCT of 19.1% w yielded the various streams in the following quantities:

102.2 pbw mixture (313) having an RCT of 19.5% w, a product (315), the C_5^- fraction of which had an RCT of 9.4% w,

20.7 pbw $C_5-350^\circ\text{C}$ atmospheric distillate (317),

75.1 pbw 350°C^+ atmospheric residue (318),

30.1 pbw $350-520^\circ\text{C}$ vacuum distillate (319),

45.0 pbw 520°C^+ vacuum residue (302),

30.6 pbw deasphalted oil (320),

14.4 pbw asphaltic bitumen (303),

2.3 pbw $C_5-350^\circ\text{C}$ atmospheric distillate (323),

11.7 pbw 350°C^+ atmospheric residue (324),

1.5 pbw $350-520^\circ\text{C}$ vacuum distillate (325),

10.2 pbw 520°C^+ vacuum residue (304),

2.2 pbw portion (312) and

8.0 pbw portion (326).

Example 2

This Example was carried out according to flow diagram B as represented by Figure IV.

100 pbw Vacuum residue (401) having an RCT of 19.8% w yielded the various streams in the following quantities:

117.6 pbw mixture (412),

71.7 pbw deasphalted oil (413),

45.9 pbw asphaltic bitumen (403),

5.9 pbw $C_5-350^\circ\text{C}$ atmospheric distillate (416),

39.1 pbw 350°C^+ atmospheric residue (417),

4.7 pbw $350-520^\circ\text{C}$ vacuum distillate (418),

34.4 pbw 520°C^+ vacuum residue (404),

5.0 pbw portion (419),

29.4 pbw portion (420) having an RCT of 41.2% w, a product (422), the C_5^- fraction of which had an RCT of 18.5% w,

4.1 pbw $C_5-350^\circ\text{C}$ atmosphere distillate (424),

23.8 pbw 350°C^+ atmospheric residue (425),

6.2 pbw $350-520^\circ\text{C}$ vacuum distillate (426) and

17.6 pbw 520°C^+ vacuum residue (402).

Claims

1. A process for the production of deasphalted oils and hydrocarbon oil distillates from asphaltene-containing hydrocarbon mixtures, characterized in that an asphaltene-containing hydrocarbon mixture (1) is subjected to a combination of the following three treatments:

a catalytic hydrotreatment (HT) in which an asphaltene-containing feed is converted into a product having a reduced asphaltene content from which one or more distillate fractions and a heavy fraction (stream 2) are separated,

a solvent deasphalting (DA) treatment in which an asphaltene-containing feed is converted into a product from which a deasphalted oil and an asphaltic bitumen (stream 3) are separated and

a thermal cracking (TC) treatment in which a feed is converted into a product which contains less than 20% w C_4^- hydrocarbons and from which one or more distillate fractions and a heavy fraction (stream 4) are separated, that stream 3 is used as the feed for the TC treatment and that stream 1 is used either

1) together with stream 4 as a feed component for the HT with stream 2 being used as the feed for the DA treatment, or

2) together with stream 2 as a feed component for the DA treatment, with stream 4 being used as the feed for the HT.

2. A process as claimed in claim 1, characterized in that a hydrocarbon mixture which boils substantially above 350°C and more than 35% w of which boils above 520°C and which has an RCT of more than 7.5% w, such as a residue obtained in the vacuum distillation of an atmospheric distillation residue from the crude mineral oil is used as stream 1.

3. A process as claimed in claim 1 or 2, characterized in that one or more vacuum distillates are separated from one or more of streams 1, 2 and 4.

4. A process as claimed in any one of claims 1-3, characterized in that the catalyst used in the HT aiming at the reduction of the asphaltene content of the feed, is a catalyst containing at least one metal chosen from the group formed by nickel and cobalt and in addition at least one metal chosen from the group formed by molybdenum and tungsten supported on a carrier, which carrier consists more than 40% w of alumina.

5. A process as claimed in any one of claims 1-4, characterized in that the HT is carried out at a temperature of from $350-450^\circ\text{C}$, a pressure of from 75-200 bar, a space velocity of from $0.1-2\text{ g.g}^{-1}.\text{h}^{-1}$ and a H_2/feed ratio of from 500-2000 Nl.kg^{-1} .

6. A process as claimed in any one of claims 1-5, characterized in that the HT is carried out in such a way that it yields a product, the C_5^- fraction of which meets the following requirements:

a) the RCT of the C_5^- fraction is 20-70% of the RCT of the feed and

(b) the difference between the weight per-



tages of hydrocarbons boiling below 350°C present in the C₅⁺ fraction and in the feed is at most 40

7. A process as claimed in any one of claims 1—6, characterized in that the DA treatment is carried out using n-butane as the solvent at a pressure of from 35—45 bar and a temperature of from 100—150°C.

8. A process as claimed in any one of claims 1—7, characterized in that the TC treatment is carried out at a temperature of from 400—525°C and a space velocity of from 0.01—5 kg fresh feed per litre cracking reactor volume per minute.

Patentansprüche

1. Ein Verfahren zur Erzeugung von Kohlenwasserstoffdestillaten aus asphaltenthaltiger Kohlenwasserstoffmischungen, dadurch gekennzeichnet, daß eine asphaltenthaltige Kohlenwasserstoffmischung (1) einer Kombination der folgenden drei Behandlungsarten unterworfen wird:

einer katalytischen Wasserstoffbehandlung (HT), in welcher eine asphaltenthaltige Zuspeisung in ein Produkt mit verringertem Asphaltengehalt umgewandelt wird, aus dem eine oder mehrere Destillatfraktion(en) und eine schwere Fraktion (Strom 2) abgetrennt werden,

einer Lösungsmittel-Entasphaltierungsbehandlung (DA), in welcher eine asphaltenthaltige Zuspeisung in ein Produkt umgewandelt wird, aus welchem eine entasphaltierte Ölfraction und eine Bitumenfraktion (Strom 3) abgetrennt werden,

einer thermischen Crackbehandlung (TC), in welcher eine Zuspeisung in ein Produkt umgewandelt wird, welches weniger als 20 Gewichtsprozent C₄⁻-Kohlenwasserstoffe enthält und aus dem eine oder mehrere Destillatfraktion(en) und eine schwere Fraktion (Strom 4) abgetrennt werden, daß Strom 3 als Zuspeisung für die TC-Behandlung verwendet wird, und daß Strom 1 entweder

1) zusammen mit Strom 4 als eine Zuspeisungskomponente für die HT-Behandlung verwendet wird, wobei Strom 2 dann als eine Zuspeisungskomponente für die DA-Behandlung eingesetzt wird, oder

2) zusammen mit Strom 2 als eine Zuspeisungskomponente für die DA-Behandlung verwendet wird, wobei der Strom 4 dann als Zuspeisung für die HT-Behandlung eingesetzt wird.

2. Ein Verfahren wie in Anspruch 1 beansprucht, dadurch gekennzeichnet, daß als Strom 1 eine Kohlenwasserstoffmischung verwendet wird, welche im wesentlichen oberhalb 350°C siedet und von der mehr als 35 Gewichtsprozent oberhalb 520°C siedet, und welche einen RCT-Wert von mehr als 7,5 Gewichtsprozent hat, wie ein Rückstand, der bei der Vakuumdestillation eines atmosphärischen Destillationsrückstandes eines Rohmineralöls erhalten worden ist.

3. Ein Verfahren wie in Anspruch 1 oder 2 beansprucht, dadurch gekennzeichnet, daß ein

oder mehrere Vakuumdestillat(e) aus einem oder mehreren der Ströme 1, 2 und 4 abgetrennt wird(werden).

4. Ein Verfahren wie in irgendeinem der Ansprüche 1 bis 3 beansprucht, dadurch gekennzeichnet, daß in der HT-Behandlung für die Verminderung des Asphaltengehaltes der Zuspeisung ein Katalysator verwendet wird, welcher mindestens ein Metall ausgewählt aus der Gruppe, welche durch Nickel und Kobalt gebildet wird, und zusätzlich mindestens ein Metall, ausgewählt aus der Gruppe, welche durch Molbdän und Wolfram gebildet wird, auf einem Träger enthält, wobei dieser Träger zu mehr als 40 Gewichtsprozent aus Aluminiumoxid besteht.

5. Ein Verfahren wie in irgendeinem der Ansprüche 1 bis 4 beansprucht, dadurch gekennzeichnet, daß die HT-Behandlung bei einer Temperatur im Bereich von 350 bis 450°C, einem Druck im Bereich von 75 bis 200 bar, einer Raumgeschwindigkeit im Bereich von 0,1 bis 2 g.g⁻¹.h⁻¹ und einem Verhältnis Wasserstoff zu Zuspeisung im Bereich von 500 bis 2000 Nl.kg⁻¹ durchgeführt wird.

6. Ein Verfahren wie in irgendeinem der Ansprüche 1 bis 5 beansprucht, dadurch gekennzeichnet, daß die HT-Behandlung in einer solchen Weise durchgeführt wird, daß ein Produkt erhalten wird, dessen C₅⁺ Fraktion den folgenden Anforderungen entspricht:

a) Der RCT-Wert der C₅⁺-Fraktion beträgt 20 bis 70% des RCT-Wertes der Zuspeisung und

b) der Unterschied im Prozentgehalt der unterhalb 350°C siedenden Kohlenwasserstoffe in der C₅⁺-Fraktion und der Zuspeisung beträgt höchstens 40.

7. Ein Verfahren wie in irgendeinem der Ansprüche 1 bis 6 beansprucht, dadurch gekennzeichnet, daß die DA-Behandlung unter Verwendung von n-Butan als Lösungsmittel bei einem Druck im Bereich von 35 bis 45 bar und bei einer Temperatur im Bereich von 100 bis 150°C durchgeführt wird.

8. Ein Verfahren wie in irgendeinem der Ansprüche 1 bis 7 beansprucht, dadurch gekennzeichnet, daß die TC-Behandlung bei einer Temperatur im Bereich von 400 bis 525°C und einer Raumgeschwindigkeit im Bereich von 0,01 bis 5 kg frischer Zuspeisung je Liter Volumen des Crackreaktors je Minute durchgeführt wird.

Revendications

1. Procédé de production d'huiles déasphaltées et de distillats d'huiles hydrocarbonées à partir de mélanges hydrocarbonés contenant des asphaltènes, caractérisé en ce qu'on soumet un mélange hydrocarboné contenant des asphaltènes (1) à une combinaison des trois traitements suivants:

un hydrotraitement catalytique (HT) où l'on transforme une charge contenant des asphaltènes en un produit ayant une teneur réduite en asphaltènes à partir duquel ou sépare une ou plusieurs fractions de distillat et une fraction lourde (courant 2),



un traitement de déasphaltage par solvant (DA) où l'on transforme une charge contenant des asphaltènes en un produit à partir duquel on sépare une huile déasphaltée et un bitume asphaltique (courant 3) et

un traitement de craquage thermique (CT) où l'on transforme une charge en un produit qui contient moins de 20% en poids (p) d'hydrocarbures C4- et à partir duquel on sépare une ou plusieurs fractions de distillat et une fraction lourde (courant 4), en ce qu'on utilise le courant 3 comme charge pour le traitement CT et en ce qu'on utilise le courant 1

1) soit avec le courant 4 comme composant de charge pour le HT, le courant 2 étant utilisé comme charge pour le traitement DA,

2) soit avec le courant 2 comme composant de charge pour le traitement DA, le courant 4 étant utilisé comme charge pour le HT.

2. Procédé selon la revendication 1, caractérisé en ce qu'on utilise comme courant 1 un mélange hydrocarboné qui a un point d'ébullition substantiellement supérieur à 350°C et dont plus de 35% p a un point d'ébullition supérieur à 520°C et qui a un RCT supérieur à 7,5% p, comme un résidu obtenu dans la distillation sous vide d'un résidu de distillation atmosphérique à partir de l'huile minérale brute.

3. Procédé selon les revendications 1 et 2, caractérisé en ce qu'on sépare un ou plusieurs distillats sous vide à partir d'un ou plusieurs des courants 1, 2 et 4.

4. Procédé selon l'une quelconque des revendications 1—3, caractérisé en ce que le catalyseur utilisé dans le HT visant à la réduction de la teneur

en asphaltènes de la charge est un catalyseur contenant au moins un métal choisi dans le groupe formé par le nickel et le cobalt et en outre au moins un métal choisi dans le groupe formé par le molybdène et le tungstène sur un support, lequel support se compose à plus de 40% p d'alumine.

5. Procédé selon l'une quelconque des revendications 1—4, caractérisé en ce que le HT est conduit à une température de 350—450°C, une pression de 75—200 bars, une vitesse spatiale de 0,1—2 g.g⁻¹.h⁻¹ et un rapport H₂/charge de 500—2000 NI.kg⁻¹.

6. Procédé selon l'une quelconque des revendications 1—5, caractérisé en ce que le HT est conduit d'une manière telle qu'il donne un produit dont la fraction C5+ répond aux exigences suivantes:

a) le RCT de la fraction C5+ est de 20—70% du RCT de la charge et

b) la différence entre les pourcentages pondéraux des hydrocarbures ayant un point d'ébullition inférieur à 350°C présents dans la fraction C5+ et dans la charge est d'au plus 40.

7. Procédé selon l'une quelconque des revendications 1—6, caractérisé en ce que le traitement DA est conduit en utilisant du n-butane comme solvant à une pression de 35—45 bars et une température de 100—150°C.

8. Procédé selon l'une quelconque des revendications 1—7, caractérisé en ce que le traitement CT est conduit à une température de 400—525°C et une vitesse spatiale de 0,01—5 kg de charge fraîche par litre de volume de réacteur de craquage par minute.

