

PROCESS FOR THE PREPARATION OF A HYDROCARBON MIXTURE

The invention relates to a process for the preparation of a hydrocarbon mixture having a Ramsbottom Carbon Test value (RCT) of a %w and an initial boiling point of T_1 °C.

The RCT is an important parameter in the assessment of the suitability of heavy hydrocarbon mixtures as feed stocks for catalytic conversion processes, such as catalytic cracking, carried out in the presence or absence of hydrogen, for the preparation of light hydrocarbon distillates, such as gasoline and kerosine. According as the feed has a higher RCT, the catalyst will be deactivated more rapidly in these processes.

Residual hydrocarbon mixtures, such as residues obtained in the distillation of a crude mineral oil and asphaltic bitumen separated in the solvent deasphalting of the said distillation residues or of residues obtained in the distillation of a hydrotreated residual fraction of a crude mineral oil generally have too high an RCT to be suitable without previous treatment for use as feeds for the above-mentioned catalytic conversion processes. Since the RCT of residual hydrocarbon mixtures is mainly determined by the percentage of asphaltenes present in the mixtures, a reduction of the RCT of these mixtures can be obtained by reducing the asphaltenes content. Basically, this may be achieved in two ways. Part of the asphaltenes may be separated from the mixture by solvent deasphalting, or part of the asphaltenes may be converted by subjecting the mixture to a catalytic hydrotreatment. For the reduction of the RCT of distillation residues the latter method is preferred, in the first place, because its yield of heavy product with a low RCT is higher and further because, in contrast to the former method, where asphaltic bitumen is obtained as a by-product, it yields a valuable C_5^+ atmospheric distillate as a by-product. In view of the fact that when the former method is applied to asphaltic bitumen, yields are low, only the latter method is eligible for

the preparation of heavy product with a low RCT from asphaltic bitumen or from mixtures of asphaltic bitumen and distillation residue. A drawback to the latter method, however, is that it gives rise to the formation of an undesirable C_4^- fraction which, moreover, contributes considerably to the hydrogen consumption of the process.

It was found that during the reduction of the RCT through catalytic hydrotreatment of heavy hydrocarbon mixtures, according as the catalytic hydrotreatment is carried out under more severe conditions in order to attain a greater RCT reduction, the parameter " C_4^- production per % RCT reduction" (for the sake of brevity hereinafter referred to as "G") at first remains virtually constant (G_c) and subsequently shows a fairly sharp increase. In view of the hydrogen consumption of the process it is however important to take care that the RCT reduction is not carried beyond the value corresponding to $G = 2 \times G_c$. This means that in practice there will be a number of cases in which it is undesirable, starting from a heavy hydrocarbon mixture, to employ nothing but a catalytic hydrotreatment for preparing a product from which, after separation of an atmospheric distillate, an oil can be obtained which has an initial boiling point of $T_1^\circ C$ and an RCT of a %w. In those cases there is nevertheless an attractive manner of preparing an oil having the afore-mentioned initial boiling point and RCT from a heavy hydrocarbon mixture. To this end the product obtained in the catalytic hydrotreatment is separated by distillation into an atmospheric distillate and an atmospheric residue having an initial boiling point of $T_1^\circ C$. The process may be continued in two ways. First, from the atmospheric residue so much asphaltic bitumen may be separated by solvent deasphalting that a deasphalted atmospheric residue is obtained which has the desired RCT of a %w. Secondly, the atmospheric residue may be separated by distillation into a vacuum distillate and a vacuum residue, and from the vacuum residue so much asphaltic bitumen may be separated by solvent deasphalting that a deasphalted

vacuum residue is obtained having an RCT which is such that, when this deasphalted vacuum residue is mixed with the previously separated vacuum distillate, an oil is obtained which has the desired RCT of a %w. The most attractive balance between yields of C_4^- fraction, C_5^+ atmospheric distillate, asphaltic bitumen and oil having an initial boiling point of $T_1^\circ\text{C}$ and an RCT of a %w is obtained when the catalytic hydrotreatment is carried out under such conditions that G lies between $1.5 \times G_c$ and $2.0 \times G_c$. When the catalytic hydrotreatment is carried out under such conditions that $G < 1.5 \times G_c$, a low C_4^- production is still obtained, but the yield of oil having an initial boiling point of $T_1^\circ\text{C}$ and an RCT of a %w in the combination process is unsatisfactory. When the catalytic hydrotreatment is carried out under such conditions that $G > 2.0 \times G_c$, a high yield of oil having an initial boiling point of $T_1^\circ\text{C}$ and an RCT of a %w is still obtained in the combination process, but it is attended with an unacceptably high C_4^- production.

G_c as well as the conditions at which G reaches a value between $1.5 \times G_c$ and $2.0 \times G_c$ may be read from a graph composed on the basis of a number of catalytic hydrotreatment scouting experiments with the asphaltenes-containing hydrocarbon mixture carried out at different severities and in which the occurring G 's have been plotted against the severities applied. Apart from one parameter e.g. the space velocity, which is variable, the other conditions in the scouting experiments are kept constant and chosen equal to those which will be used when the process is applied in practice.

The present patent application therefore relates to a process for the preparation of a hydrocarbon mixture with an RCT of a %w and an initial boiling point of $T_1^\circ\text{C}$, in which an asphaltenes-containing hydrocarbon mixture is subjected to a catalytic hydrotreatment, the product obtained being separated by distillation into an atmospheric distillate and an atmospheric residue having an initial boiling point of $T_1^\circ\text{C}$, in which either a deasphalted atmospheric residue having the

desired RCT of a %w is obtained from the said atmospheric residue by solvent deasphalting, or in which the atmospheric residue is first separated by distillation into a vacuum distillate and a vacuum residue, from which vacuum residue
5 asphaltic bitumen is separated by solvent deasphalting such that a deasphalted vacuum residue is obtained having an RCT such that, when this latter deasphalted vacuum residue is mixed with the said vacuum distillate, a mixture having the desired RCT of a %w is obtained, the catalytic hydrotreatment being carried out
10 under such conditions that the C_4^- production per % RCT reduction (G) lies between $1.5 \times G_c$ and $2.0 \times G_c$. G_c represents the virtually constant value of G which appears when the catalytic hydrotreatment is carried out at low severity.

As regards the way in which RCT's of hydrocarbon mixtures
15 are determined, the following three cases may be distinguished.

- a) The viscosity of the hydrocarbon mixture to be investigated is so high that it is impossible to determine the RCT by ASTM method D 524. In this case, the CCT (Conradson Carbon Test value) of the mixture is determined by ASTM method
20 D 189, and the RCT is computed from the CCT according to the formula:
$$RCT = 0.649 \times (CCT)^{1.144}.$$
- b) The viscosity of the hydrocarbon mixture to be investigated is such that the RCT can still be determined according to
25 the ASTM D 524 method, but this method gives an RCT value which lies above 20.0 %w. In this case, as in the case mentioned under a), the CCT of the mixture is determined by ASTM method D 189 and the RCT is computed from the CCT according to the formula mentioned under a).
- 30 c) The viscosity of the hydrocarbon mixture to be investigated is such that the RCT can be determined by ASTM method D 524 and this method gives an RCT value not higher than 20.0 %w. In this case the value thus found is taken to be the RCT of the mixture concerned.

In practice, for the determination of the RCT's of vacuum distillates, atmospheric residues, deasphalted distillation residues and mixtures of vacuum distillates and deasphalted distillation residues, the direct method described under c) will in many cases be sufficient. In the determination of the RCT of vacuum residues both the direct method described under c) and the indirect method described under b) are used. In the determination of the RCT of asphaltic bitumen the indirect method described under a) is usually the only one eligible.

The process according to the invention is a two-step process in which reduction of the RCT is attained through reduction of the asphaltenes content. In the first step of the process the asphaltenes content is reduced by converting part of the asphaltenes by means of a catalytic hydrotreatment. In the second step of the process the asphaltenes content is reduced by separating part of the asphaltenes by means of solvent deasphalting. Asphaltenes containing hydrocarbon mixtures usually contain an appreciable percentage of metals, especially vanadium and nickel. When such mixtures are subjected to a catalytic treatment, e.g. a catalytic hydrotreatment for RCT reduction, as in the process according to the invention, these metals will be deposited on the RCT-reduction catalyst, thus shortening its life. In view of this, asphaltenes-containing hydrocarbon mixtures having a vanadium + nickel content of more than 50 ppmw should preferably be subjected to demetallization before being contacted with the RCT-reduction catalyst. This demetallization may very suitably be carried out by contacting the mixture in the presence of hydrogen, with a catalyst consisting of 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, on a carrier substantially consisting of silica, are eligible for the purpose. Very suitable demetallization catalysts are those which meet certain given requirements as regards their porosity and particle size

and which are described in Netherlands patent application No. 7309387. When in the process according to the invention a catalytic demetallization in the presence of hydrogen is applied to the hydrocarbon mixture, this demetallization may be carried out in a separate reactor. Since the catalytic demetallization and the catalytic RCT reduction can be carried out under the same conditions, both processes may very suitably be carried out in the same reactor containing, successively, a bed of demetallization catalyst and a bed of RCT-reduction catalyst.

It should be noted that in the catalytic demetallization the reduction of the metal content is accompanied by some reduction of the RCT. The same applies to the catalytic RCT reduction in which the RCT reduction is accompanied by some reduction of the metal content. In this patent application, RCT reduction should be taken to be the total RCT reduction occurring in the catalytic hydrotreatment (i.e. including the RCT reduction occurring in a possible catalytic demetallization process).

Suitable catalysts for carrying out the catalytic RCT reduction 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 on a carrier, which carrier consists more than 40 %w of alumina. Very suitable RCT-reduction catalysts are those which comprise the metal combination nickel/molybdenum or cobalt/molybdenum on alumina as the carrier.

The catalytic RCT reduction is preferably carried out at a temperature of 300-500°C, a pressure of 50-300 bar, a space velocity of $0.02-10 \text{ g.g}^{-1}.\text{h}^{-1}$ and a H_2 /feed ratio of 100-5000 Nl/kg . Particular preference is given to carrying out the catalytic RCT reduction at a temperature of 350-450°C, a pressure of 75-200 bar, a space velocity of $0.1-2 \text{ g.g}^{-1}.\text{h}^{-1}$ and a H_2 /feed ratio of 500-2000 Nl/kg . As regards the conditions to be used in a catalytic demetallization process in the presence of hydrogen, to be carried out if necessary, the same preference

applies as that stated hereinbefore for the catalytic RCT reduction.

The desired RCT reduction in the first step of the process according to the invention may, for instance, be achieved by application of the space velocity pertaining to that RCT reduction, which can be read from a graph composed on the basis of a number of catalytic hydrotreatment scouting experiments with the asphaltenes-containing hydrocarbon mixture carried out at different space velocities and in which the RCT reductions achieved have been plotted against the space velocities used. Apart from the space velocity, which is variable, the other conditions in the scouting experiments are kept constant and chosen equal to those which will be used when the process according to the invention is applied in practice.

The second step of the process according to the invention is a solvent deasphalting step applied to a residue from the distillation of the hydrotreated product of the first step. The distillation residue to which the solvent deasphalting step is applied may be an atmospheric residue or a vacuum residue from the hydrotreated product. Preferably, a vacuum residue from the hydrotreated product is used for the purpose. Suitable solvents for carrying out the solvent deasphalting are paraffinic hydrocarbons having 3-6 carbon atoms per molecule, such as n-butane and mixtures thereof, such as mixtures of propane with n-butane and mixtures of n-butane with n-pentane. Suitable solvent/oil weight ratios lie between 7:1 and 1:1 and in particular between 4:1 and 2:1. The solvent deasphalting is preferably carried out at a pressure between 20 and 100 bar. When n-butane is used as the solvent, the deasphalting is preferably carried out at a pressure of 35-45 bar and a temperature of 100-150°C.

When the RCT reduction in the second step of the process according to the invention takes place by solvent deasphalting of an atmospheric residue, the desired RCT of the deasphalted atmospheric residue may be attained, for instance, by using the deasphalting temperature pertaining to that RCT, which can be

read from a graph composed on the basis of a number of de-asphalting scouting experiments with the atmospheric residue carried out at different temperatures in which the RCT's of the deasphalted atmospheric residues obtained have been plotted
 5 against the temperatures applied. Apart from the temperature, which is variable, the other conditions in the scouting experiments are kept constant and chosen equal to those which will be used when the process according to the invention is applied in practice.

10 When the RCT reduction in the second step of the process according to the invention takes place by solvent deasphalting of a vacuum residue, after which the deasphalted vacuum residue is mixed with the vacuum distillate separated earlier, the RCT and the quantity of the deasphalted vacuum residue should be
 15 adjusted to the quantity and the RCT of the vacuum distillate as follows. When a given quantity of vacuum distillate (VD) of A pbw having a given RCT_{VD} is available, then, in order to obtain a mixture M having a given RCT_M by mixing the vacuum distillate with deasphalted vacuum residue (DVR), B pbw of deasphalted
 20 vacuum residue will have to be prepared, its RCT_{DVR} being such that it obeys the relation:

$$\frac{A \times RCT_{VD} + B \times RCT_{DVR}}{A + B} = RCT_M$$

or, expressed otherwise,

$$A(RCT_M - RCT_{VD}) = B(RCT_{DVR} - RCT_M).$$

In the equation mentioned hereinabove the left-hand member is known. In addition, in the right-hand member RCT_M is known. On the basis of a number of deasphalting scouting experiments
 25 carried out with the vacuum residue at, for instance, different temperatures, a graph can be composed in which the term $B(RCT_{DVR} - RCT_M)$ has been plotted against the temperature used. The

temperature to be applied in the deasphalting in the second step of the process according to the invention may be read from this graph, this being the temperature at which the term

$B(RCT_{DVR} - RCT_M)$ has the given value $A(RCT_M - RCT_{VD})$. Apart from

- 5 the temperature, which is variable, the other conditions in the scouting experiments on deasphalting are kept constant and chosen equal to those which will be applied when the process according to the invention is used in practice.

- Besides the RCT, the metal content is also an important
10 parameter in assessing the suitability of heavy hydrocarbon oils as feeds for catalytic conversion processes, in the presence or absence of hydrogen, for the preparation of light hydrocarbon distillates, such as gasoline and kerosine. According as the feed has a higher metal content, the catalyst will be de-
15 activated more rapidly in these processes. As a rule, residual feed mixtures have not only too high an RCT, but also too high a metal content to be suitable, without treatment, as feeds for the afore-mentioned catalytic conversion processes. The product obtained in the process according to the invention is a de-
20 asphalted atmospheric residue or a mixture of a vacuum distillate and a deasphalted vacuum residue, which product, in addition to a low RCT, has a very low metal content. This is due to a considerable extent to the fact that the metal-containing distillation residue which is subjected to solvent deasphalting
25 has been catalytically hydrotreated. For, the solvent deasphalting of such metal-containing residues shows a very high metal-removing selectivity.

- As examples of asphaltenes-containing hydrocarbon mixtures which may be used as feed for the process according to the
30 invention the following may be mentioned:

- a) atmospheric residues obtained in the distillation of a crude mineral oil,
- b) vacuum residues obtained in the distillation of a crude mineral oil,

- c) asphaltic bitumen separated in the solvent deasphalting of the residues mentioned under a) and b),
- d) asphaltic bitumen separated in the solvent deasphalting of residues obtained in the distillation of a hydrotreated residual fraction of a crude mineral oil,
- 5 e) mixtures of two or more of the heavy hydrocarbon mixtures mentioned under a) - d),
- f) heavy crude oils,
- g) heavy hydrocarbon mixtures extracted from tar sands,
- 10 h) residues ex thermal cracking, and
- i) mixtures of one or more of the asphaltenes-rich hydrocarbon mixtures mentioned under a) - h) with one or more asphaltenes-poor or asphaltenes-free hydrocarbon mixtures such as aromatic extracts ex lubricating oil production and cycle oils and slurry oils ex catalytic cracking.
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As asphaltenes-containing hydrocarbon mixtures to be used as feed for the process according to the invention the following six are preferred:

Feed 1

- 20 An atmospheric residue obtained in the distillation of a crude mineral oil.

The investigation has shown that the RCT reductions in the catalytic hydrotreatment in which for G values are reached which correspond with $1.5 \times G_c$ and $2.0 \times G_c$, are dependent on T_1 , the RCT of the atmospheric residue (b %w) and the percentage by weight of the atmospheric residue which boils below 520°C (d %w), and are given by the following relation (relation 1)

$$\text{RCT reduction} = \frac{b-c}{b} \times 100 =$$

$$\frac{51.6 - 0.526 \times d - 0.115 \times T_1 + 2.55 \times b + 0.00115 \times T_1 \times d}{(1.426 - 1.15 \times 10^{-3} \times T_1)(1 - 0.01 \times d)} \pm 5$$

where c is the RCT of the atmospheric residue with an initial boiling point of $T_1^\circ\text{C}$ of the hydrotreated product.

Feed 2

A vacuum residue obtained in the distillation of a crude mineral oil.

The investigation has shown that the RCT reductions in the catalytic hydrotreatment in which for G values are reached which correspond with $1.5 \times G_c$ and $2.0 \times G_c$, are dependent on T_1 , the RCT of the vacuum residue (b %w) and the 5 %w boiling point of the vacuum residue ($T_5^\circ\text{C}$), and are given by the following relation (relation 2)

$$\text{RCT reduction} = \frac{b-c}{b} \times 100 =$$

$$\frac{73.5 - 0.108 \times T_1 + 2.55 \times b - 0.05 \times T_5}{1.4 - 1.08 \times 10^{-3} \times T_1} \pm 5$$

where c is the RCT of the atmospheric residue with an initial boiling point of $T_1^\circ\text{C}$ of the hydrotreated product.

Feed 3

An asphaltic bitumen separated in the solvent deasphalting of a distillation residue from a crude mineral oil.

The investigation has shown that the RCT reductions in the catalytic hydrotreatment in which for G values are reached which correspond with $1.5 \times G_c$ and $2.0 \times G_c$, are dependent on T_1 , the RCT of the asphaltic bitumen (b %w) and the average molecular weight (M) of the asphaltic bitumen, and are given by the following relation (relation 3)

$$\text{RCT reduction} = \frac{b-c}{b} \times 100 =$$

$$\frac{-48.5 - 0.108 \times T_1 + 32.1 \times \log M + (18.6 - 5.36 \times \log M) \times b}{1.4 - 1.08 \times 10^{-3} \times T_1} \pm 5.2$$

where c is the RCT of the atmospheric residue with an initial boiling point of T_1 °C of the hydrotreated product.

Feed 4

A mixture of an atmospheric residue obtained in the distillation of a crude mineral oil and an asphaltic bitumen separated in the solvent deasphalting of a residue obtained in the distillation
5 of a hydrotreated residual fraction of a crude mineral oil, which mixture comprises less than 50 pbw of the asphaltic bitumen per 100 pbw of the atmospheric residue.

The investigation has shown that the RCT reductions in the catalytic hydrotreatment in which for G values are reached which
10 correspond to $1.5 \times G_c$ and $2.0 \times G_c$, are dependent on

- 1) T_1 ,
 - 2) the RCT of the atmospheric residue (b %w),
 - 3) the percentage by weight of the atmospheric residue boiling below 520°C (f %w),
 - 15 4) the RCT of the asphaltic bitumen (c %w), and
 - 5) the asphaltic bitumen/atmospheric residue mixing ratio in the feed mixture, expressed in pbw of the asphaltic bitumen per 100 pbw of the atmospheric residue (r pbw),
- and are given by the following relation (relation 4)

$$\text{RCT reduction} = \frac{d-e}{d} \times 100 =$$

$$100 - \frac{P^{1.8} \times (91 - 0.9 \times f - 2.55 \times b) + (1 - P)(118 - 1.18 \times f)}{(1.426 - 1.15 \times 10^{-3} \times T_1 + 1.25 \times 10^{-3} \times r)(1 - 0.01 \times f)} \pm 5 \times \frac{100 + r}{100}$$

where

$$P = \frac{100 \times b}{100 \times b + r \times c}$$

d = the RCT of the feed mixture, and

e = the RCT of the atmospheric residue with an initial boiling point of T_1 °C of the hydrotreated product.

Feed 5

- A mixture of a vacuum residue obtained in the distillation of a crude mineral oil and an asphaltic bitumen separated in the solvent deasphalting of a residue obtained in the distillation of a hydrotreated residual fraction of a crude mineral oil, which mixture comprises less than 50 pbw of the asphaltic bitumen per 100 pbw of the vacuum residue.

The investigation has shown that the RCT reductions in the catalytic hydrotreatment in which for G values are reached which correspond to $1.5 \times G_c$ and $2.0 \times G_c$, are dependent on

- 1) T_1 ,
 - 2) the RCT of the vacuum residue (b %w),
 - 3) the 5 %w boiling point of the vacuum residue ($T_5^\circ\text{C}$),
 - 4) the RCT of the asphaltic bitumen (c %w), and
 - 15 5) the asphaltic bitumen/vacuum residue mixing ratio in the feed mixture, expressed in pbw of the asphaltic bitumen per 100 pbw of the vacuum residue (r pbw),
- and are given by the relation (relation 5)

$$\text{RCT reduction} = \frac{d-e}{d} \times 100 =$$

$$100 - \frac{P^{1.8} \times (66.5 - 2.55 \times b + 0.05 \times T_5) + 118 \times (1 - P)}{1.4 - 1.08 \times 10^{-3} \times T_1 + 1.4 \times 10^{-3} \times r} \pm 5 \times \frac{100 + r}{100}$$

where

$$P = \frac{100 \times b}{100 \times b + r \times c}$$

d = the RCT of the feed mixture, and

e = the RCT of the atmospheric residue with an initial boiling point of T_1 °C of the hydrotreated product.

Feed 6

A mixture of an asphaltic bitumen I separated in the solvent deasphalting of a residue obtained in the distillation of a crude mineral oil and an asphaltic bitumen II separated in the solvent deasphalting of a residue obtained in the distillation of a hydrotreated residual fraction of a crude mineral oil which mixture comprises less than 50 pbw of asphaltic bitumen II per 100 pbw of asphaltic bitumen I.

The investigation has shown that the RCT reductions in the catalytic hydrotreatment in which for G values are reached which correspond to $1.5 \times G_c$ and $2.0 \times G_c$, are dependent on

- 1) T_1 ,
 - 2) the RCT of the asphaltic bitumen I (b %w),
 - 3) the average molecular weight of the asphaltic bitumen I (M),
 - 4) the RCT of the asphaltic bitumen II (c %w), and
 - 5) the asphaltic bitumen II/asphaltic bitumen I mixing ratio in the feed mixture, expressed in pbw of the asphaltic bitumen II per 100 pbw of the asphaltic bitumen I (r pbw),
- and are given by the relation (relation 6)

$$\text{RCT reduction} = \frac{d-e}{d} \times 100 =$$

$$100 - \frac{p^{1.8} \times [188.5 - 32.1 \times \log M - (18.6 - 5.36 \times \log M) \times b] + 111 \times (1 - p)}{1.4 - 1.08 \times 10^{-3} \times T_1 + 1.4 \times 10^{-3} \times r} \pm 5.2 \times \frac{100 + r}{r}$$

where

$$p = \frac{100 \times b}{100 \times b + r \times c}$$

d = the RCT of the feed mixture, and

e = the RCT of the atmospheric residue with an initial boiling point of $T_1^\circ\text{C}$ of the hydrotreated product.

The average molecular weight M of the asphaltic bitumen I used as feed component in feed 6 as well as the average molecular weight M of the asphaltic bitumen used as feed 3 are determined by ASTM method D 3592-77 using toluene as solvent.

5 The relations 1-6 mentioned above offer an opportunity of determining whether, in view of the maximum acceptable value of G (corresponding to $2.0 \times G_c$), it is possible by catalytic hydrotreatment alone, starting from the feeds 1-6, to prepare a product from which, by distillation, an atmospheric residue can
10 be obtained which has a given initial boiling point of $T_1^\circ\text{C}$ and a given RCT of $a\%$. If, according to the relations, this proves impossible and, therefore, the combination route has to be applied, the relations further indicate the limits between which, in the catalytic hydrotreatment of the combination route,
15 the RCT reductions should be chosen to ensure optimum efficiency of the combination route.

The feeds 4-6 are composed of two blending components. One of these blending components (blending component I) is selected from the group consisting of atmospheric residues obtained in
20 the distillation of a crude mineral oil, vacuum residues obtained in the distillation of a crude mineral oil and asphaltic bitumen separated in the solvent deasphalting of a residue obtained in the distillation of a crude mineral oil. The other blending component (blending component II) is an asphaltic
25 bitumen separated in the solvent deasphalting of a residue obtained in the distillation of a hydrotreated residual fraction of a crude mineral oil. Examples of the latter residual fractions are atmospheric residues and vacuum residues obtained in the distillation of a crude mineral oil and asphaltic bitumen
30 separated in the solvent deasphalting of these residues. A very attractive embodiment of the process according to the invention in which one of the feeds 4-6 is used, is that in which the blending component II used as a component of the feed for the first step is the asphaltic bitumen obtained in the solvent

deasphalting in the second step. The conditions for attaining the desired RCT reduction in the first step of the process, with recirculation of asphaltic bitumen, may be determined as follows. The relation found is used to determine the RCT reduction to be employed in the catalytic hydrotreatment in order to ensure optimum efficiency in the combination process, when blending component I is the only feed used. The space velocity to be used for the purpose is determined on the basis of a number of catalytic hydrotreatment experiments using blending component I as the feed. Using this space velocity, in the combination process, an oil is prepared which has the desired RCT of a %w and the desired initial boiling point of $T_1^{\circ}\text{C}$, and an asphaltic bitumen (asphaltic bitumen A) is obtained as a by-product. Subsequently, the relation found is used to determine the RCT reduction to be employed in the catalytic hydrotreatment in order to ensure optimum efficiency in the combination process when a mixture of blending component I and asphaltic bitumen A having the desired ratio r is used as the feed. The space velocity to be used for the purpose is determined on the basis of a number of catalytic hydrotreatment scouting experiments using the mixture of blending component I and asphaltic bitumen A as the feed. Using this space velocity in the combination process an oil is prepared which has the desired RCT of a %w and the desired initial boiling point of $T_1^{\circ}\text{C}$, and an asphaltic bitumen (asphaltic bitumen B) is obtained as a by-product. These experiments are repeated optionally once or several times, in each case using the asphaltic bitumen separated from a preceding series of experiments as the mixing component for blending component I (at constant values of r) in a following series of experiments, until the moment has come when two successive series of experiments yield separated asphaltic bitumens having virtually equal RCT's. Thus the space velocity is determined which is required for the application in actual practice of the process according to the invention with recirculation of asphaltic bitumen. Generally, two or three

series of experiments are sufficient to produce the stationary state.

The invention is now illustrated with the aid of the following examples.

5 EXAMPLE 1

In the investigation two atmospheric residues were used which had been obtained in the distillation of crude mineral oils (Atmospheric residues A and B).

10 Atmospheric residue A had an RCT of 10 %w (determined by ASTM method D 524), a vanadium + nickel content of 70 ppmw and a percentage boiling below 520°C of 50 %w.

Atmospheric residue B had an RCT of 15.6 %w (determined by ASTM method D 524), a vanadium + nickel content of 500 ppmw and a percentage boiling below 520°C of 29.4 %w.

15 As regards the question whether it is possible, in view of the maximum permissible value of G, starting from atmospheric residue A, to prepare by nothing but catalytic hydrotreatment a product from which, by distillation, an atmospheric residue can be obtained which has an initial boiling point of 370°C and an
20 RCT lower than that of atmospheric residue A, application of relation 1 in the form

$$\frac{b-c}{b} \times 100 = F_{\max}$$

(where $F_{\max}$ is the maximum value of the right-hand member of the relation), with substitution of $b=10$, $T=370$ and $d=50$, shows that this is quite feasible provided that the atmospheric residue
25 with an initial boiling point of 370°C to be prepared has an RCT (c) higher than 3.6 %w. This means, for instance, that, starting from atmospheric residue A, for the preparation of an atmospheric residue having an initial boiling point of 370°C and an RCT (c) of 4.5 %w a catalytic hydrotreatment alone will be
30 sufficient.

If, however, from atmospheric residue A an oil is to be prepared having an initial boiling point of 370°C and a much

more reduced RCT of 1.5 %w a catalytic hydrotreatment alone is not sufficient in view of the maximum permissible value of G. Then, in addition to the catalytic hydrotreatment, a solvent deasphalting treatment should be applied. Application of

5 relation 1, in the form:

maximum RCT reduction = $F_{\max}$, and

minimum RCT reduction = $F_{\min}$

(where $F_{\max}$ and $F_{\min}$ are the maximum and the minimum value, respectively, of the right-hand member of the relation), with

10 substitution of $b=10$, $T=370$ and $d=50$, shows that for optimum utilization of the combination process care should be taken that the RCT reduction in the catalytic hydrotreatment is between 54.1 and 64.1%.

With the object of preparing atmospheric residues having an
15 initial boiling point of 370°C and different RCT's (c), atmospheric residue A was subjected to catalytic hydrotreatment in thirteen experiments. The experiments were carried out in a 1000 ml reactor containing two fixed catalyst beds of a total volume of 600 ml. The first catalyst bed consisted of a
20 Ni/V/SiO₂ catalyst containing 0.5 pbw of nickel and 2.0 pbw of vanadium per 100 pbw of silica. The second catalyst bed consisted of a Co/Mo/Al₂O₃ catalyst containing 4 pbw of cobalt and 12 pbw of molybdenum per 100 pbw of alumina. The weight ratio between the Ni/V/SiO₂ and Co/Mo/Al₂O₃ catalysts was 1:3. All the experi-
25 ments were carried out at a temperature of 390°C, a pressure of 125 bar and a H₂/oil ratio of 1000 Nl/kg. Various space velocities were used in the experiments. The results of Experiments 1-13 at run hour 450 are listed in Table A.

For each experiment the table gives the space velocity
30 used, the RCT reduction $\frac{(b-c)}{b} \times 100$ achieved and the corre-

sponding C₄⁻ production (calculated as %w on feed).

Experiments 1-12 were carried out in pairs, the difference in space velocity between the two experiments of each pair being such as to achieve a difference in RCT reduction

of about 1.0%. The table further gives the C_4^- production per % RCT reduction (G) for each pair of experiments.

TABLE A

Experiment No.	Space velocity, $\text{g.g}^{-1}.\text{h}^{-1}$	RCT reduction, %	C_4^- production, %w on feed	G, %w
1	1.50	31.9	0.481	0.015
2	1.40	32.9	0.496	
3	2.42	20.0	0.300	0.015
4	2.31	21.3	0.319	
5	1.07	40.2	0.603	0.016
6	1.03	41.1	0.617	
7	0.61	53.5	0.901	0.023
8	0.57	54.7	0.929	
9	0.40	63.4	1.164	0.030
10	0.37	64.6	1.200	
11	0.30	70.0	1.432	0.057
12	0.27	71.1	1.495	
13	0.50	59.0	1.030	

Only Experiments 8, 9 and 13 are experiments according to the invention. The other experiments have been included for reasons of comparison. As can be seen in Table A, in Experiments 1-2, 3-4 and 5-6, G remains virtually constant (G_c). In Experiments 7-8 and 9-10, in which RCT reductions were achieved of about 54 and 64%, respectively, G was about $1.5 G_c$ and $2.0 G_c$, respectively.

The products obtained in the catalytic hydrotreatment carried out according to Experiments 5, 11 and 13 were separated by successive atmospheric distillation and vacuum distillation into a C_4^- fraction, a $H_2S + NH_3$ fraction, a $C_5-370^\circ C$ atmospheric distillate, a $370-520^\circ C$ vacuum distillate and a $520^\circ C^+$ vacuum residue. The vacuum residues were deasphalted with n-butane at a pressure of 40 bar and a solvent/oil weight ratio of 3:1, and the deasphalted vacuum residues obtained were mixed with the corresponding vacuum distillates. The results (of which only Experiment 16 is an experiment according to the invention) are listed in Table B.

TABLE B

Experiment No.	14	15	16
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H₂-treated product from

Experiment No.	5	11	13
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Distillation

Yield of products calculated

on 100 pbw feed, pbw

C ₄ ⁻	0.60	1.43	1.03
H ₂ S + NH ₃	2.9	3.4	3.2
C ₅ - 370°C	8.2	11.7	10.5
370-520°C (vacuum distillate)	56.3	58.0	58.1
520°C ⁺ (vacuum residue)	33.3	27.7	28.9
RCT of the vacuum distillate, %w	0.4	0.3	0.3
RCT of the vacuum residue, %w	15.4	8.8	13.6

Deasphalting

Temperature, °C	130	129	133
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Yield of deasphalted vacuum

residue, pbw	21.6	22.1	21.8
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Yield of asphaltic bitumen, pbw	11.7	5.6	7.1
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RCT of the deasphalted vacuum

residue, %w	4.4	4.6	4.8
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Mixing

Yield of mixture of vacuum

distillate and deasphalted

vacuum residue, pbw	77.9	80.1	79.9
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Initial boiling point of the

mixture, °C	370	370	370
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RCT of the mixture, %w	1.5	1.5	1.5
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Application of relation 1, in the form:

$$\frac{b-c}{b} \times 100 = F_{\max}$$

with substitution of $b=15.6$, $T=370$ and $d=29.4$, shows that this is quite feasible to prepare an atmospheric residue with an initial boiling point of 370°C and an RCT lower than that of atmospheric residue B by catalytic hydrotreatment and distillation of the product so obtained, provided that the atmospheric residue to be prepared has an RCT (c) higher than 4.7 %w.

If from atmospheric residue B however an oil is to be prepared which has an initial boiling point of 370°C and a much more reduced RCT of 2.5 %w, a catalytic hydrotreatment alone is insufficient in view of the maximum permissible value of G. Then, in addition to the catalytic hydrotreatment a solvent deasphalting step should be applied. Application of relation 1, in the form:

$$\begin{aligned} \text{maximum RCT reduction} &= F_{\max}, \text{ and} \\ \text{minimum RCT reduction} &= F_{\min} \end{aligned}$$

with substitution of $b=15.6$, $T=370$ and $d=29.4$, shows that for optimum utilization of the combination process care should be taken that the reduction in the catalytic hydrotreatment is between 60.0 and 70.0%.

With the object of preparing an oil having an initial boiling point of 370°C and an RCT of 2.5 %w from atmospheric residue B this atmospheric residue B was subjected to a catalytic hydrotreatment in a similar way as described for Experiments 1-13, using the same catalysts. The reaction conditions were slightly different, viz. a temperature of 395°C , a pressure of 150 bar, a space velocity of $1.05 \text{ g.g}^{-1}.\text{h}^{-1}$ and a H_2/oil ratio of 1000 Nl/kg. The RCT reduction was 65%. The product of the catalytic hydrotreatment was separated likewise as described hereinbefore by consecutive atmospheric distillation and vacuum distillation into several fractions. The 520°C^+ vacuum residue was deasphalted with n-butane at a temperature of 115°C , a pressure of 40 bar and a solvent/oil weight ratio of 3:1, and

the deasphalted vacuum residue obtained was mixed with the vacuum distillate. The results of this experiment No. 17 according to the invention are given hereinafter.

Experiment No. 17

Distillation

Yield of products calculated on 100 pbw feed, pbw

C ₄ -	0.98
H ₂ S + NH ₃	1.5
C ₅ - 370°C	14.2
370-520°C (vacuum distillate)	48.3
520°C ⁺ (vacuum residue)	32.6

RCT of the vacuum distillate, %w	0.5
RCT of the vacuum residue, %w	12.9

Deasphalting

Yield of deasphalted vacuum

residue, pbw 26.8

Yield of asphaltic bitumen, pbw 5.8

RCT of the deasphalted vacuum

residue, %w 6.1

Mixing

Yield of mixture of vacuum

distillate and deasphalted

vacuum residue, pbw 75.1

Initial boiling point of the

mixture, °C 370

RCT of the mixture, %w 2.5

EXAMPLE 2

In the example two different vacuum residues were used:

(i) Vacuum residue A with an RCT of 19 %w (determined by ASTM

method D 524), a vanadium + nickel content of 160 ppmw and a 5 %w boiling point of 500°C, and

- (ii) Vacuum residue B with an RCT of 11 %w (determined by ASTM method D 524), a vanadium + nickel content of 20 ppmw and a 5 %w boiling point of 520°C.

From vacuum residue A an oil having an initial boiling point of 370°C and an RCT of 2.5 %w cannot be prepared by catalytic hydrotreatment alone in view of the maximum permissible value of G. Then, in addition to the catalytic hydrotreatment, a solvent deasphalting treatment should be applied.

Application of relation 2 in the form:

maximum RCT reduction = $F_{\max}$, and

minimum RCT reduction = $F_{\min}$

- 15 (where $F_{\max}$ and $F_{\min}$ are the maximum and the minimum value, respectively, of the right-hand member of the relation), with substitution of $b=19$, $T_1=370$ and $T_5=500$, shows that for optimum utilization of the combination process care should be taken that the RCT reduction in the catalytic hydrotreatment is between 20 52.0 and 62.0%.

With the object of preparing atmospheric residues having an initial boiling point of 370°C and different RCT's (c), vacuum residue A was subjected to catalytic hydrotreatment in thirteen experiments in a similar way as described for Experiments 1-13, 25 using the same catalysts in the weight ratio indicated. The reaction conditions were: a temperature of 385°C, a pressure of 150 bar and a H_2 /oil ratio of 1000 Nl/kg. Various space velocities were used in the experiments. The results of Experiments 18-30 at run hour 500 are listed in Table C.

TABLE C

Experiment No.	Space velocity, $\text{g} \cdot \text{g}^{-1} \cdot \text{h}^{-1}$	RCT reduction, %	C_4 production, %w on feed	G, %w
18	0.91	30.5	0.801	0.027
19	0.87	31.5	0.828	
20	1.36	20.0	0.525	0.027
21	1.30	21.2	0.557	
22	0.60	39.9	1.061	0.028
23	0.58	41.1	1.095	
24	0.38	51.5	1.466	0.040
25	0.36	52.4	1.502	
26	0.26	61.8	1.983	0.054
27	0.24	62.5	2.021	
28	0.17	70.0	3.015	0.113
29	0.15	71.1	3.139	
30	0.30	57.0	1.700	

Only Experiments 25, 26 and 30 are experiments according to the invention. The other experiments have been included for reasons of comparison. As can be seen in Table C in Experiments 18-19, 20-21 and 22-23, G remains virtually constant (G_c). In 5. Experiments 24-25 and 26-27, in which RCT reductions were achieved of about 52 and 62%, respectively, G was about $1.5 G_c$ and $2.0 G_c$, respectively.

The products obtained in the catalytic hydrotreatment carried out according to Experiments 22, 28 and 30 were 10 separated by consecutive atmospheric distillation and vacuum distillation into several fractions as described hereinbefore. The vacuum residues were deasphalted with n-butane and the deasphalted vacuum residues so obtained were mixed with the corresponding vacuum distillates. The results of these 15 experiments of which only Experiment 33 is an experiment according to the invention, are listed in Table D.

TABLE D

Experiment No.	31	32	33
H ₂ -treated product from Experiment No.	22	28	30
<u>Distillation</u>			
Yield of products calculated on 100 pbw feed, pbw			
C ₄ ⁻	1.06	3.02	1.70
H ₂ S + NH ₃	3.8	5.1	4.5
C ₅ - 370°C	5.8	10.0	8.3
370-520°C (vacuum distillate)	23.5	39.0	34.0
520°C ⁺ (vacuum residue)	67.1	45.2	53.0
RCT of the vacuum distillate, %w	0.4	0.4	0.4
RCT of the vacuum residue, %w	15.2	10.3	13.2
<u>Deasphalting</u>			
Temperature, °C	137	125	133
Yield of deasphalted vacuum residue, pbw			
	41.0	36.2	38.0
Yield of asphaltic bitumen, pbw			
	26.1	9.0	15.0
RCT of the deasphalted vacuum residue, %w			
	3.7	4.8	4.4
<u>Mixing</u>			
Yield of mixture of vacuum distillate and deasphalted vacuum residue, pbw			
	64.5	75.2	72.0
Initial boiling point of the mixture, °C			
	370	370	370
RCT of the mixture, %w			
	2.5	2.5	2.5

A catalytic hydrotreatment alone is insufficient to prepare from vacuum residue B an oil with an initial boiling point of 370°C and an RCT of 3 %w in view of the maximum permissible value of G. In addition to the catalytic hydro-
5 treatment a solvent deasphalting step has to be applied.

Application of relation 2, in the form:

maximum RCT reduction = $F_{\max}$, and

minimum RCT reduction = $F_{\min}$

shows that for optimum utilization of the combination process
10 care should be taken that the reduction in the catalytic hydro-
treatment is between 30.6 and 40.6%.

Vacuum residue B was subjected to a catalytic hydro-
treatment to prepare an oil having an initial boiling point of
370°C and an RCT of 3.0 %w from it. The experiment No. 34 was
15 carried out in a 1000 ml reactor containing a fixed catalyst bed
of 600 ml volume of the same Co/Mo/Al₂O₃ catalyst as used in
Example 1. Reaction conditions were: a temperature of 390°C, a
pressure of 125 bar, a space velocity of 1.0 g.g⁻¹.h⁻¹ and a
H₂/oil ratio of 1000 Nl/kg. The RCT reduction was 35.5%. The
20 520°C⁺ vacuum residue obtained after vacuum distillation of the
product of the catalytic hydrotreatment was deasphalted with
n-butane at a temperature of 127°C, a pressure of 40 bar and a
solvent/oil weight ratio of 3:1, and the deasphalted vacuum
residue obtained was mixed with the 370°-520°C vacuum
25 distillate. The results of this experiment according to the
invention are given hereinafter.

Experiment No. 34-

Distillation

Yield of products calculated
on 100 pbw feed, pbw

C_4^-	1.4
$H_2S + NH_3$	1.0
$C_5 - 370^\circ C$	3.5
370-520°C (vacuum distillate)	20.6
520°C ⁺ (vacuum residue)	71.2
RCT of the vacuum distillate, %w	0.3
RCT of the vacuum residue, %w	9.1

Deasphalting

Yield of deasphalted vacuum residue, pbw	56.0
Yield of asphaltic bitumen, pbw	15.2
RCT of the deasphalted vacuum residue, %w	4.0

Mixing

Yield of mixture of vacuum distillate and deasphalted vacuum residue, pbw	76.6
Initial boiling point of the mixture, °C	370
RCT of the mixture, %w	3.0

EXAMPLE 3

In the following experiments two asphaltic bitumens were used.

Asphaltic bitumen A had been obtained through deasphalting
5 with propane of a vacuum residue from a crude mineral oil. It
had an RCT of 25.4 %w (computed from the CCT determined by ASTM
method D 189), an average molecular weight of 1400 (determined

by ASTM method D 3592/77, using toluene as the solvent) and a vanadium + nickel content of 250 ppmw.

Asphaltic bitumen B had been obtained by deasphalting with n-butane of a vacuum residue from a crude mineral oil. It had an
5 RCT of 48.0 %w (computed from the CCT determined by ASTM method D 189), an average molecular weight of 2000 (determined by ASTM method D 8592/77, using toluene as the solvent) and a vanadium + nickel content of 420 ppmw.

Catalytic hydrotreatment alone is not sufficient to prepare
10 from asphaltic bitumen A an oil having an initial boiling point of 370°C and an RCT of 3.0 %w in view of the maximum permissible value of G. Then, in addition to the catalytic hydrotreatment, a solvent deasphalting treatment should be applied. Application of relation 3, in the form:

15 maximum RCT reduction = $F_{\max}$, and
 minimum RCT reduction = $F_{\min}$

shows that for optimum utilization of the combination process care should be taken that the RCT reduction in the catalytic hydrotreatment is between 51.0 and 61.4%.

20 Asphaltic bitumen A was subjected to catalytic hydro-treatment in thirteen experiments to prepare atmospheric residues having an initial boiling point of 370°C and different RCT's (c). The experiments were similar to those described for Experiments 1-13, the weight ratio between the Ni/V/SiO₂ and
25 Co/Mo/Al₂O₃ catalysts however being 1:2. The reaction conditions were: a temperature of 400°C, a pressure of 145 bar and a H₂/oil ratio of 1000 NI/kg, and varying space velocities. The results of Experiments 35-46 at run hour 450 are listed in Table E.

TABLE E

Experiment No.	Space velocity, $\text{g.g}^{-1}.\text{h}^{-1}$	RCT reduction, %	C_4 production, %w on feed	G, %w
35	0.61	30.2	1.054	0.030
36	0.58	31.3	1.087	
37	0.91	19.8	0.689	0.030
38	0.88	20.7	0.716	
39	0.40	39.8	1.390	0.032
40	0.38	41.0	1.428	
41	0.27	50.8	1.880	0.044
42	0.25	51.7	1.920	
43	0.18	60.6	2.528	0.060
44	0.17	61.8	2.600	
45	0.11	70.5	3.996	0.212
46	0.10	71.5	4.208	
47	0.22	56.0	2.220	

Only Experiments 42, 43 and 47 are experiments according to the invention. The other experiments have been included for reasons of comparison. As can be seen in Table E in Experiments 35-36, 37-38 and 39-40, G remains virtually constant (G_c). In
5 Experiments 41-42 and 43-44, in which RCT reductions were achieved of about 51 and 61%, respectively, G was about 1.5 G_c and 2.0 G_c , respectively.

The products obtained in the catalytic hydrotreatment carried out according to Experiments 39, 45 and 47 were
10 separated by consecutive atmospheric distillation and vacuum distillation into separate fractions. The 520°C⁺ vacuum residues were deasphalted with n-butane and the deasphalted vacuum residues obtained were mixed with the corresponding 370-520°C vacuum distillates. The results are listed in Table F,
15 Experiment 50 being according to the invention.

TABLE F

Experiment No.	48	49	50
H ₂ -treated product from Experiment No.	39	45	47
<u>Distillation</u>			
Yield of products calculated on 100 pbw feed, pbw			
C ₄ ⁻	1.39	4.00	2.22
H ₂ S + NH ₃	3.0	4.0	3.4
C ₅ - 370°C	13.9	19.4	17.0
370-520°C (vacuum distillate)	13.2	22.0	18.4
520°C ⁺ (vacuum residue)	70.0	53.1	61.0
RCT of the vacuum distillate, %w	0.5	0.3	0.4
RCT of the vacuum residue, %w	18.1	10.5	14.5
<u>Deasphalting</u>			
Temperature, °C	132	130	132
Yield of deasphalted vacuum residue, pbw			
	39.8	41.9	41.5
Yield of asphaltic bitumen, pbw			
	30.2	11.2	18.5
RCT of the deasphalted vacuum residue, %w			
	3.8	4.4	4.2
<u>Mixing</u>			
Yield of mixture of vacuum distillate and deasphalted vacuum residue, pbw			
	53.0	63.9	59.9
Initial boiling point of the mixture, °C			
	370	370	370
RCT of the mixture, %w			
	3.0	3.0	3.0

A catalytic hydrotreatment alone is insufficient to prepare from asphaltic bitumen B an oil having an initial boiling point of 370°C and an RCT of 4 %w in view of the maximum permissible value of G. In addition to the catalytic hydrotreatment a solvent deasphalting step should be applied. Application of relation 3, in the form:

maximum RCT reduction = $F_{\max}$, and

minimum RCT reduction = $F_{\min}$

shows that for optimum utilization of the combination process care should be taken that the reduction in the catalytic hydrotreatment is between 56.1 and 66.5%.

Asphaltic bitumen B was subjected to a catalytic hydrotreatment to prepare an oil having an initial boiling point of 370°C and an RCT of 4.0 %w from it. The experiment was similar to those described for Experiments 1-13, the weight ratio between the Ni/V/SiO₂ and Co/Mo/Al₂O₃ catalysts however being 1:1. Reaction conditions were: a temperature of 390°C, a pressure of 150 bar, a space velocity of 0.41 g.g⁻¹.h⁻¹ and a H₂/oil ratio of 1000 Nl/kg. The RCT reduction was 61.0%. The 520°C⁺ vacuum residue obtained after vacuum distillation of the product of the catalytic hydrotreatment was deasphalted with n-butane at a temperature of 120°C, a pressure of 40 bar and a solvent/oil weight ratio of 3:1, and the deasphalted vacuum residue obtained was mixed with the 370°-520°C vacuum distillate. The results of this experiment according to the invention are given hereinafter.

Experiment No. 51

Distillation

Yield of products calculated on 100 pbw feed, pbw

C_4^-	3.7
$H_2S + NH_3$	6.1
$C_5 - 370^\circ C$	19.9
370-520°C (vacuum distillate)	17.0
520°C ⁺ (vacuum residue)	55.6
RCT of the vacuum distillate, %w	0.6
RCT of the vacuum residue, %w	24.2

Deasphalting

Yield of deasphalted vacuum

residue, pbw	33.9
Yield of asphaltic bitumen, pbw	21.7
RCT of the deasphalted vacuum residue, %w	5.7

Mixing

Yield of mixture of vacuum

distillate and deasphalted

vacuum residue, pbw	50.9
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Initial boiling point of the

mixture, °C	370
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RCT of the mixture, %w	4.0
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EXAMPLE 4

In this experiment a mixture AB was used which had been obtained by mixing 100 pbw of an atmospheric residue A and 15 pbw of an asphaltic bitumen B. Atmospheric residue A had an RCT of 9.8 %w (determined by ASTM method D 524), and a vanadium + nickel content of 95 ppmw and boiled below 520°C to an extent of 50 %w. Asphaltic bitumen B had an RCT of 35 %w (calculated from

the CCT determined by ASTM method D 189) and a vanadium + nickel content of 110 ppmw. Asphaltic bitumen B was obtained by solvent deasphalting with n-butane of a vacuum residue obtained in the distillation of a hydrotreated mineral oil vacuum residue.

5 A catalytic hydrotreatment alone is not sufficient to prepare from mixture AB an oil having an initial boiling point of 370°C and an RCT of 1.5 %w in view of the maximum permissible value of G. Then, in addition to the catalytic hydrotreatment, a solvent deasphalting treatment should be applied. Application of
10 relation 4, in the form:

 maximum RCT reduction = $F_{\max}$, and

 minimum RCT reduction = $F_{\min}$

with substitution of $b=9.8$, $c=35$, $r=15$, $T_1=370$ and $f=50$, shows that for optimum utilization of the combination process care
15 should be taken that the RCT reduction in the catalytic hydro-treatment is between 34.6 and 46.2%.

 A mixture AB was subjected to catalytic hydrotreatment in eleven experiments to prepare atmospheric residues having an initial boiling point of 370°C and different RCT's (e). The
20 experiments were similar to those described for Experiments 18-30, the weight ratio between the $Ni/V/SiO_2$ and $Co/Mo/Al_2O_3$ catalysts however being 1:2.5. The reaction conditions were: a temperature of 385°C, a pressure of 150 bar and a H_2 /oil ratio of 1000 Nl/kg, with varying space velocities. The results of
25 Experiments 52-62 at run hour 425 are listed in Table G.

TABLE G

Experiment No.	Space velocity, $\text{g.g}^{-1}.\text{h}^{-1}$	RCT reduction,* %	C_4 production, %w on feed	G, %w
52	5.31	10.1	0.217	0.021
53	4.84	11.0	0.236	
54	2.09	22.3	0.475	0.022
55	2.02	23.1	0.493	
56	1.19	34.2	0.838	0.032
57	1.13	35.4	0.876	
58	0.68	46.1	1.280	0.042
59	0.65	47.0	1.318	
60	0.41	60.3	2.057	0.086
61	0.40	61.8	2.168	
62	0.86	40.5	1.030	

* RCT reduction = $\frac{d-e}{d} \times 100\%$

Only Experiments 57, 58 and 62 are experiments according to the invention. The other experiments have been included for reasons of comparison. As can be seen in Table G in Experiments 52-53 and 54-55, G remains virtually constant (G_c). In Experiments 56-57 and 58-59, in which RCT reductions were achieved of about 35 and 47%, respectively, G was about $1.5 \times G_c$ and $2.0 \times G_c$, respectively.

The products obtained in the catalytic hydrotreatment carried out according to Experiments 54, 60 and 62 were separated by consecutive atmospheric distillation and vacuum distillation into separate fractions and the 520°C^+ vacuum residues were deasphalted with n-butane under standard conditions. The results (of which only Experiment 65 is an experiment according to the invention) are listed in Table H.

TABLE H

Experiment No.	63	64	65
H ₂ -treated product from Experiment No.	54	60	62

Distillation

Yield of products calculated
on 100 pbw feed, pbw

C ₄ ⁻	0.5	2.1	1.0
H ₂ S + NH ₃	1.6	3.1	2.8
C ₅ - 370°C	9.5	14.0	12.3
370-520°C (vacuum distillate)	43.7	50.1	48.8
520°C ⁺ (vacuum residue)	45.2	32.0	36.1
RCT of the vacuum distillate, %w	0.4	0.3	0.3
RCT of the vacuum residue, %w	19.7	12.9	17.9

Deasphalting

Temperature, °C	135	132	133
Yield of deasphalted vacuum residue, pbw	22.0	22.4	21.8
Yield of asphaltic bitumen, pbw	23.2	9.6	14.3
RCT of the deasphalted vacuum residue, %w	3.7	4.2	4.2

Mixing

Yield of mixture of vacuum distillate and deasphalted vacuum residue, pbw	65.7	72.5	70.6
Initial boiling point of the mixture, °C	370	370	370
RCT of the mixture, %w	1.5	1.5	1.5

Three further experiments (Experiments 66-68) were carried out to prepare an oil having an initial boiling point of 370°C

and an RCT of 1.5 %w. In the experiments three different residual feedstocks were subjected to a catalytic hydrotreatment in the same reactor as described for Experiments 1-13 and applying the same reaction conditions and catalysts at the 5 weight ratio indicated there. The products from the catalytic hydrotreatment were further treated as described for Experiments 14, 15 and 16.

Experiment 66

The feed used in this experiment was atmospheric residue C. 10 Atmospheric residue C obtained in the distillation of a crude mineral oil, had an RCT of 10 %w (determined by ASTM method D 524) and a vanadium + nickel content of 70 ppmw, and boiled below 520°C to an extent of 50 %w. Application of relation 4, in the form:

15 maximum RCT reduction = $F_{\max}$, and
 minimum RCT reduction = $F_{\min}$

shows that for optimum utilization of the combination process care should be taken that the RCT reduction in the catalytic hydrotreatment is between 54.1 and 64.1%. In the catalytic 20 hydrotreatment of Experiment 66 the space velocity applied was $0.50 \text{ g.g}^{-1}.\text{h}^{-1}$ and the RCT reduction achieved was 59%. In the solvent deasphalting of Experiment 66 an asphaltic bitumen D was separated which had an RCT of 41 %w.

Experiment 67

25 The feed used in this experiment was a mixture CD obtained by mixing 100 pbw of atmospheric residue C with 12 pbw of asphaltic bitumen D obtained in the above Experiment 66.

Application of relation 4 in the form:

 maximum RCT reduction = $F_{\max}$, and
30 minimum RCT reduction = $F_{\min}$

shows that for optimum utilization of the combination process care should be taken that the RCT reduction in the catalytic hydrotreatment is between 36.5 and 47.7%. In the catalytic hydrotreatment of Experiment 67 the space velocity used was 35 $0.43 \text{ g.g}^{-1}.\text{h}^{-1}$ and the RCT reduction achieved was 42.1%. In the

solvent deasphalting an asphaltic bitumen E was separated which had an RCT of 39 %w.

Experiment 68

5 The feed used in this experiment was a mixture CE obtained by mixing 100 pbw of atmospheric residue C with 12 pbw of asphaltic bitumen E obtained in the above Experiment 67.

Application of relation 4 in the form:

maximum RCT reduction = $F_{\max}$, and

minimum RCT reduction = $F_{\min}$

10 shows that for optimum utilization of the combination process care should be taken that the RCT reduction in the catalytic hydrotreatment is between 37.1 and 48.3%. In the catalytic hydrotreatment of Experiment 68 the space velocity used was $0.43 \text{ g.g}^{-1}.\text{h}^{-1}$ and the RCT reduction achieved was 42.7%. In the
15 solvent deasphalting an asphaltic bitumen F was separated which had an RCT of 39 %w. Since the RCT of asphaltic bitumen F is equal to that of asphaltic bitumen E, this is the moment when in recycling the asphaltic bitumen the process has reached its stationary state. The results of Experiments 66-68 are listed in
20 Table I.

TABLE I

Experiment No.	66	67	68
<u>Distillation</u>			
Yield of products calculated on 100 pbw feed, pbw			
C ₄ ⁻	1.03	0.92	0.93
H ₂ S + NH ₃	3.2	3.0	3.0
C ₅ - 370°C	10.5	9.8	9.9
370-520°C (vacuum distillate)	58.1	51.9	52.0
520°C ⁺ (vacuum residue)	28.9	36.1	35.9
RCT of the vacuum distillate, %w	0.3	0.3	0.3
RCT of the vacuum residue, %w	13.6	18.3	17.9
<u>Deasphalting</u>			
Temperature, °C	133	135	136
Yield of deasphalted vacuum residue, pbw	21.8	21.6	21.8
Yield of asphaltic bitumen, pbw	7.1	14.5	14.1
RCT of the deasphalted vacuum residue, %w	4.8	4.4	4.3
RCT of the asphaltic bitumen, %w	41	39	39
<u>Mixing</u>			
Yield of mixture of vacuum distillate and deasphalted vacuum residue, pbw	79.9	73.5	73.8
Initial boiling point of the mixture, °C	370	370	370
RCT of the mixture, %w	1.5	1.5	1.5

EXAMPLE 5

A heavy mixture AB was used which had been obtained by mixing 100 pbw of a vacuum residue A and 30 pbw of an asphaltic

57

bitumen B. Vacuum residue A had an RCT of 19 %w (determined by ASTM method D 524), a vanadium + nickel content of 180 ppmw and a 5% boiling point of 520°C. Asphaltic bitumen B had an RCT of 35 %w (calculated from the CCT determined by ASTM method D 189) and a vanadium + nickel content of 110 ppmw. It was obtained by solvent deasphalting with n-butane of a vacuum residue obtained in the distillation of a hydrotreated mineral oil vacuum residue.

A catalytic hydrotreatment alone is not sufficient to prepare from mixture AB an oil having an initial boiling point of 370°C and an RCT of 2.5 %w in view of the maximum permissible value of G. In addition to the catalytic hydrotreatment, a solvent deasphalting treatment should be applied. Application of relation 5, in the form:

15 maximum RCT reduction = $F_{\max}$, and
 minimum RCT reduction = $F_{\min}$

shows that for optimum utilization of the combination process care should be taken that the RCT reduction in the catalytic hydrotreatment is between 34.0 and 47.0 %w.

20 The mixture AB was subjected to catalytic hydrotreatment in eleven experiments to prepare atmospheric residues having an initial boiling point of 370°C and different RCT's (e). The experiments were similar to those described for Experiments 1-13, the weight ratio between the Ni/V/SiO_2 and $\text{Co/Mo/Al}_2\text{O}_3$ catalysts however being 1:2. The reaction conditions were: a temperature of 380°C, a pressure of 170 bar and a H_2 /oil ratio of 1000 Nl/kg, varying space velocities being used. The results of Experiments 69-79 at run hour 400 are listed in Table J.

For each experiment the table gives the space velocity used, the RCT reduction ($\frac{d-e}{d} \times 100$) achieved and the

corresponding C_4^- production (calculated as %w on feed). Experiments 69-78 were carried out in pairs, the difference in space velocity between the two experiments of each pair being such as to achieve a difference in RCT reduction of about 1.0%.

The table further gives the C_4^- production per % RCT reduction (G) for each pair of experiments.

TABLE J

Experiment No.	Space velocity, $\text{g.g}^{-1}.\text{h}^{-1}$	RCT reduction,* %	C_4^- production, %w on feed	G, %w
69	2.95	10.2	0.380	0.037
70	2.69	11.1	0.413	
71	1.16	22.4	0.832	0.038
72	1.12	23.2	0.860	
73	0.66	33.5	1.410	0.056
74	0.63	34.3	1.454	
75	0.38	46.8	2.240	0.074
76	0.36	47.7	2.306	
77	0.23	58.5	3.370	0.125
78	0.22	59.3	3.470	
79	0.48	40.8	1.800	

$$* \text{ RCT reduction} = \frac{d-e}{d} \times 100\%$$

Only Experiments 74, 75 and 79 are experiments according to the invention. The other experiments have been included for reasons of comparison. As can be seen in Table J in Experiments 69-70 and 71-72, G remains virtually constant (G_c). In Experiments 73-74 and 75-76, in which RCT reductions were achieved of about 34 and 47%, respectively, G was about $1.5 \times G_c$ and $2.0 \times G_c$, respectively.

The products obtained in the catalytic hydrotreatment according to Experiments 71, 77 and 79 were further treated as hereinbefore described for Experiments 14, 15 and 16. The results (of which only Experiment 82 is an experiment according to the invention) are listed in Table K.

TABLE K

Experiment No.	80	81	82
H ₂ -treated product from Experiment No.	71	77	79

Distillation

Yield of products calculated
on 100 pbw feed, pbw

C ₄ ⁻	0.8	3.4	1.8
H ₂ S + NH ₃	2.2	4.1	3.5
C ₅ - 370°C	8.0	12.8	11.0
370-520°C (vacuum distillate)	22.9	32.0	29.4
520°C ⁺ (vacuum residue)	67.2	49.9	55.8
RCT of the vacuum distillate, %w	0.4	0.3	0.3
RCT of the vacuum residue, %w	23.5	15.2	20.3

Deasphalting

Temperature, °C	134	130	131
Yield of deasphalted vacuum residue, pbw	30.4	33.9	32.4
Yield of asphaltic bitumen, pbw	36.8	16.0	23.4
RCT of the deasphalted vacuum residue, %w	4.1	4.6	4.5

Mixing

Yield of mixture of vacuum distillate and deasphalted vacuum residue, pbw	53.3	65.9	61.8
Initial boiling point of the mixture, °C	370	370	370
RCT of the mixture, %w	2.5	2.5	2.5

EXAMPLE 6

Three experiments (Experiments 83-85) were carried out with the object of preparing an oil having an initial boiling point of 370°C and an RCT of 2.5 %w and to investigate the feasibility of recycle of the asphaltic bitumen produced to the catalytic hydrotreatment. In the experiments three different residual feedstocks were subjected to a catalytic hydrotreatment in the same reactor and applying the same reaction conditions as described for Experiments 18-30. The products from the catalytic hydrotreatment were further treated as described for Experiments 14, 15 and 16.

Experiment 83

The feed used in this experiment was the vacuum residue A of Example 5. Application of relation 5 shows that for optimum utilization of the combination process care should be taken that the RCT reduction in the catalytic hydrotreatment is between 52 and 62%. In the catalytic hydrotreatment of Experiment 83 the space velocity applied was $0.30 \text{ g.g}^{-1}.\text{h}^{-1}$ and the RCT reduction achieved was 57%. In the solvent deasphalting of Experiment 83 an asphaltic bitumen C was separated which had an RCT of 36 %w.

Experiment 84

The feed used in this experiment was a mixture AC obtained by mixing 100 pbw of vacuum residue A with 20 pbw of asphaltic bitumen C obtained in the above Experiment 83. Application of relation 5 shows that for optimum utilization of the combination process care should be taken that the RCT reduction in the catalytic hydrotreatment is between 38.4 and 50.4%. In the catalytic hydrotreatment of Experiment 84 the space velocity applied was $0.29 \text{ g.g}^{-1}.\text{h}^{-1}$ and the RCT reduction achieved was 45%. In the solvent deasphalting an asphaltic bitumen D was separated which had an RCT of 39 %w.

Experiment 85

The feed used in this experiment was a mixture AD obtained by mixing 100 pbw of vacuum residue A with 20 pbw of asphaltic bitumen D obtained in the above Experiment 84. Application of

relation 5 shows that for optimum utilization of the combination process care should be taken that the RCT reduction in the catalytic hydrotreatment is between 37.8 and 49.8%. In the catalytic hydrotreatment of Experiment 85 the space velocity 5 applied was $0.28 \text{ g.g}^{-1}.\text{h}^{-1}$ and the RCT reduction achieved was 44%. In the solvent deasphalting an asphaltic bitumen E was separated which had an RCT of 39 %w. Since the RCT of asphaltic bitumen E is equal to that of asphaltic bitumen D, this is the moment when in recycling the asphaltic bitumen the process has 10 reached its stationary state. The results of Experiments 83-85 are listed in Table L.

TABLE L

Experiment No.	83	84	85
<u>Distillation</u>			
Yield of products calculated on 100 pbw feed, pbw			
C ₄ ⁻	1.70	1.56	1.58
H ₂ S + NH ₃	4.5	3.9	3.9
C ₅ - 370°C	8.3	7.4	7.2
370-520°C (vacuum distillate)	34.0	30.1	29.9
520°C ⁺ (vacuum residue)	53.0	58.5	58.7
RCT of the vacuum distillate, %w	0.4	0.4	0.4
RCT of the vacuum residue, %w	13.2	18.0	18.7
<u>Deasphalting</u>			
Temperature, °C	133	133	132
Yield of deasphalted vacuum residue, pbw	38.0	35.1	34.6
Yield of asphaltic bitumen, pbw	15.0	23.4	24.1
RCT of the deasphalted vacuum residue, %w	4.4	4.3	4.3
RCT of the asphaltic bitumen, %w	36	39	39
<u>Mixing</u>			
Yield of mixture of vacuum distillate and deasphalted vacuum residue, pbw	72.0	65.2	64.5
Initial boiling point of the mixture, °C	370	370	370
RCT of the mixture, %w	2.5	2.5	2.5

EXAMPLE 7

A heavy mixture AB was used which had been obtained by mixing 100 pbw of an asphaltic bitumen A and 35 pbw of an asphaltic bitumen B. Asphaltic bitumen A obtained by

solvent deasphalting with propane of a mineral oil vacuum residue had an RCT of 25.4 %w (calculated from the CCT determined by ASTM method D 189), a vanadium + nickel content of 250 ppmw and an average molecular weight of 1400. Asphaltic bitumen B had an RCT of 40 %w (calculated from the CCT determined by ASTM method D 189) and a vanadium + nickel content of 125 ppmw. It was obtained by solvent deasphalting with n-butane of a vacuum residue obtained in the distillation of a hydrotreated asphaltic bitumen which latter asphaltic bitumen was obtained by solvent deasphalting of a mineral oil vacuum residue.

A catalytic hydrotreatment alone is not sufficient to prepare from mixture AB an oil having an initial boiling point of 370°C and an RCT of 3.0 %w in view of the maximum permissible value of G. In addition to the catalytic hydrotreatment, a solvent deasphalting treatment should be applied. Application of relation 6 shows that for optimum utilization of the combination process care should be taken that the RCT reduction in the catalytic hydrotreatment is between 36.7 and 50.7%.

The residual feed mixture AB was subjected to catalytic hydrotreatment in eleven experiments to prepare atmospheric residues having an initial boiling point of 370°C and different RCT's (e). The experiments were similar to those described for Experiments 18-30, the weight ratio between the Ni/V/SiO₂ and Co/Mo/Al₂O₃ catalysts however being 1:2. All other reaction conditions were identical. The results of Experiments 86-96 at run hour 430 are listed in Table M.

TABLE M

Experiment No.	Space velocity, $\text{g.g}^{-1}.\text{h}^{-1}$	RCT reduction, %	C_4 production, %w on feed	G, %w
86	1.29	10.2	0.226	0.022
87	1.18	11.1	0.246	
88	0.62	20.4	0.468	0.023
89	0.60	21.7	0.489	
90	0.34	36.3	0.894	0.033
91	0.32	37.4	0.930	
92	0.19	50.5	1.427	0.044
93	0.18	51.3	1.462	
94	0.11	65.6	2.295	0.072
95	0.10	66.5	2.360	
96	0.25	43.5	1.150	

Only Experiments 91, 92 and 96 are experiments according to the invention. The other experiments have been included for reasons of comparison. As can be seen in Table M in Experiments 86-87 and 88-89, G remains virtually constant (G_c). In Experiments 90-91 and 92-93, in which RCT reductions were achieved of about 37 and 51%, respectively, G was about $1.5 \times G_c$ and $2.0 \times G_c$, respectively.

The products obtained in the catalytic hydrotreatment carried out according to Experiments 89, 94 and 96 were further treated as described hereinbefore for Experiments 14, 15 and 16. The results (of which only Experiment 99 is an experiment according to the invention) are listed in Table N.

TABLE N

Experiment No.	97	98	99
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H₂-treated product from

Experiment No.	89	94	96
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Distillation

Yield of products calculated
on 100 pbw feed, pbw

C ₄ ⁻	0.5	2.3	1.1
H ₂ S + NH ₃	2.0	4.2	3.5
C ₅ - 370°C	9.1	14.7	13.2
370-520°C (vacuum distillate)	18.2	24.2	22.7
520°C ⁺ (vacuum residue)	71.2	57.6	61.3
RCT of the vacuum distillate, %w	0.3	0.3	0.3
RCT of the vacuum residue, %w	28.7	14.1	22.5

Deasphalting

Temperature, °C	131	130	128
Yield of deasphalted vacuum residue, pbw	29.4	38.4	34.0
Yield of asphaltic bitumen, pbw	41.8	19.2	27.3
RCT of the deasphalted vacuum residue, %w	4.7	4.7	4.8

Mixing

Yield of mixture of vacuum distillate and deasphalted vacuum residue, pbw	47.6	62.6	56.7
Initial boiling point of the mixture, °C	370	370	370
RCT of the mixture, %w	3.0	3.0	3.0

EXAMPLE 8

Two experiments were carried out with the object of preparing an oil having an initial boiling point of 370°C and an RCT of 3.0 %w and to investigate the feasibility of recycle of the asphaltic bitumen produced to the catalytic hydrotreatment. In these experiments two different residual feedstocks were subjected to a catalytic hydrotreatment in a 1000 ml reactor containing two fixed catalyst beds of a total volume of 600 ml. The catalyst beds consisted of the same Ni/V/SiO₂ and Co/Mo/Al₂O₃ catalysts as were used in Example 1, the weight ratio however being 1:2. The reaction conditions were: a temperature of 400°C, a pressure of 145 bar and a H₂/oil ratio of 1000 Nl/kg. The products from the catalytic hydrotreatment were further treated as described for Experiments 14, 15 and 16.

15 Experiment 100

The feed used in this experiment was asphaltic bitumen A of Example 7. Application of relation 6 shows that for optimum utilization of the combination process care should be taken that the RCT reduction in the catalytic hydrotreatment is between 51.0 and 61.4%. In the catalytic hydrotreatment of Experiment 100 the space velocity applied was 0.22 g.g⁻¹.h⁻¹ and the RCT reduction achieved was 56%. In the solvent deasphalting of Experiment 100 an asphaltic bitumen C was separated which had an RCT of 36 %w.

25 Experiment 101

The feed used in this experiment was a mixture AC obtained by mixing 100 pbw of asphaltic bitumen A with 25 pbw of asphaltic bitumen C obtained in the above Experiment 100. Application of relation 6 shows that for optimum utilization of the combination process care should be taken that the RCT reduction in the catalytic hydrotreatment is between 41.0 and 54.0%. In the catalytic hydrotreatment of Experiment 101 the space velocity applied was 0.21 g.g⁻¹.h⁻¹, and the RCT reduction achieved was 47.5%. In the solvent deasphalting an asphaltic bitumen D was separated which had an RCT of 36 %w.

Since the RCT of asphaltic bitumen D is equal to that of asphaltic bitumen C, this is the moment when in recycling the asphaltic bitumen the process has reached its stationary state. The results of Experiments 100 and 101 are listed in Table O.

TABLE O

Experiment No.	100	101
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Distillation

Yield of products calculated
on 100 pbw feed, pbw

C_4^-	2.22	2.0
$H_2S + NH_3$	3.4	2.9
$C_5 - 370^\circ C$	17.0	14.4
$370-520^\circ C$ (vacuum distillate)	18.4	16.0
$520^\circ C^+$ (vacuum residue)	61.0	66.7
RCT of the vacuum distillate, %w	0.4	0.4
RCT of the vacuum residue, %w	14.5	17.9

Deasphalting

Temperature, $^\circ C$	132	133
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Yield of deasphalted vacuum
residue, pbw

	41.5	38.0
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Yield of asphaltic bitumen, pbw	19.5	28.7
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RCT of the deasphalted vacuum
residue, %w

	4.2	4.1
--	-----	-----

RCT of the asphaltic bitumen, %w

	36	36
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Mixing

Yield of mixture of vacuum
distillate and deasphalted

vacuum residue, pbw	59.9	54.0
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Initial boiling point of the
mixture, $^\circ C$

	370	370
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RCT of the mixture, %w

	3.0	3.0
--	-----	-----

EXAMPLE 9

A heavy mixture ABC was used which had been obtained by mixing 55 pbw of an atmospheric residue A with 30 pbw of a vacuum residue B and with 15 pbw of an asphaltic bitumen C.

5 Atmospheric bitumen A which was obtained in the distillation of a crude mineral oil, had an RCT of 10 %w (determined by ASTM method 524), a vanadium + nickel content of 70 ppmw and a percentage boiling below 520°C of 50 %w. Vacuum residue B which was obtained in the distillation of a crude mineral oil, had an
10 RCT of 20.6 %w (computed from the CCT determined by ASTM method D 189), a vanadium + nickel content of 170 ppmw and a 5 %w boiling point of 500°C. Asphaltic bitumen C had been obtained in the deasphalting with propane of a mineral oil vacuum residue. It had an RCT of 25.4 %w (computed from the CCT determined by
15 ASTM method D 189), an average molecular weight of 1400 (determined by ASTM method D 3592-77, using toluene as the solvent) and a vanadium + nickel content of 250 ppmw.

The mixture ABC had an RCT of 15.5 %w, a vanadium + nickel content of 127 ppmw and 29.5 %w of the mixture boiled below
20 520°C.

The mixture ABC with an RCT of 15.5 %w (b) was subjected to catalytic hydrotreatment in fifteen experiments to prepare atmospheric residues having an initial boiling point of 370°C and different RCT's (c). The experiments were similar to those
25 described for Experiments 1-13, the weight ratio between the Ni/V/SiO_2 and $\text{Co/Mo/Al}_2\text{O}_3$ catalysts however being 1:2. The reaction conditions were: a temperature of 400°C, a pressure of 160 bar and a H_2 /oil ratio of 1500 Nl/kg, varying space velocities being used. The results of Experiments 102-116 at run
30 hour 250 are listed in Table P.

TABLE P

Experiment No.	Space velocity, $\text{g.g}^{-1}.\text{h}^{-1}$	RCT reduction, %	C_4 production, %w on feed	G, %w
102	11.4	10.4	0.166	0.016
103	10.4	11.3	0.181	
104	6.05	19.8	0.312	0.016
105	5.62	21.0	0.331	
106	2.62	39.7	0.652	0.017
107	2.53	40.6	0.668	
108	1.69	50.2	0.836	0.018
109	1.61	51.5	0.859	
110	1.13	59.9	1.037	0.024
111	1.08	60.9	1.061	
112	0.70	70.2	1.316	0.032
113	0.67	70.9	1.339	
114	0.37	80.1	1.908	0.131
115	0.35	81.1	2.039	
116	0.90	65.0	1.165	

- 62 -

Of Experiments 102-116 only Experiments 111, 112 and 116 are experiments according to the invention. The other experiments have been included for reasons of comparison. As can be seen in Table P in Experiments 110-111 and 112-113, in which RCT 5 reductions were achieved of about 60 and 70%, respectively, G was about 1.5 G_c and 2.0 G_c , respectively.

The product obtained in the catalytic hydrotreatment carried out according to Experiment 116 was further separated by successive atmospheric distillation, vacuum distillation and 10 solvent deasphalting as described hereinbefore. The results are listed hereinafter.

Experiment No. 117

H₂-treated product from
Experiment No.

116

Distillation

Yield of products calculated
on 100 pbw feed, pbw

C ₄ ⁻	1.17
H ₂ S + NH ₃	2.2
C ₅ - 370°C	13.3
370-520°C (vacuum distillate)	47.0
520°C ⁺ (vacuum residue)	33.9
RCT of the vacuum distillate, %w	0.5
RCT of the vacuum residue, %w	12.3

Deasphalting ¹⁾

Yield of deasphalted vacuum
residue, pbw

27.6

Yield of asphaltic bitumen, pbw

6.3

RCT of the deasphalted vacuum
residue, %w

5.8

Mixing

Yield of mixture of vacuum
distillate and deasphalted
vacuum residue, pbw

74.6

Initial boiling point of the
mixture, °C

370

RCT of the mixture, %w

2.5

- 1) solvent = n-butane
solvent/oil weight ratio = 3:1
temperature, 118°C
pressure = 41 bar

74

C L A I M S

1. A process for the preparation of a hydrocarbon mixture having an RCT of a %w and an initial boiling point of $T_1^{\circ}\text{C}$, characterized in that an asphaltenes-containing hydrocarbon mixture is subjected to a catalytic hydrotreatment for reducing
5 its RCT, the product obtained being separated by distillation into an atmospheric distillate and an atmospheric residue having an initial boiling point of $T_1^{\circ}\text{C}$, that either a deasphalted atmospheric residue having the desired RCT of a %w is obtained from the said atmospheric residue by solvent deasphalting or
10 that the atmospheric residue is first separated by distillation into a vacuum distillate and a vacuum residue, from which vacuum residue asphaltic bitumen is separated by solvent deasphalting such that a deasphalted vacuum residue is obtained having an RCT such that, when this latter deasphalted vacuum residue is mixed
15 with the said vacuum distillate, a mixture is obtained which has the desired RCT of a %w, the catalytic hydrotreatment being carried out under such conditions that the C_4^- production per % RCT reduction ("G") lies between $1.5 \times G_c$ and $2.0 \times G_c$ as defined.
- 20 2. A process as claimed in claim 1, characterized in that in the catalytic hydrotreatment for the reduction of the RCT a catalyst is used which comprises 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
25 tungsten on a carrier, which carrier consists more than 40 %w of alumina.
3. A process as claimed in claim 2, characterized in that in the catalytic hydrotreatment for the reduction of the RCT a catalyst is used which comprises the metal combination nickel-
30 molybdenum or cobalt-molybdenum on alumina as the carrier.
4. A process as claimed in claims 2-3, characterized in that the asphaltenes-containing hydrocarbon mixture has a vanadium + nickel content of more than 50 ppmw and that in the catalytic hydrotreatment this mixture is contacted with two successive
35 catalysts, the first catalyst being a demetallization catalyst



* C L M S *

consisting more than 80 %w of silica and the second catalyst being an RCT reduction catalyst as described in claim 2 or 3.

5. A process as claimed in claim 4, characterized in that the demetallization catalyst comprises the metal combination nickel-
5 vanadium on silica as the carrier.

6. A process as claimed in any one of claims 1-5, characterized in that the catalytic hydrotreatment is carried out at a temperature of from 300-500°C, a pressure of from 50-300 bar, a space velocity of from 0.02-10 g.g⁻¹.h⁻¹ and a H₂/feed ratio of from
10 100-5000 NL/kg.

7. A process as claimed in claim 6, characterized in that the catalytic hydrotreatment 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 NL/kg.

15 8. A process as claimed in any one of claims 1-7, characterized in that the solvent deasphalting is applied to a vacuum residue from the hydrotreated product.

9. A process as claimed in any one of claims 1-8, characterized in that the solvent deasphalting is carried out using n-butane
20 as solvent, at a pressure of from 35-45 bar and a temperature of from 100-150°C.

10. A process as claimed in any one of claims 1-9, characterized in that an asphaltic bitumen separated in the solvent deasphalting of a residue obtained in the distillation of a hydrotreated
25 residual fraction of a crude mineral oil, which asphaltic bitumen is used as a mixing component in the feed for the first step of the process, originates from the solvent deasphalting carried out in the second step of the process.

11. A process as claimed in claim 1 for the preparation of a
30 hydrocarbon mixture suitable for use as feed for a catalytic conversion process, such as catalytic cracking, carried out in the presence or absence of hydrogen for the preparation of light hydrocarbon distillates, such as gasoline and kerosine, which hydrocarbon mixture is prepared substantially as described
35 hereinbefore with reference to the Examples.

12. Hydrocarbon mixtures prepared according to a process as described in claim 11.

