

12 **EUROPEAN PATENT APPLICATION**

21 Application number: 83200869.2

51 Int. Cl.<sup>3</sup>: C 10 G 67/04

22 Date of filing: 14.06.83

30 Priority: 13.07.82 NL 8202827

43 Date of publication of application:  
25.01.84 Bulletin 84/4

64 Designated Contracting States:  
BE DE FR GB IT SE

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54 Process for the production of low-asphaltenes hydrocarbon mixtures.

57 Deasphalted oils and hydrocarbon oil distillates are produced from asphaltenes-containing hydrocarbon mixtures by a process comprising converting an asphaltenes-containing hydrocarbon mixture using a catalytic hydrotreatment into a product with a reduced asphaltenes content which is separated by distillation into one or more distillate fractions and a residual fraction, which is subjected to two-step solvent deasphalting.

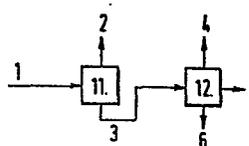


FIG. 1A-1

PROCESS FOR THE PRODUCTION OF LOW-ASPHALTENES  
HYDROCARBON MIXTURES

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

The atmospheric distillation of crude mineral oil for the  
5 preparation of light hydrocarbon oil distillates, such as gas-  
oline, kerosine and gasoil, yields an asphaltenes-containing  
residue as a by-product. At first such residues, which, in  
addition to asphaltenes, generally contain a considerable pro-  
portion of sulphur and metals, used to find application as fuel  
10 oils. In view of the need of light hydrocarbon oil distillates  
and shrinking oil reserves, various treatments have already been  
proposed which aimed at producing light hydrocarbon oil distillates  
from atmospheric residues. For instance, solvent deasphalting  
(for the sake of brevity hereinafter referred to as "DA") may be  
15 used to separate from an atmospheric residue a deasphalted oil  
which may be subjected to catalytic cracking in the presence or  
in the absence of hydrogen. Another option is to separate an  
atmospheric residue by vacuum distillation into a vacuum distil-  
late and a vacuum residue, to separate a deasphalted oil from the  
20 vacuum residue using DA and to subject both the vacuum distillate  
and the deasphalted oil to catalytic cracking in the presence or  
in the absence of hydrogen.

A drawback to the conventional DA treatment, in which an  
asphaltenes-containing feed is separated in one step into a  
25 deasphalted oil as the desired main product and an asphaltic  
bitumen as a by-product, is that if a sufficiently high yield of  
deasphalted oil is to be realised, one must generally accept a  
deasphalted oil of unsatisfactory quality. In this connection the  
quality of the deasphalted oil should be taken to be its suita-  
30 bility to be converted into hydrocarbon oil distillates by  
catalytic cracking in the presence or in the absence of hydrogen.  
This suitability becomes better according as the deasphalted oil  
has, among other things, lower asphaltenes, metal and sulphur  
contents. By subjecting a deasphalted oil of unsatisfactory

quality to a pretreatment, it may still be rendered suitable for conversion into hydrocarbon oil distillates by catalytic cracking in the presence or in the absence of hydrogen.

It has been found that the above-mentioned drawback of the conventional DA treatment can be overcome to some extent by carrying out the DA treatment as a two-step process, in which the asphaltenes-containing hydrocarbon mixture is separated into a high-quality deasphalted oil (for the sake of brevity hereinafter referred to as "deasphalted oil 1"), a deasphalted oil of lower quality (for the sake of brevity hereinafter referred to as "deasphalted oil 2") and an asphaltic bitumen. Deasphalted oil 1 differs from deasphalted oil 2 mainly by its considerably lower asphaltenes, metal and sulphur contents. Comparison of the results of the one-step process with those of the two-step process shows that, starting from the same quantity of an asphaltenes-containing hydrocarbon mixture for the preparation of the same total quantity of deasphalted oil, which deasphalted oil in the case of the one-step process is of unsatisfactory quality, the two-step process yields two deasphalted oils, of which deasphalted oil 1 is suitable, such as it is, for conversion into hydrocarbon oil distillates by catalytic cracking in the presence or in the absence of hydrogen. Although the two-step process produces a deasphalted oil of unsatisfactory quality as well, it does so in considerably smaller quantities than the one-step process.

Since DA treatment has proved in practice to be suitable for the production of deasphalted oils from a variety of asphaltenes-containing hydrocarbon mixtures and since it has also been found that a two-step DA treatment gives better results than a one-step process, investigations were carried out into whether a combination of the two-step DA treatment and a pretreatment of the asphaltenes-containing feed can produce a better result than using nothing but a two-step DA treatment. One of the pretreatments investigated was a catalytic hydrotreatment (for the sake of brevity hereinafter referred to as "HT") in which the asphaltenes-containing feed is converted into a product having a reduced

asphaltenes content, from which one or more distillate fractions are separated whilst the residue is used as the feed for the two-step DA treatment. In the assessment of the results it is in the first place the yield and quality of the deasphalted oils and the asphaltic bitumen that play a role. Then, the yield of light product is of great importance as well. In this connection the quality of the asphaltic bitumen should be taken to be its suitability to serve as fuel oil component. This suitability is better according as the asphaltic bitumen has lower metal and sulphur contents and lower viscosity and density.

In the investigation a comparison was made between the results obtained in the production of deasphalted oils (and possibly a hydrocarbon oil distillate) starting from equal quantities of an asphaltenes-containing hydrocarbon mixture using a) nothing but two-step DA treatment and b) two-step DA treatment preceded by a HT, whilst during the DA treatments the conditions were chosen such that both procedures yielded equal quantities of deasphalted oil 1. Considering the quantities and qualities of the various products obtained in the two procedures, the following may be observed:

- 1) The deasphalted oil 1 obtained according to procedure b) has considerably lower metal and sulphur contents than the deasphalted oil 1 obtained according to procedure a).
- 2) Procedure b) produces a lower yield of deasphalted oil 2 than procedure a).
- 3) The deasphalted oil 2 obtained according to procedure b) has considerably lower metal and sulphur contents than the deasphalted oil 2 obtained according to procedure a).
- 4) Procedure b) produces a considerably lower yield of asphaltic bitumen than procedure a).
- 5) In procedure b) a substantial yield of hydrocarbon oil distillate is obtained.

Considering the better quality of the deasphalted oils, the lower yield of the by-product asphaltic bitumen and the high yield of hydrocarbon oil distillate, procedure b) is much to be

preferred to procedure a).

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 a HT is used to convert an asphaltenes-containing hydrocarbon mixture into a product with a reduced asphaltenes content which is separated by distillation into one or more distillate fractions and a residual fraction and in which two-step DA is used to separate the residual fraction into a deasphalted oil 1 of high quality, a deasphalted oil 2 of lower quality and an asphaltic bitumen.

In the process according to the invention the feed used is an asphaltenes-containing hydrocarbon mixture. A suitable parameter for the assessment of the asphaltenes content of a hydrocarbon mixture and for the reduction of the asphaltenes content which occurs when a HT is applied to an asphaltenes-containing hydrocarbon mixture, is the Ramsbottom Carbon Test value (RCT). The higher the asphaltenes content of the hydrocarbon mixture, the higher the RCT. The process is preferably applied to hydrocarbon mixtures which substantially boil above 350°C and more than 35 %w of which boils above 520°C and which have an RCT of more than 7.5 %w. Examples of such hydrocarbon mixtures are residues obtained in the distillation of crude mineral oils and heavy hydrocarbon mixtures obtained from shale and tar sand. If required, the process may also be applied to heavy crude mineral oils, to residues obtained in the distillation of products developed in the thermal cracking of hydrocarbon mixtures and to asphaltic bitumen obtained in the solvent deasphalting of asphaltenes-containing hydrocarbon mixtures. The process according to the invention is very suitable for application to residues obtained in the vacuum distillation of atmospheric distillation residues of crude mineral oils. The process according to the invention is also very suitable for application to residues obtained in the vacuum distillation of atmospheric distillation residues of products developed in the thermal cracking of asphalt-

enes-containing hydrocarbon mixtures. If the feed available for the process according to the invention is an atmospheric distillation residue, then 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 can be subjected to thermal cracking or to catalytic cracking in the presence or in the absence of hydrogen to convert it into light hydrocarbon oil distillates.

10       Asphaltenes-containing hydrocarbon mixtures generally contain a considerable proportion of metals, in particular vanadium and nickel. If such hydrocarbon mixtures are subjected to a catalytic treatment, for instance a HT for the reduction of the asphaltenes content, as in the process according to the invention, these metals will deposit on the catalyst used in the HT and thus shorten its life. In view of this, asphaltenes-containing hydrocarbon mixtures with a vanadium + nickel content of more than 50 parts per million by weight (ppmw) should preferably be subjected to demetallization 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 consisting more than 80 %w of silica. Both catalysts consisting entirely of silica and catalysts containing one or more metals having hydrogenating activity, in particular a combination of nickel and vanadium, present on a carrier support substantially consisting of silica, are suitable for the purpose. If in the process according to the invention a catalytic demetallization in the presence of hydrogen is applied to an asphaltene-containing feed, this demetallization may be carried out in a separate reactor. However, since the catalytic demetallization and the HT for the reduction of the asphaltenes content can be carried out under the same conditions, the two processes may also very suitably be carried out in the same reactor, which will contain a bed of the demetallization catalyst and a bed of the catalyst used in the HT, successively.

Suitable catalysts for carrying out the HT are those 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. Very suitable catalysts for use in the HT are those comprising the metal combinations nickel/molybdenum or cobalt/molybdenum on alumina as a 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<sup>-1</sup>.h<sup>-1</sup> and in particular of from 0.1-2 g.g<sup>-1</sup>.h<sup>-1</sup> and a H<sub>2</sub>/feed ratio of from 100-5000 Nl.kg<sup>-1</sup> and in particular of from 500-2000 Nl.kg<sup>-1</sup>. As regards the conditions used in a possible catalytic demetallization in the presence of hydrogen, the same preference applies as that stated hereinbefore for the HT for the reduction of the asphaltenes content.

The HT is preferably carried out in such a manner that it yields a product the C<sub>5</sub><sup>+</sup> fraction of which meets the following requirements:

- a) the RCT of the C<sub>5</sub><sup>+</sup> fraction is 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 C<sub>5</sub><sup>+</sup> 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 normally accompanied with some reduction of the RCT and some formation of C<sub>5</sub>-350°C product. A similar phenomenon is seen in the HT, in which the reduction of RCT and the formation of C<sub>5</sub>-350°C product are normally accompanied with some reduction of the metal content. As regards the requirements mentioned hereinbefore under a) and b), these relate to the total RCT reduction and C<sub>5</sub>-350°C product formation (viz. including those occurring in a possible catalytic demetallization).

In the HT a product with a reduced asphaltenes content is obtained from which one or more distillate fractions and

a heavy fraction are separated. The distillate fractions separated from the product may be atmospheric distillates only, but it is preferred to separate a vacuum distillate from the product as well. This vacuum distillate may be converted into light hydrocarbon oil distillates in the manners indicated hereinbefore.

In the process according to the invention two-step DA treatment is applied to a distillation residue obtained as one of the products of the HT. Suitable solvents for carrying out the DA treatment are waxy hydrocarbons having 3-7 carbon atoms per molecule, such as propane, n-butane isobutane, n-pentane, isopentane and mixtures thereof, such as mixtures of propane and n-butane and mixtures of n-butane and isobutane. Suitable solvent/oil weight ratios lie between 7:1 and 1:1. The DA treatment is preferably carried out at elevated temperature and pressure. The two-step DA treatment may essentially be carried out in two ways.

According to the first embodiment the residue from the HT to be treated is subjected to extraction under mild conditions in which the residue is separated into a deasphalted oil 1 and a "light" asphaltic bitumen and subsequently the light asphaltic bitumen is subjected in the second step to a second extraction in which it is separated into a deasphalted oil 2 and the final asphaltic bitumen as a by-product. The same solvent can be used in both steps and the degree of extraction is controlled with the aid of the temperature (temperature in the first step higher than in the second step). Different solvents may also be used, for instance propane in the first step and n-butane in the second step.

According to the second embodiment the residue from the HT to be treated is subjected to extraction under severe conditions in which the residue is separated into a deasphalted oil and the final asphaltic bitumen as a by-product and subsequently the deasphalted oil is separated in the second step into a deasphalted oil 1 and a deasphalted oil 2. To this end the mixture of deasphalted oil and solvent coming from the extractor

need only be fed into a settler in which a higher temperature prevails than that used in the first step.

For carrying out the process according to the invention a number of embodiments are suitable. Each one of these embodi-  
5 ments may be assigned to one of two main classes, depending on whether the asphaltenes-containing feed is subjected to the HT immediately (class I) or whether the asphaltenes-containing feed is first subjected to thermal cracking (for the sake of brevity hereinafter referred to as TC) and the HT is applied to  
10 a residual fraction of the thermally cracked product (class II).

The embodiments belonging to class I may further be arranged according to whether the apparatus in which the process is carried out is confined to a HT zone and a two-step DA zone (class IA) or whether the apparatus in addition to a HT zone and a two-step DA  
15 zone also includes a TC zone (class IB), a CC zone (IC) or both a TC zone and a CC zone (class ID), in which the deasphalted oil 2 and/or the asphaltic bitumen separated in the two-step DA zone, are further processed.

The term "CC" as used hereinbefore should be taken to refer  
20 to a special type of catalytic cracking for the preparation of light hydrocarbon oil distillates, in which the feed used is a deasphalted oil 2. This feed is distinguished from the feed which is normally used in a catalytic cracking process by the fact that the deasphalted oil 2 has, among other things, a much higher RCT  
25 and a much higher metal content.

The embodiments belonging to class IA may further be arranged as follows:

IA - 1: The deasphalted oil 2 and the asphaltic bitumen are separated as final products.

30 IA - 2: The deasphalted oil 2 is recirculated to the HT.

IA - 3: The asphaltic bitumen is recirculated to the HT.

The embodiments belonging to class IB may further be arranged as follows:

35 IB - 1: The deasphalted oil 2 is used as the feed for the TC treatment and a residual fraction of the thermally cracked product is recirculated to the HT.

IB - 2: The deasphalted oil 2 is used as the feed for the TC treatment and a residual fraction of the thermally cracked product, together with the asphaltic bitumen, is recirculated to the HT.

5 IB - 3: The asphaltic bitumen is used as the feed for the TC treatment and a residual fraction of the thermally cracked product is recirculated to the HT.

10 IB - 4: Both the deasphalted oil 2 and the asphaltic bitumen are used as feed components for the TC treatment and a residual fraction of the thermally cracked product is recirculated to the HT.

The embodiments belonging to class IC may be arranged as follows:

15 IC - 1: The deasphalted oil 2 was used as the feed for the CC treatment and a residual fraction of the catalytically cracked product is recirculated to the HT.

20 IC - 2: The deasphalted oil 2 is used as the feed for the CC treatment and a residual fraction of the catalytically cracked product, together with the asphaltic bitumen, is recirculated to the HT.

As regards the embodiment belonging to class ID:

25 ID : The deasphalted oil 2 is used as the feed for the CC treatment, the asphaltic bitumen is used as the feed for the TC treatment and a residual fraction of the catalytically cracked product is recirculated, together with a residual fraction of the thermally cracked product, to the HT.

The embodiments belonging to class II may further be arranged as follows:

30 II - 1: The deasphalted oil 2 and the asphaltic bitumen are separated as final products.

II - 2: The deasphalted oil 2 is recirculated to the TC treatment.

II - 3: The deasphalted oil 2 is recirculated to the HT.

II - 4: The asphaltic bitumen is recirculated to the TC treatment.

II - 5: The asphaltic bitumen is recirculated to the HT.

35 II - 6: The deasphalted oil 2 and the asphaltic bitumen are recirculated to the TC treatment.

II - 7: The deasphalted oil 2 is recirculated to the HT and the asphaltic bitumen is recirculated to the TC treatment.

II - 8: The deasphalted oil 2 is recirculated to the TC treatment and the asphaltic bitumen is recirculated to the HT.

5 The various embodiments of the process according to the invention are represented schematically in Figures IA - 1 to IA - 3 inclusive, IB - 1 to IB - 4 inclusive, IC - 1, IC - 2, ID and II - 1 to II - 8 inclusive. In the figures the various streams and the various zones are indicated by the following  
10 numerals:

stream 1 = asphaltenes-containing feed  
" 2 = hydrocarbon oil distillate ex HT  
" 3 = residue ex HT  
" 4 = deasphalted oil 1 ex DA treatment  
15 " 5 = deasphalted oil 2 ex DA treatment  
" 6 = asphaltic bitumen ex DA treatment  
" 7 = hydrocarbon oil distillate ex TC treatment  
" 8 = residue ex TC treatment  
" 9 = hydrocarbon oil distillate ex CC treatment  
20 " 10 = residue ex CC treatment  
zone 11 = HT  
" 12 = DA  
" 13 = TC  
" 14 = CC

25 In the embodiments where the object is to obtain as complete as possible a conversion of the asphaltenes-containing feed into deasphalted oil and hydrocarbon oil distillates, it is preferred to separate what is called a bleed stream from one of the heavy streams in the process. In this way the build-up of  
30 undesirable heavy components during the process can be prevented.

Carrying out the process according to the invention by using a TC treatment and/or a CC treatment yields cracked products from which one or more distillate fractions are separated. These distillate fractions may be atmospheric distillates only, but  
35 preferably a vacuum distillate should also be separated from the

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cracked products. This vacuum distillate may be converted into light hydrocarbon oil distillates by the methods mentioned hereinbefore.

5 If the process according to the invention is carried out in an apparatus which includes a TC zone, whilst the streams which are fed into this TC zone consist of one or more relatively low-asphaltenes streams - such as a deasphalted oil 2 - as well as of one or more relatively asphaltene-rich streams - such as asphaltic bitumen separated in the process and/or the asphaltene-  
10 containing feed which is to be processed with the aid of the process - , it is preferred to use a TC zone which includes two cracking units and to crack the types of feed separately into products from which one or more distillate fractions and a residual fraction are separated. When a TC zone is used which  
15 includes two cracking units, a heavy fraction of the cracked product coming from the cracking unit in which a relatively low-asphaltenes feed is processed, is preferably recirculated to that cracking unit. When a TC zone is used which includes two  
20 cracking units, then, from the product obtained in the cracking unit in which the relatively asphaltene-rich feed is cracked, a relatively low-asphaltenes heavy fraction may be separated, if desired, and the latter may be used as a feed component for the cracking unit in which the relatively low-asphaltenes feed  
25 is processed. When a TC zone is used which includes two cracking units, it is not necessary for the distillation of the cracked products (atmospheric distillation and optionally vacuum distillation) to be carried out in separate distillation units. If desired, the cracked products or fractions thereof may be combined and distilled together.

30 Five flow diagrams for the preparation of deasphalted oils and hydrocarbon oil distillates from asphaltene-containing hydrocarbon mixtures will hereinafter be explained in more detail with the aid of Figures III-VII.

Flow diagram A (based on embodiment IA-1).

See Figure III

The process is carried out in an apparatus consisting of a HT zone composed of a catalytic hydrotreatment unit (11), an atmospheric distillation unit (15) and a vacuum distillation unit (16) and a two-step DA zone (12), successively.

An asphaltenes-containing hydrocarbon mixture (1), together with hydrogen (20), is subjected to a catalytic hydrotreatment. The hydrotreated product (21) is separated by atmospheric distillation into a gas fraction (22), an atmospheric distillate (2A) and an atmospheric residue (23). The atmospheric residue (23) is separated by vacuum distillation into a vacuum distillate (2B) and a vacuum residue (3). The vacuum residue (3) is separated by two-step de-asphalting into a deasphalted oil 1 (stream 4), a deasphalted oil 2 (stream 5) and an asphaltic bitumen (6).

Flow diagram B (based on embodiment IB-3).

See Figure IV

The process is carried out in an apparatus consisting of a HT zone composed of a catalytic hydrotreatment unit (11), an atmospheric distillation unit (15) and a vacuum distillation unit (16), a two-step DA zone (12) and a TC zone composed of a thermal cracking unit (13), a second atmospheric distillation unit (17) and a second vacuum distillation unit (18), successively.

An asphaltenes-containing hydrocarbon mixture (1) is mixed with a recirculation stream (8) and the mixture (29), together with hydrogen (20), is subjected to a catalytic hydrotreatment. The hydrotreated product (21) is separated by atmospheric distillation into a gas fraction (22), an atmospheric distillate (2A) and an atmospheric residue (23). The atmospheric residue (23) is separated by vacuum distillation into a vacuum distillate (2B) and a vacuum residue (3). The vacuum residue (3) is separated by two-step solvent deasphalting into a deasphalted oil 1 (stream 4), a deasphalted oil 2 (stream 5) and an asphaltic bitumen (6). The asphaltic bitumen (6) is divided into two portions (30) and (31). Portion (30) is subjected to thermal cracking. The thermally

cracked product (24) is separated by atmospheric distillation into a gas fraction (25), an atmospheric distillate (7A) and an atmospheric residue (26). The atmospheric residue (26) is separated by vacuum distillation into a vacuum distillate (7B) and a vacuum residue (8).

Flow diagram C (based on embodiment IC-1)

See Figure V

The process is carried out in an apparatus consisting of a HT zone composed of a catalytic hydrotreatment unit (11), an atmospheric distillation unit (15) and a vacuum distillation unit (16), a two-step DA zone (12) and a CC zone composed of a catalytic cracking unit (14) and a second atmospheric distillation unit (19), successively.

An asphaltene-containing hydrocarbon mixture (1) is mixed with a recirculation stream (10) and the mixture (32), together with hydrogen (20), is subjected to a catalytic hydrotreatment. The hydrotreated product (21) is separated by atmospheric distillation into a gas fraction (22), an atmospheric distillate (2A) and an atmospheric residue (23). The atmospheric residue (23) is separated by vacuum distillation into a vacuum distillate (2B) and a vacuum residue (3). The vacuum residue (3) is separated by two-step solvent deasphalting into a deasphalted oil 1 (stream 4), a deasphalted oil 2 (stream 5) and an asphaltic bitumen (6). The deasphalted oil 2 (stream 5) is subjected to catalytic cracking. The catalytically cracked product (27) is separated by atmospheric distillation into a gas fraction (28), an atmospheric distillate (9) and an atmospheric residue (10).

Flow diagram D (based on embodiment ID).

See Figure VI

The process is carried out in an apparatus consisting of a HT zone composed of a catalytic hydrotreatment unit (11), an atmospheric distillation unit (15) and a vacuum distillation unit (16), a two-step DA zone (12), a TC zone composed of a thermal cracking unit (13), a second atmospheric distillation unit (17) and a second vacuum distillation unit (18) and a CC zone composed of a

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catalytic cracking unit (14) and a third atmospheric distillation unit (19), successively.

An asphaltenes-containing hydrocarbon mixture (1) is mixed with a recirculation stream (34) and the mixture (33), together with  
5 hydrogen (20), is subjected to a catalytic hydrotreatment. The hydrotreated product (21) is separated by atmospheric distillation into a gas fraction (22), an atmospheric distillate (2A) and an atmospheric residue (23). The atmospheric residue (23) is separated  
10 by vacuum distillation into a vacuum distillate (2B) and a vacuum residue (3). The vacuum residue (3) is separated by two-step solvent deasphalting into a deasphalted oil 1 (stream 4), a deasphalted oil 2 (stream 5) and an asphaltic bitumen (6). The asphaltic bitumen (6) is divided into two portions (30) and (31). Portion (30) is subjected to thermal cracking. The thermally cracked  
15 product (24) is separated by atmospheric distillation into a gas fraction (25), an atmospheric distillate (7A) and an atmospheric residue (26). The atmospheric residue (26) is separated by vacuum distillation into a vacuum distillate (7B) and a vacuum residue (8). The deasphalted oil 2 (stream 5) is subjected to catalytic cracking.  
20 The catalytically cracked product (27) is separated by atmospheric distillation into a gas fraction (28), an atmospheric distillate (9) and an atmospheric residue (10). Streams (8) and (10) are mixed to form the recirculation stream (34).

Flow diagram E (based on embodiment II-1)

25 See Figure VII

The process is carried out in an apparatus consisting of a TC zone composed of a thermal cracking unit (13), an atmospheric distillation unit (17) and a vacuum distillation unit (18), a HT zone composed of a catalytic hydrotreatment unit (11), a second atmospheric dis-  
30 tillation unit (15) and a second vacuum distillation unit (16) and a two-step DA zone (12), successively. An asphaltenes-containing hydrocarbon mixture (1) is subjected to thermal cracking. The thermally cracked product (24) is separated by atmospheric distillation into a gas fraction (25), an atmospheric distillate (7A) and an

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atmospheric residue (26). The atmospheric residue (26) is separated by vacuum distillation into a vacuum distillate (7B) and a vacuum residue (8). The vacuum residue (8), together with hydrogen (20), is subjected to a catalytic hydrotreatment. The hydrotreated product (21) is separated by atmospheric distillation into a gas fraction (22), an atmospheric distillate (2A) and an atmospheric residue (23). The atmospheric residue (23) is separated by vacuum distillation into a vacuum distillate (2B) and a vacuum residue (3). The vacuum residue (3) is separated by two-step solvent deasphalting into a deasphalted oil 1 (stream 4), a deasphalted oil 2 (stream 5) and an asphaltic bitumen (6).

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

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

In the process according to the invention the starting material was an asphaltenes-containing hydrocarbon mixture obtained as a residue in the vacuum distillation of an atmospheric distillation residue of a crude mineral oil. The vacuum residue boiled substantially above 520°C and had an RCT of 18.8 %w, an overall vanadium and nickel content of 167 ppmw and a sulphur content of 5.4 %w. The process was carried out according to the flow diagrams A-E. The following conditions were used in the various zones.

In all the flow diagrams the catalytic hydrotreatment unit consisted of two reactors, the first of which was filled with a Ni/V/SiO<sub>2</sub> catalyst containing 0.5 parts by weight (pbw) of nickel and 2.0 pbw of vanadium per 100 pbw of silica and the second of which was filled with a Ni/Mo/Al<sub>2</sub>O<sub>3</sub> catalyst containing 4 pbw of nickel and 12 pbw of molybdenum per 100 pbw of alumina. The catalysts were used in a volume ratio 1:4. The HT was carried out at a hydrogen pressure of 150 bar, a space velocity (measured over the two reactors) of 0.5 kg of feed per

litre of catalyst per hour, a  $H_2$ /feed ratio of 1000 Nl per kg and an average temperature of  $410^\circ C$  in the first reactor and  
5  $390^\circ C$  in the second reactor.

In all the flow diagrams the two-step DA treatment was carried out by contacting the feed to be deasphalted in the first step (in an extractor) with a n-butane/isobutane mixture (weight ratio 65:35) at a temperature of  $110^\circ C$ , a pressure of 40 bar and  
10 a solvent/oil weight ratio of 2:1 and, after the asphaltic bitumen has been separated off, separating the deasphalted oil in a second step (in a settler) at a temperature of  $140^\circ C$  and a pressure of 40 bar into a deasphalted oil 1 and a deasphalted oil 2.

15 In flow diagrams B, D and E, respectively, the TC treatment was carried out in a cracking coil at a pressure of 10 bar, a space velocity of 0.4 kg of fresh feed per litre of cracking coil volume per minute and at a temperature of  $460^\circ C$  (measured at the outlet of the cracking coil).

20 In flow diagrams C and D, respectively, the CC treatment was carried out at a temperature of  $510^\circ C$ , a pressure of 2.2 bar, a space velocity of  $2 \text{ kg} \cdot \text{kg}^{-1} \cdot \text{h}^{-1}$  and a catalyst renewal rate of 1.0 pbw of catalyst per 1000 pbw of oil and using a zeolite cracking catalyst.

25 For comparison, an experiment was carried out in which the vacuum residue was subjected to two-step DA treatment for producing a deasphalted oil 1 and a deasphalted oil 2, using no previous HT (Example 6) and also an experiment in which the vacuum residue was subjected to a one-step DA treatment for preparing a de-  
30 asphalted oil 3, using no previous HT (Example 7). In Example 6 the two-step DA treatment was carried out in substantially the same way as described in the Examples 1-5, with the distinction that the temperature prevailing in the settler described in Example 6 was  $144^\circ C$ . The one-step DA treatment described in  
35 Example 7 was carried out in the same way as the first step of the two-step DA treatment as described in the Examples 1-6.

In all the experiments the asphaltenes-containing hydrocarbon

mixture (1) used as starting material was 100 pbw of vacuum residue.

The quantities of the various streams obtained in the experiments described in the Examples 1-5 and the RCT's of certain streams are given in Table I.

Table II lists the yields of final products obtained in the experiments described in Examples 1-7.

Table III lists the properties of the final products obtained in the experiments described in Examples 1-7.

TABLE I

Example No.	1	2	3	4	5
Example carried out according to flow diagram No.	A	B	C	D	E
Flow diagram represented in Figure No.	III	IV	V	VI	VII
<u>Quantities in pbw</u>					
C <sub>5</sub> - 350°C atmosph. distillate (2A)	20.8	20.9	21.6	21.8	14.4
C <sub>5</sub> - 350°C " " (7A)	-	0.4	-	0.4	10.4
C <sub>5</sub> - 350°C " " (9)	-	-	10.2	12.1	-
350 - 520°C vacuum distillate (2B)	31.4	31.6	33.4	33.8	21.9
350 - 520°C " " (7B)	-	0.5	-	0.5	16.5
deasphalted oil 1 (stream 4)	22.0	23.5	23.2	24.8	16.8
deasphalted oil 2 (stream 5)	16.5	18.1	14.4	18.1	12.2
asphaltic bitumen (6)	7.3	53.9	8.5	49.5	5.8
520°C <sup>+</sup> vacuum residue (8)	-	50.0	-	45.6	73.1
370°C <sup>+</sup> atmospheric residue (10)	-	-	3.1	4.4	-
portion (30)	-	50.9	-	46.5	-
" (31)	-	3.0	-	3.0	-
<u>RCT's of various streams in %w</u>					
C <sub>5</sub> <sup>+</sup> fraction of product (21)	4.6	21.4	4.3	21.8	6.5
mixture (29)	-	30.7	-	-	-
" (32)	-	-	18.3	-	-
" (33)	-	-	-	31.3	-
520°C <sup>+</sup> vacuum residue (8)	-	-	-	-	25.7

TABLE II

Example No.	1	2	3	4	5	6	7
<u>Yields in pbw</u>							
hydrocarbon oil distillates	52.2	53.4	65.2	68.6	63.2	-	-
deasphalted oil 1	22.0	23.5	23.2	24.8	16.8	22.0	-
" " 2	16.5	18.1	-	-	12.2	40.2	-
" " 3	-	-	-	-	-	-	62.2
asphaltic bitumen	7.3	3.0	8.5	3.0	5.8	37.8	37.8

TABLE III

Example No.	1	2	3	4	5	6	7
deasphalted oil 1	2.2	3.4	2.1	3.2	2.5	1.8	-
" " 2	8.5	13.5	-	-	9.2	8.2	-
" " 3	-	-	-	-	-	-	5.9
asphaltic bitumen	36.8	52.5	52.0	60.5	52.7	39.5	39.5
RCT, %w							
deasphalted oil 1	0.3	1.2	0.2	3.2	1.1	2.9	-
" " 2	2.2	3.4	-	-	3.3	26	-
" " 3	-	-	-	-	-	-	18
asphaltic bitumen	115	86	84	88	151	411	411
V+Ni content, ppmw							
deasphalted oil 1	0.26	0.73	0.25	0.63	1.0	3.2	-
" " 2	0.38	0.94	-	-	1.6	4.5	-
" " 3	-	-	-	-	-	-	4.1
asphaltic bitumen	1.9	2.5	2.1	2.5	5.8	7.2	7.2
Sulphur content, %w							

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With reference to Tables I-III the following should be noted.

The advantage of a two-step DA treatment over a one-step DA treatment becomes evident upon comparison of the results described in the Examples 6 and 7.

The advantage of applying a HT to the feed for the two-step DA treatment becomes evident upon comparison of the results described in the Examples 1 and 6.

Comparison of the results described in the Examples 1 and 2 shows that application of a TC treatment to the asphaltic bitumen and recirculation of the residue ex TC treatment to the HT produces higher yields of hydrocarbon oil distillates and deasphaltered oils.

Comparison of the results described in the Examples 1 and 2 shows that application of a CC treatment to the deasphaltered oil 2 and recirculation of the residue ex CC treatment to the HT produces considerably higher yields of hydrocarbon oil distillates.

Example 4, describing experiments in which both a TC treatment and a CC treatment are used, provides a combination of the advantages mentioned for Examples 2 and 3.

Comparison of Examples 1 and 5 shows that application of a TC treatment to the feed for the HT produces considerably higher yields of hydrocarbon oil distillates.

C L A I M S

1. A process for the production of deasphalted oils and hydrocarbon oil distillates from asphaltenes-containing hydrocarbon mixtures, characterized in that a catalytic hydrotreatment is used to convert an asphaltenes-containing hydrocarbon mixture  
5 into a product with a reduced asphaltenes content which is separated by distillation into one or more distillate fractions and a residual fraction and that two-step solvent deasphalting is used to separate the residual fraction into a deasphalted oil 1 of high quality, a deasphalted oil 2 of lower quality and an  
10 asphaltic bitumen.
2. A process as claimed in claim 1, characterized in that the feed used is 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, preferably a residue  
15 obtained in the vacuum distillation of an atmospheric distillation residue of a crude mineral oil.
3. A process as claimed in claim 1 or 2, characterized in that in the catalytic hydrotreatment for the reduction of the asphaltenes content a catalyst is used which comprises at least  
20 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, more than 40 %w of which carrier consists of alumina, preferably the metal combination nickel/molybdenum or cobalt/molybdenum supported on  
25 alumina as carrier.
4. A process as claimed in claim 3, characterized in that when use is made of a feed for the catalytic hydrotreatment which has a vanadium + nickel content of more than 50 ppmw, this feed is contacted with two successive catalysts, the first of which is  
30 a demetallization catalyst consisting more than 80 %w of silica and the second of which is an asphaltenes conversion catalyst as described in claim 3.
5. A process as claimed in any one of claims 1-4, character-

ized in that the catalytic hydrotreatment is carried out at a temperature of 350-450°C, a pressure of 75-200 bar, a space velocity of 0.1-2 g.g<sup>-1</sup>.h<sup>-1</sup> and a H<sub>2</sub>/feed ratio of 500-2000 Nl.kg<sup>-1</sup>.

6. A process as claimed in any one of claims 1-5, characterized  
5 in that the catalytic hydrotreatment is carried out in such a way that a product is obtained the C<sub>5</sub><sup>+</sup> fraction of which meets the following requirements:

- a) the RCT of the C<sub>5</sub><sup>+</sup> fraction is 20-70% of the RCT of the feed and
- 10 b) the difference between the percentages by weight of hydrocarbons boiling above 350°C present in the C<sub>5</sub><sup>+</sup> fraction and in the feed is at most 40.

7. A process as claimed in any one of claims 1-6, characterized  
15 in that the two-step solvent deasphalting is carried out by subjecting the residual fraction separated from the product of the catalytic hydrotreatment in the first step to extraction under mild conditions in which it is separated into a deasphalted oil 1 and a "light" asphaltic bitumen and by subjecting the light asphaltic bitumen in the second step to a second extraction  
20 treatment in which it is separated into a deasphalted oil 2 and the final asphaltic bitumen as a by-product of the process.

8. A process as claimed in any one of claims 1-7, characterized  
25 in that the two-step solvent deasphalting is carried out by subjecting the residual fraction separated from the product of the catalytic hydrotreatment in the first step to extraction under severer conditions in which it is separated into a deasphalted oil and the final asphaltic bitumen as a by-product of the process and separating deasphalted oil in the second step into a deasphalted oil 1 and a deasphalted oil 2.

30 9. A process as claimed in any one of claims 1-8, characterized in that the deasphalted oil 2 or the asphaltic bitumen is used as a feed component for the catalytic hydrotreatment.

10. A process as claimed in any one of claims 1-9, characterized  
35 in that the deasphalted oil 2 and/or the asphaltic bitumen is subjected to thermal cracking and that a distillation residue of

the thermally cracked product, preferably both a distillation residue of the thermally cracked product and the asphaltic bitumen, is (are) used as a feed component for the catalytic hydrotreatment.

- 5 11. A process as claimed in any one of claims 1-9, characterized in that the deasphalted oil 2 is subjected to catalytic cracking and that a distillation residue of the catalytically cracked product, either or not together with the asphaltic bitumen, is used as a feed component for the catalytic hydro-
- 10 treatment.
12. A process as claimed in any one of claims 1-9, characterized in that the deasphalted oil 2 is subjected to catalytic cracking, that the asphaltic bitumen is subjected to thermal cracking and that both a distillation residue of the catalytically
- 15 cracked product and a distillation residue of the thermally cracked product are used as feed components for the catalytic hydrotreatment.
13. A process as claimed in any one of claims 1-9, characterized in that the asphaltenes-containing hydrocarbon mixture which
- 20 serves as the feed for the process is first subjected to thermal cracking and that a distillation residue of the thermally cracked product is used as the feed for the catalytic hydrotreatment.
14. A process as claimed in claim 13, characterized in that the deasphalted oil 2 or the asphaltic bitumen is used as a feed
- 25 component for the thermal cracking or for the catalytic hydro-treatment.
15. A process as claimed in claim 13, characterized in that both the deasphalted oil 2 and the asphaltic bitumen are used as feed components for the thermal cracking.
- 30 16. A process as claimed in claim 13, characterized in that the deasphalted oil 2 is used as a feed component either for the thermal cracking or for the catalytic hydrotreatment, whilst the asphaltic bitumen is used as a feed component either for the catalytic hydrotreatment or for the thermal cracking, respectively.
- 35 17. A process for the production of deasphalted oils and

hydrocarbon oil distillates from asphaltenes-containing hydrocarbon mixtures, as claimed in claim 1, substantially as described hereinbefore and in particular with reference to Examples 1-5.

18. Deasphalted oils and hydrocarbon oil distillates whenever  
5 produced according to a process as described in claim 17.

19. Apparatuses for carrying out the process as claimed in claim 17 corresponding substantially with those represented schematically in Figures I-VII.

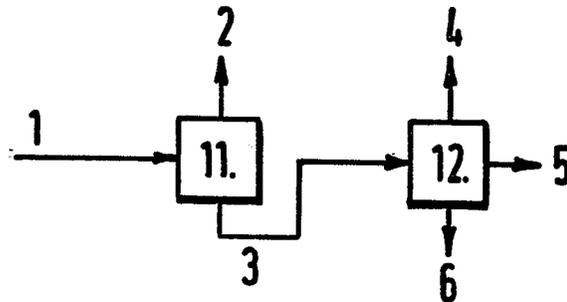


FIG. IA-1

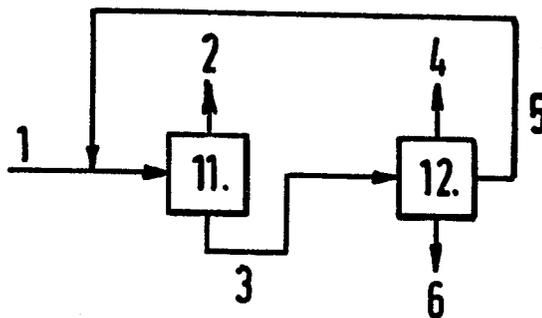


FIG. IA-2

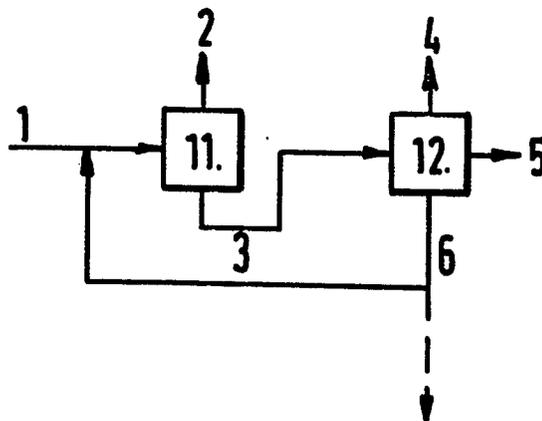


FIG. IA-3

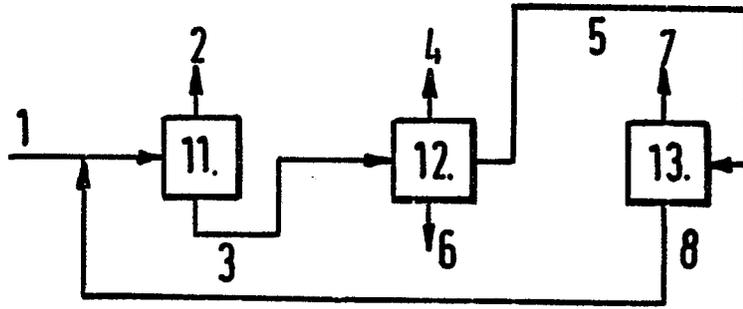


FIG. IB-1

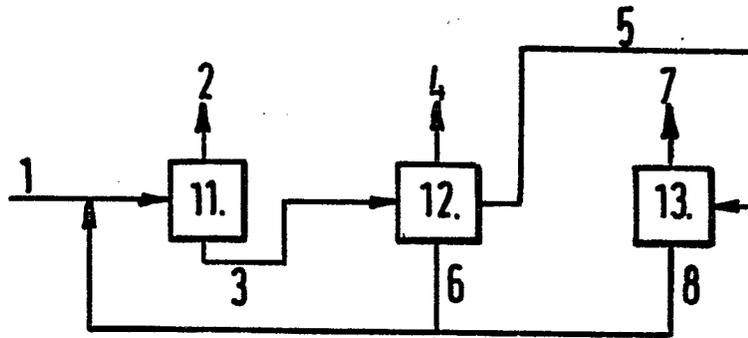


FIG. IB-2

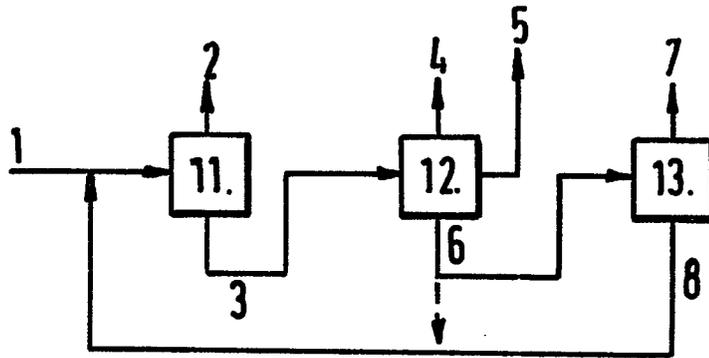


FIG. IB-3

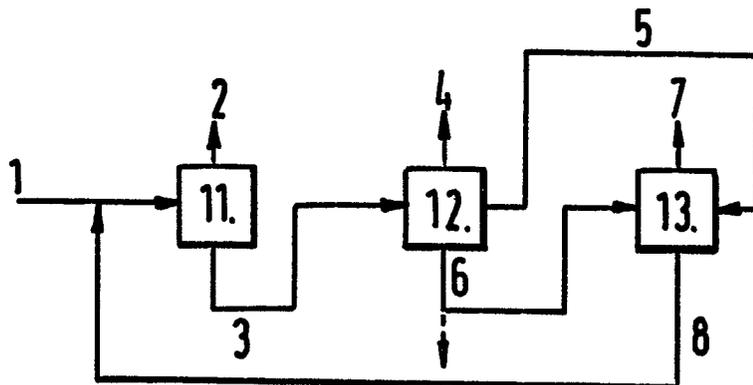


FIG. IB-4

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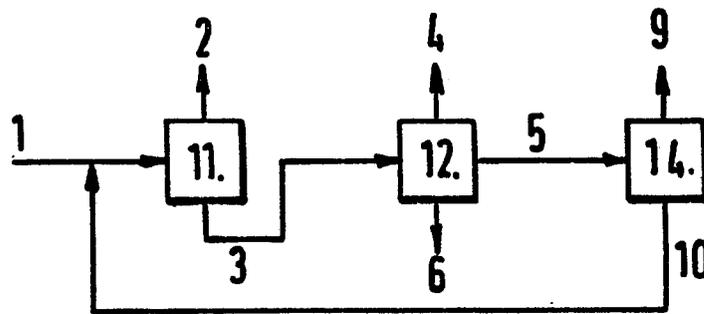


FIG.IC-1

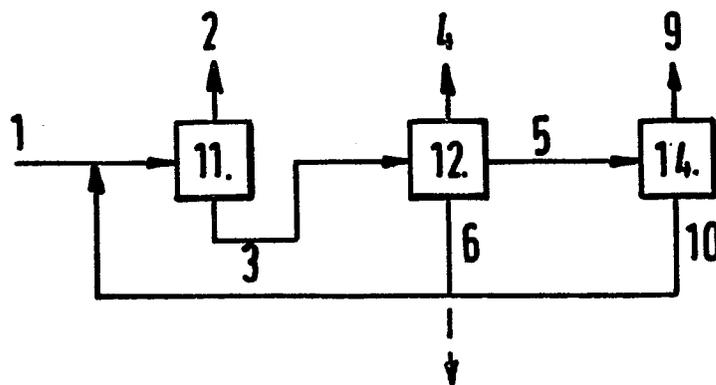


FIG.IC-2

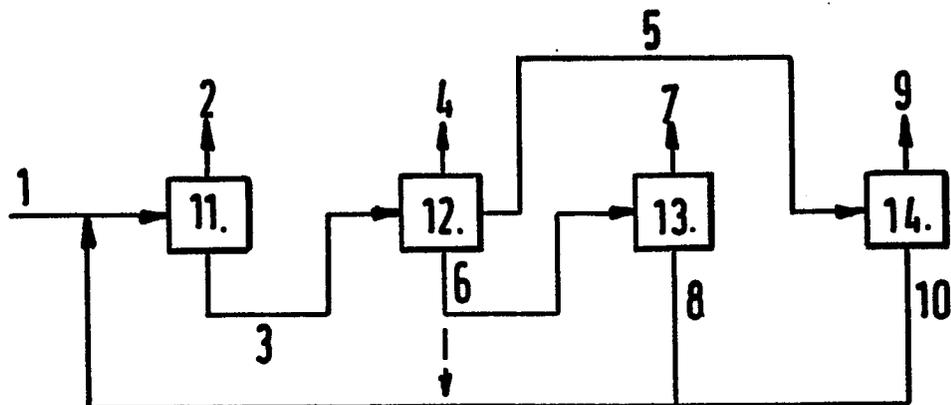


FIG.ID

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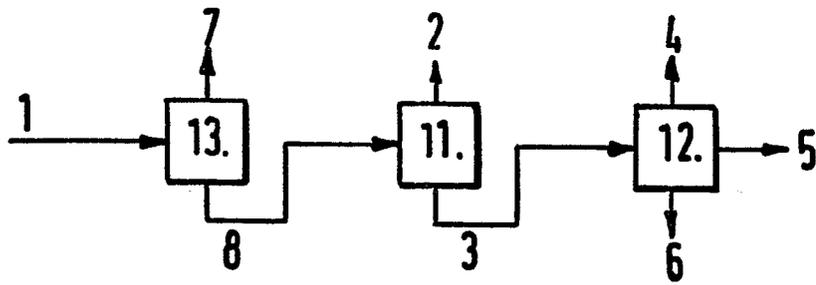


FIG. II-1

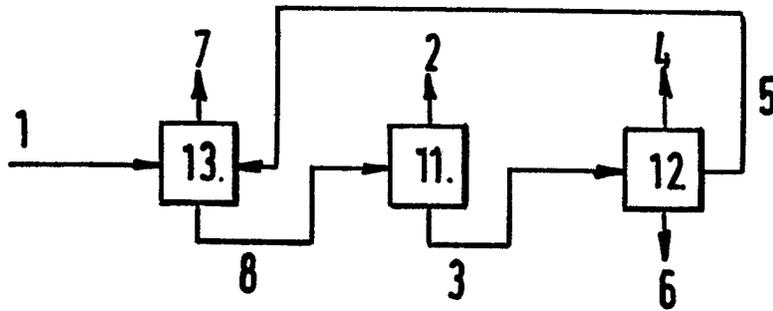


FIG. II-2

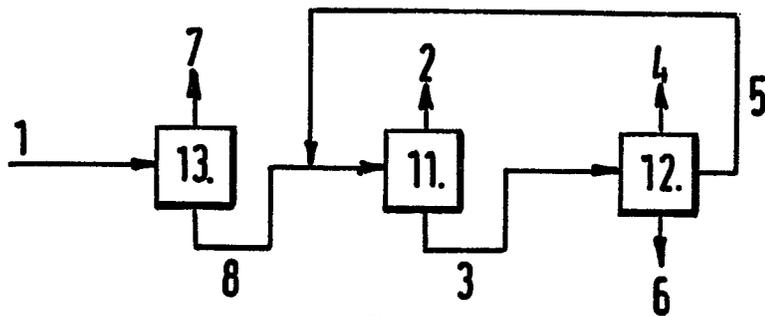


FIG. II-3

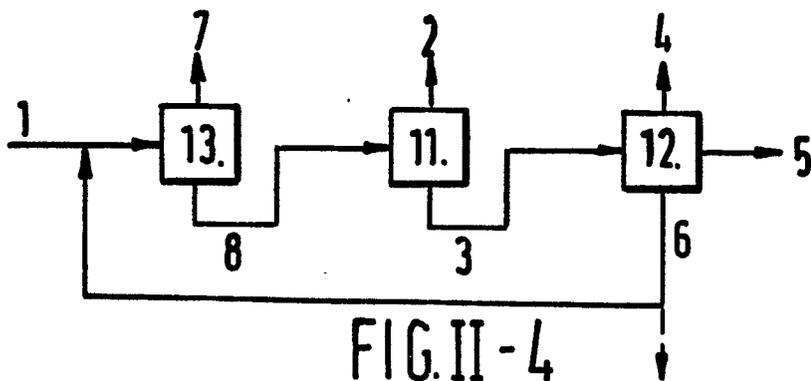


FIG. II-4

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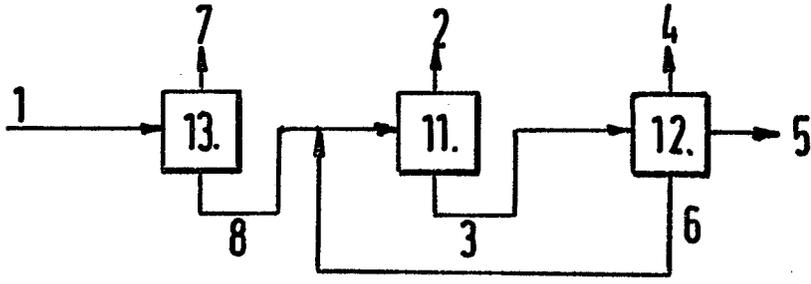


FIG. II-5

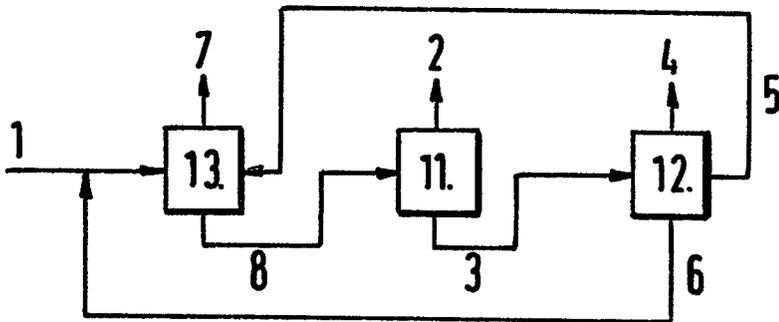


FIG. II-6

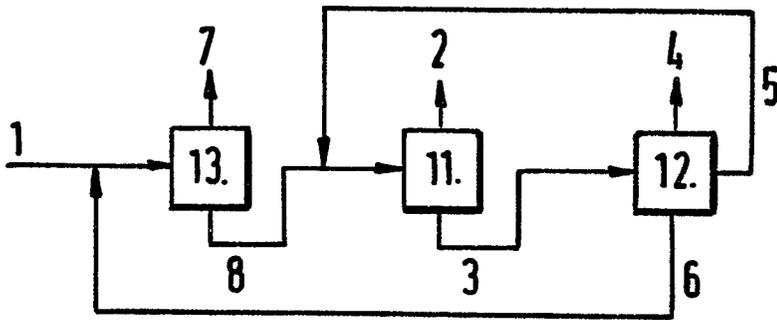


FIG. II-7

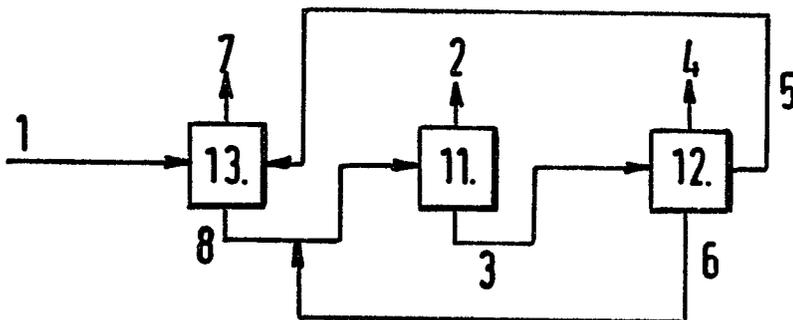


FIG. II-8

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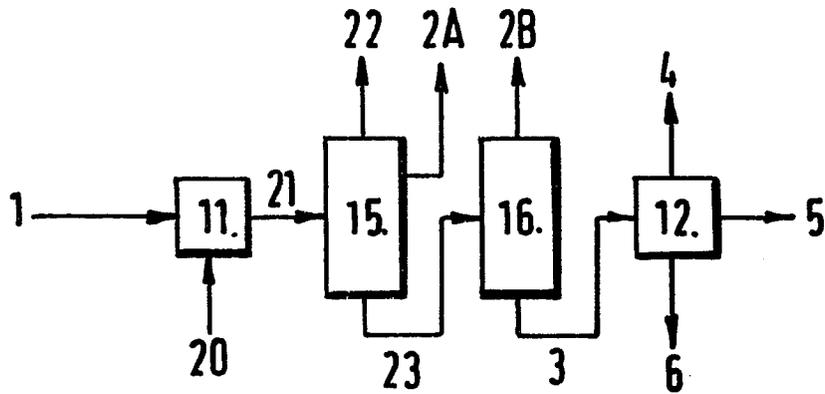


FIG. III

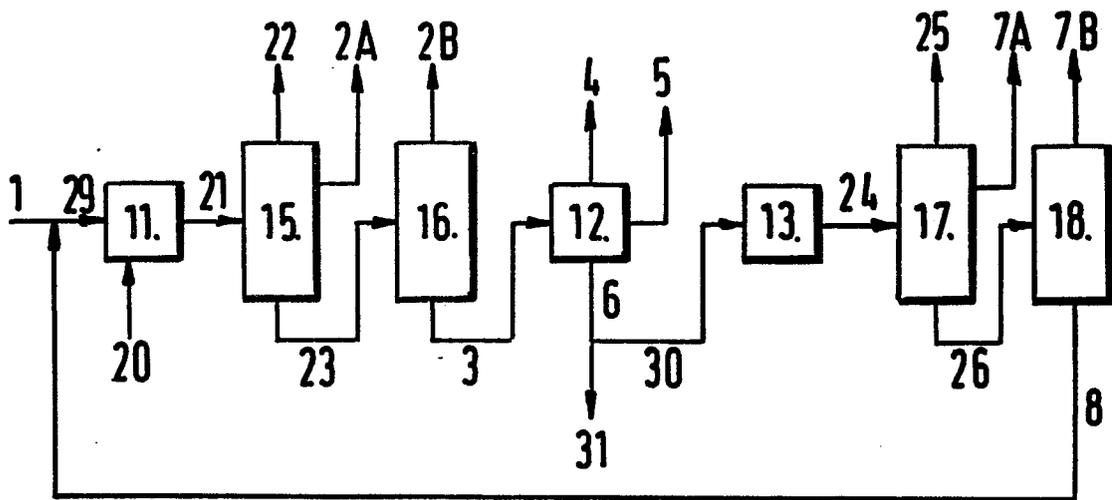


FIG. IV

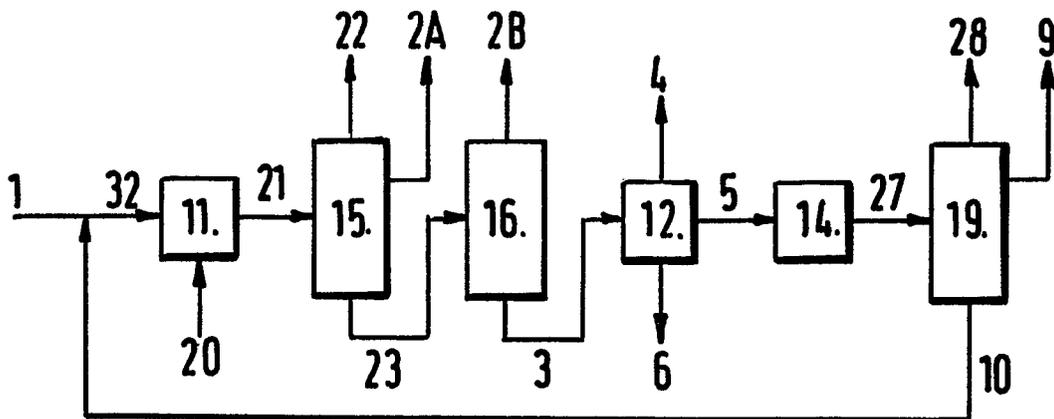


FIG. V

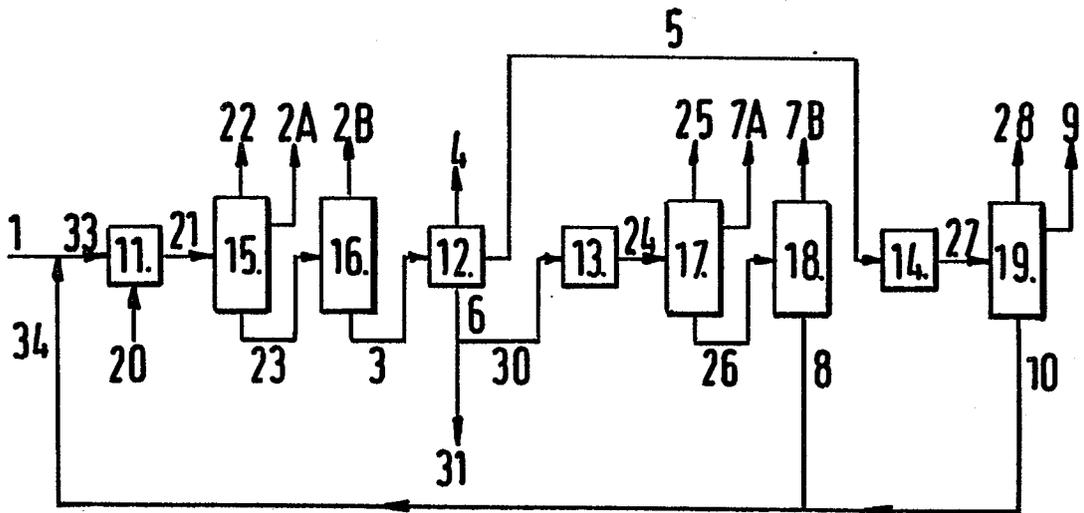


FIG. VI

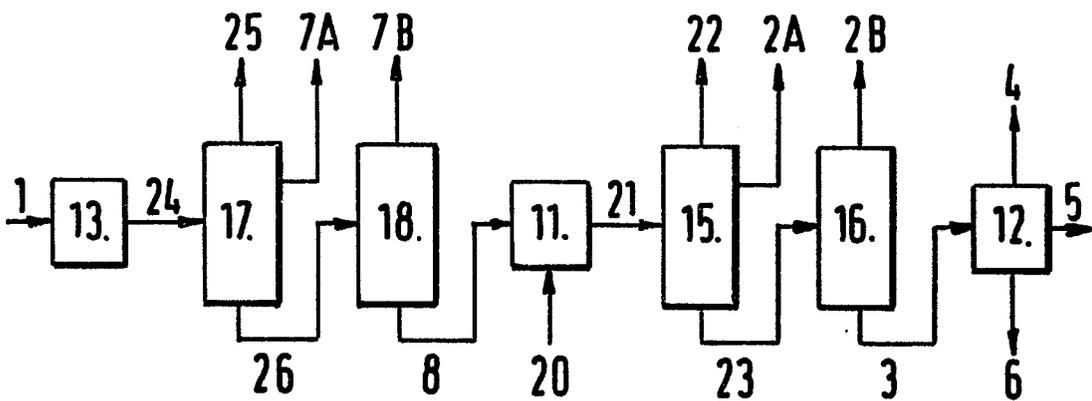


FIG. VII



DOCUMENTS CONSIDERED TO BE RELEVANT			EP 83200869.2
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 3)
A	<p>US - A - 4 191 636 (FUKUI et al.)</p> <p>* Claims 1-6,10,11; column 4, line 10 - column 6, line 2 *</p> <p>--</p>	1-5,9,17,18	C 10 G 67/04
A	<p>GB - A - 2 031 011 (CHIYODA CHEMICAL ENGINEERING &amp; CONSTRUCTION COMPANY LIMITED)</p> <p>* Claims; page 1, line 38 - page 2, line 58 *</p> <p>--</p>	1-5,17,18	
A	<p>GB - A - 1 563 276 (SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V.)</p> <p>* Claims; page 1, line 1 - page 3, line 10 *</p> <p>--</p>	1-5,9-18	
A	<p>GB - A - 1 560 148 (SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V.)</p> <p>* Claims; page 1, line 1 - page 3, line 20 *</p> <p>--</p>	1-5,9-18	<p>TECHNICAL FIELDS SEARCHED (Int. Cl. 3)</p> <p>C 10 G 67/00</p> <p>C 10 G 69/00</p> <p>C 10 G 47/00</p> <p>C 10 G 45/00</p>
A	<p>GB - A - 1 557 955 (SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V.)</p> <p>* Claims; page 1, line 1 - page 3, line 55 *</p> <p>--</p>	1-5,9-18	
The present search report has been drawn up for all claims			
Place of search		Date of completion of the search	Examiner
VIENNA		14-10-1983	STÖCKLMAYER
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone</p> <p>Y : particularly relevant if combined with another document of the same category</p> <p>A : technological background</p> <p>O : non-written disclosure</p> <p>P : intermediate document</p> <p>T : theory or principle underlying the invention</p> <p>E : earlier patent document, but published on, or after the filing date</p> <p>D : document cited in the application</p> <p>L : document cited for other reasons</p> <p>&amp; : member of the same patent family, corresponding document</p>			



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**EUROPEAN SEARCH REPORT**

**0099141**

Application number

EP 83200869.2

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. Cl. <sup>3</sup> )
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
P,A	EP - A2 - 0 068 543 (SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V.) * Totality; especially claims * ----	1-5,9,17,18	
			TECHNICAL FIELDS SEARCHED (Int. Cl. <sup>3</sup> )