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(54) **Process for preparing one or more light hydrocarbon oil distillates.**

(57) A process for preparing one or more light hydrocarbon oil distillates comprising:

- a) hydrocracking (2) a first hydrocarbon oil fraction (1)
- b) catalytically cracking (12) a second hydrocarbon oil fraction (11) substantially identical to the first hydrocarbon oil fraction or differing therefrom,
- c) separating the product obtained in step b) by means of distillation (14) into one or more distillates (15,16) and a residue (18)
- d) subjecting the residue obtained in step c) together with the first hydrocarbon oil fraction to the hydrocracking in step a), and
- e) isolating one or more light hydrocarbon oil distillates from the products obtained in steps a) and b).

**EP 0 436 253 A1**

## PROCESS FOR PREPARING ONE OR MORE LIGHT HYDROCARBON OIL DISTILLATES

The present invention relates to a process for preparing one or more light hydrocarbon oil distillates from a hydrocarbonaceous feedstock.

In the atmospheric distillation of crude mineral oil, as applied on a large scale in refineries in the preparation of light hydrocarbon oil distillates, for example gasoline fractions, a residual oil is obtained as a by-product. Gasolines, as referred to herein, are those fractions having a boiling range at atmospheric pressure between that of n-pentane and 220 °C. To increase the yield of light hydrocarbon oil distillates from the crude oil concerned, a heavy hydrocarbon oil distillate can be separated from said residual oil by vacuum distillation, which hydrocarbon oil distillate can be converted in a relatively simple way by hydrocracking or catalytic cracking into one or more light hydrocarbon oil distillates.

A process is described in Oil and Gas Journal, Feb. 16, 1987, pp 55-66, which meets the increasing demands for middle distillates, i.e. those having an atmospheric boiling range from between 180 °C and 370 °C.

It has now been found that, among the light hydrocarbon oil distillates, gasoline fractions are obtained in a surprisingly high yield when integrating the steps of hydrocracking and catalytic cracking in a specific manner.

The present invention therefore relates to a process for preparing one or more light hydrocarbon oil distillates comprising:

- a) hydrocracking a first hydrocarbon oil fraction,
- b) catalytically cracking a second hydrocarbon oil fraction substantially identical to the first hydrocarbon oil fraction or differing therefrom,
- c) separating the product obtained in step b) by means of distillation into one or more distillates and a residue,
- d) subjecting the residue obtained in step c) together with the first hydrocarbon oil fraction to the hydrocracking in step a), and
- e) isolating one or more light hydrocarbon oil distillates from the product obtained in steps a) and b).

In Figures 1 and 2 suitable embodiments of the process according to the present invention are schematically shown, in which reference numerals relating to corresponding parts are the same.

Referring to Figure 1, a heavy vacuum hydrocarbon oil distillate is introduced via a line 1 into a hydrocracker 2 in which the oil is hydrocracked (step a)). The product obtained in hydrocracker 2 is withdrawn therefrom via a line 3 and introduced via this line into a distillation column 4. From the distillation column 4 a gas fraction is withdrawn via a line 5, a gasoline fraction via a line 6, a kerosine fraction via a line 7, a gas oil fraction via a line 8 and a residue via a line 9. Hydrogen is introduced into the hydrocracker 2 via a line 10. A substantially identical heavy vacuum hydrocarbon oil distillate is introduced via a line 11 into a catalytic cracker 12 in which the distillate is catalytically cracked (step b)). The product obtained in catalytic cracker 12 is withdrawn therefrom via a line 13 and introduced via this line into a distillation column 14 from which a gasoline fraction is withdrawn via a line 15 and a middle distillate fraction via a line 16. Catalyst with coke deposited thereupon is withdrawn from the catalytic cracker via a line 17, subjected to a regeneration treatment and recycled thereafter via a line not shown to the catalytic cracker. From the distillation column 14 a residue is withdrawn via a line 18 and a gas fraction via a line 19. The residues from columns 4 and 14 are introduced via the lines 18 and 1 into the hydrocracker 2 in which the residues are hydrocracked (step d). In this way the residues obtained in steps a) and b) are hydrocracked in step d) advantageously together with the heavy vacuum hydrocarbon oil distillate.

Referring to Figure 2, a heavy vacuum hydrocarbon distillate is introduced into the hydrocracker 2 via a line 1a and line 1, and into the catalytic cracker 12 via line 1a and line 11. Moreover, the residue which is withdrawn from column 4 is introduced via line 9 and line 11 into the catalytic cracker 12. In this way the residue obtained from the distillation column 14 is hydrocracked in step a) together with a further quantity of heavy vacuum hydrocarbon oil distillate, whilst the residue obtained from the distillation column 4 is catalytically cracked in step b) together with a further quantity of heavy vacuum hydrocarbon oil distillate. This use of the hydrocracker and the catalytic cracker results in a surprisingly high yield of gasoline.

The hydrocarbon oil fractions to be converted in the process according to the present invention may be any vacuum hydrocarbon oil distillate obtained from crude mineral oil. Preferably, the vacuum hydrocarbon oil distillate is a vacuum oil having a boiling range at atmospheric pressure in the range of from 220 °C to 700 °C. Such oils may be a mixture of gas oils obtained by vacuum distillation (i.e. at sub-atmospheric pressure) and gas oils obtained by distillation at atmospheric pressure. Suitably the hydrocarbon oil fractions to be converted in the process according to the present invention comprise at least 10 %wt of

material boiling above 540 °C. In another suitable embodiment of the process according to the present invention the first hydrocarbon oil fraction is less heavy than the second hydrocarbon oil fraction. Suitably, the first hydrocarbon oil fraction comprises at most 10 %wt of material boiling above 540 °C, for instance a light vacuum hydrocarbon oil distillate, whilst the second hydrocarbon oil fraction comprises at least 10 %wt of material boiling above 540 °C, for instance a heavy vacuum hydrocarbon oil distillate. Preferably, the product obtained in step a) is separated by means of distillation into one or more distillates and a residue which is subsequently subjected together with the second hydrocarbon oil fraction to the catalytic cracking in step b). In another preferred embodiment of the process according to the present invention, the product obtained in step a) is separated by means of distillation into one or more distillates and a residue which is subsequently subjected together with the residue obtained in step b) and the first hydrocarbon oil fraction to the hydrocracking in step a).

The hydrocracking in step a) is carried out using a catalyst system which comprises at least a catalyst comprising at least one metal of the group consisting of Ni, Mo and Co on a carrier, preferably alumina, in the presence of hydrogen at a temperature of from 350-450 °C, a pressure of from 10-300 bar, a space velocity of from 0.02-10 g.g<sup>-1</sup>.h<sup>-1</sup> and a H<sub>2</sub>/feed ratio of from 100-5000 NI.kg<sup>-1</sup>. Very suitable catalysts comprise cobalt and molybdenum on alumina or nickel and molybdenum on alumina.

The hydrocracking in step a) can suitably be carried out in a stacked-bed catalyst system comprising as upper bed catalyst a catalyst as described hereinabove and as lower bed catalyst for instance a metal-containing zeolite Y. The lower bed catalyst preferably comprises Ni and/or W on a zeolite Y.

In the process according to the present invention a considerable portion of the feed to the catalytic cracker is converted into distillate fractions. In the catalytic cracking process, which is preferably carried out in the presence of a zeolitic catalyst, coke is deposited on the catalyst. This coke is removed from the catalyst by burning off during a catalyst regeneration step, whereafter the regenerated catalyst is recycled to the catalytic cracker. Catalytic cracking can suitably be carried out at a temperature of 400-900 °C and a pressure in the range of 1-10 bar.

In a suitable embodiment of the present invention the catalytic cracking in step b) is attractively carried out by contacting the second hydrocarbon oil fraction with a zeolitic catalyst comprising a zeolite with a pore diameter of 0.3 to 0.7 nm at a temperature above 480 °C during less than 10 seconds. In this way high yields of lower olefins (C<sub>2</sub>-C<sub>4</sub>) can be co-produced. Ethylene and propylene are valuable starting materials for chemical processes, while C<sub>4</sub> olefins can find use as a starting material for alkylating and/or oligomerization procedures in order to produce high octane gasoline and/or middle distillates. Isobutene can usefully be converted to methyl t-butyl ether.

Suitably, the minimum contact time is 0.1 second. Very good results are obtainable with a process in which the second hydrocarbon oil fraction is contacted with the zeolitic catalyst during 0.2 to 6 seconds.

The temperature during the catalytic cracking reaction is relatively high. It is this combination of high temperature and short contact time which allows a high conversion to olefins. A preferred temperature range is 480 to 900 °C, more preferably 550 to 800 °C.

The zeolitic catalyst to be used in step b) may comprise one or more zeolites with a pore diameter of from 0.3 to 0.7 nm, preferably from 0.5 to 0.7 nm. The catalyst suitably further comprises a refractory oxide that serves as binder material. Suitable refractory oxides include alumina, silica, silica-alumina, magnesia, titania, zirconia and mixtures thereof. Alumina is especially preferred. The weight ratio of refractory oxide and zeolite suitably ranges from 10:90 to 90:10, preferably from 50:50 to 85:15. The zeolitic catalyst may comprise up to about 40% by weight of further zeolites with a pore diameter above 0.7 nm. Suitable examples of such zeolites include the faujasite-type zeolites, zeolite beta, zeolite omega and in particular zeolite X and Y. Suitably, the zeolitic catalyst consists substantially of a zeolite with a pore diameter of from 0.3 to 0.7 nm.

The term zeolite in this specification is not to be regarded as comprising only crystalline aluminium silicates. The term also includes crystalline silica (silicalite), silicoaluminophosphates (SAPO), chromosilicates, gallium silicates, iron silicates, aluminium phosphates (ALPO), titanium aluminosilicates (TAPO) and iron aluminosilicates.

Examples of zeolites that may be used in step b) of the process of the present invention and that have a pore diameter of 0.3 to 0.7 nm, include SAPO-4 and SAPO-11, which are described in US-A-4,440,871, ALPO-11, described in US-A-4,310,440, TAPO-11, described in US-A-4,500,651, TASO-45, described in EP-A-229,295, boron silicates, described in e.g. US-A-4,254,297, aluminium silicates like erionite, ferrierite, theta and the ZSM-type zeolites such as ZSM-5, ZSM-11, ZSM-12, ZSM-35, ZSM-23, and ZSM-38. Preferably, the zeolite is selected from the group consisting of crystalline metal silicates having a ZSM-5 structure, ferrierite, erionite and mixtures thereof. Suitable examples of crystalline metal silicates with ZSM-5 structure are aluminium, gallium, iron, scandium, rhodium and/or scandium silicates as described in e.g.

GB-B-2,110,559.

The weight ratio of the catalyst used in step b) relative to the fraction of the mixture of hydrocarbons to be converted (catalyst/oil ratio, g/g) may vary widely, for example up to 150 kg of catalyst per kg of the fraction of the mixture of hydrocarbons or even more.

5 The present invention will now be illustrated by means of the following Examples. In the Examples the boiling points are given at atmospheric pressure.

#### Example 1

10 A process was carried out in accordance with the flow diagram as schematically shown in Figures 1 . The feed, an Arabian heavy flashed distillate, conducted through line 1 had the following properties:

|    |                              |               |
|----|------------------------------|---------------|
|    | <b>initial boiling point</b> | <b>350 °C</b> |
| 15 | <b>11 %wt recovered at</b>   | <b>400 °C</b> |
|    | <b>65 %wt recovered at</b>   | <b>500 °C</b> |
|    | <b>92 %wt recovered at</b>   | <b>575 °C</b> |
| 20 | <b>final boiling point</b>   | <b>650 °C</b> |

The hydrocracking in step a) was carried out at a temperature of 370 °C, a pressure of 120 bar, a weight hourly space velocity of 1 kg.kg<sup>-1</sup>.h<sup>-1</sup> and a hydrogen/feed ratio of 1000 NI.kg<sup>-1</sup>. The catalyst system used comprised a stacked-bed of which the upper bed catalyst comprised 2.8 %wt Ni and 12.8 %wt Mo (both on total catalyst) on alumina as carrier, and the lower bed catalyst comprised 8.2 %wt W and 2.6 %wt Ni (both on total catalyst) on a zeolite Y as carrier. The upper bed catalyst had a surface area of 171 m<sup>2</sup>/g, a pore volume of 0.46 ml/g and a compacted bulk density of 0.84 g/ml. The lower bed catalyst had a surface area of 492 m<sup>2</sup>/g, a pore volume of 0.43 ml/g and a compacted bulk density of 0.64 kg/l.

The same feed as described hereinabove was conducted through the line 11.

30 The catalytic cracking in step b) is carried out at a temperature of 530 °C, a pressure of 1 bar, and a Voorhies severity of 4.5. The zeolitic catalyst used comprised a zeolite Y. The catalyst had a surface area of 113 m<sup>2</sup>/g, a pore volume of 0.29 ml/g and a bulk density of 0.43 ml/g.

The catalytic cracker 12 is operated so as to obtain the maximum gasoline yield and to produce in total 7 %wt of coke.

35 90 pbw of the above feed in line 1 and 10 pbw of the above feed in line 11 yielded the various product fractions in the following quantities: 8.9 pbw gas fraction (line 5), 57.9 pbw gasoline fraction (line 6), 15.0 pbw kerosine fraction (line 7), 12.5 pbw gas oil fraction (line 8), 40 31.6 pbw residue fraction (line 9), 2.4 pbw gas fraction (line 19), 4.1 pbw gasoline fraction (line 15), 1.8 pbw middle distillate fraction (line 16), 1.1 pbw residue fraction (line 18).

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#### Example 2

A process was carried out in accordance with the flow diagram as schematically shown in Figure 2. The same feed was used as in Example 1. The hydrocracking in step a) was carried out in substantially the same manner as described in Example 1. The catalytic cracking in step b) using the same catalyst as applied in Example 1 was carried out at a temperature of 490 °C, a pressure of 2 bar, and a Voorhies severity of 2.5. The catalytic cracker 12 is operated so as to obtain the maximum gasoline yield and to produce in total 4 %wt of coke.

100 pbw of the feed in line 1a yielded the various (product) fractions in the following quantities:

55 90 pbw heavy flashed distillate fraction (line 1),  
10 pbw heavy flashed distillate fraction (line 11),  
5.0 pbw gas fraction (line 5),  
18.1 pbw gasoline fraction (line 6),

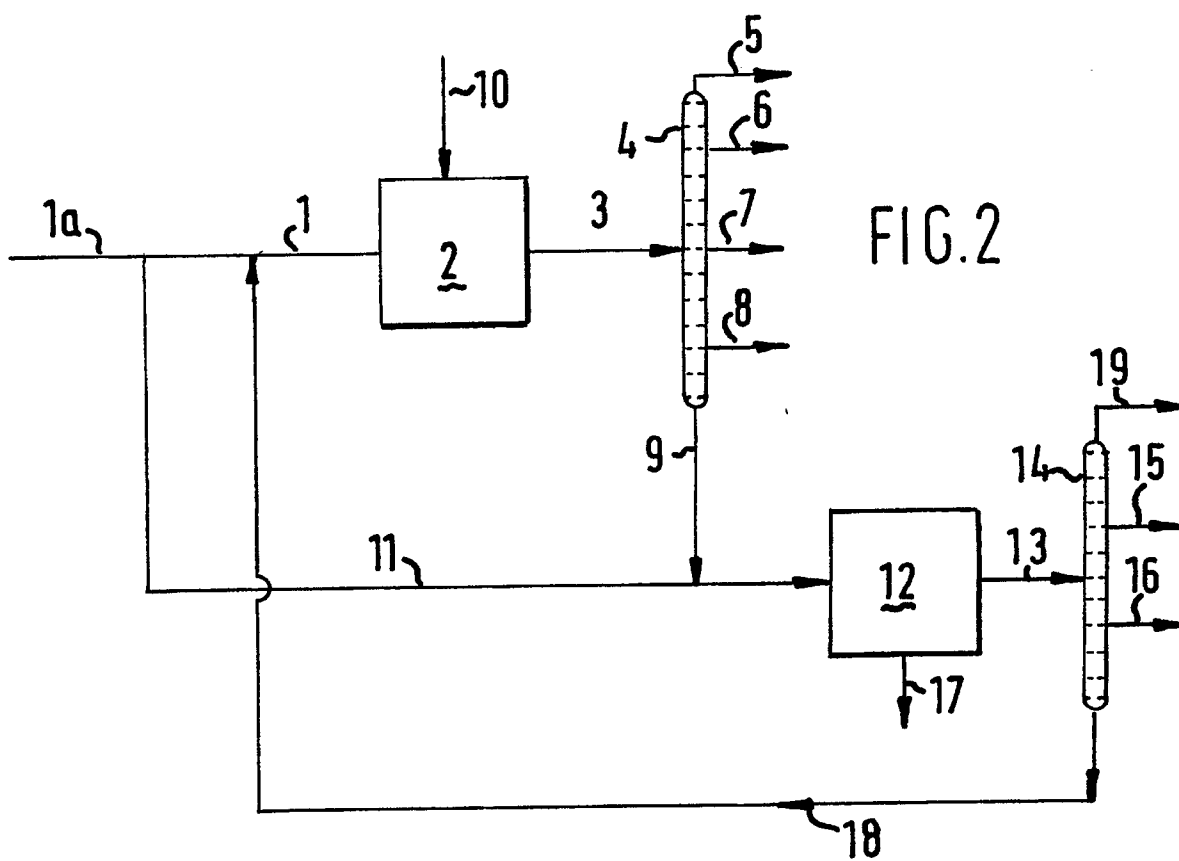
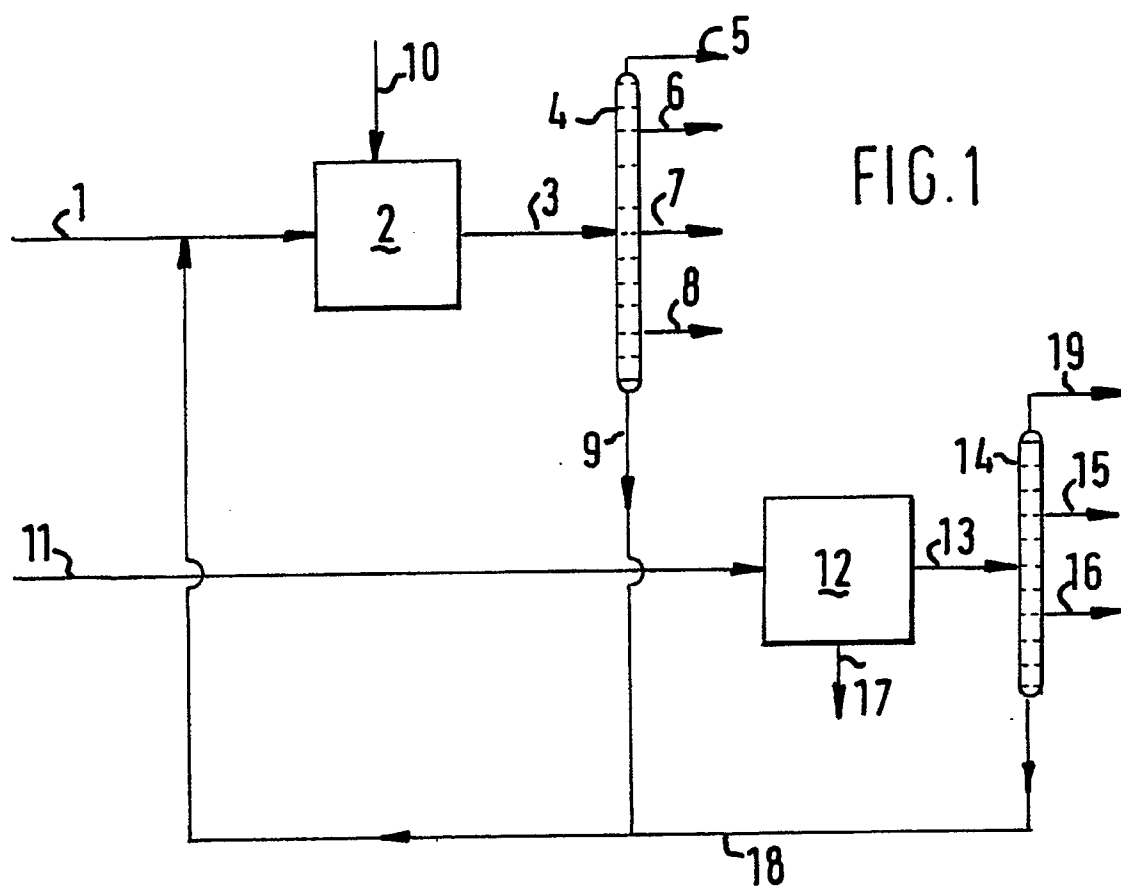
- 11.5 pbw kerosine fraction (line 7),  
 15.3 pbw gas oil fraction (line 8),  
 43.7 pbw residue fraction (line 9),  
 11.1 pbw gas fraction (line 19),  
 5 30.3 pbw gasoline fraction (line 15),  
 8.1 pbw middle distillate fraction (line 16),  
 1.9 pbw residue fraction (line 18).

### Claims

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1. A process for preparing one or more light hydrocarbon oil distillates comprising:
  - a) hydrocracking a first hydrocarbon oil fraction,
  - b) catalytically cracking a second hydrocarbon oil fraction substantially identical to the first hydrocarbon oil fraction or differing therefrom,
  - 15 c) separating the product obtained in step b) by means of distillation into one or more distillates and a residue,
  - d) subjecting the residue obtained in step c) together with the first hydrocarbon oil fraction to the hydrocracking in step a), and
  - e) isolating one or more light hydrocarbon oil distillates from the product obtained in steps a) and b).
- 20 2. A process according to claim 1, wherein both the first and the second hydrocarbon oil fraction comprise at least 10 %wt of material boiling above 540 °C.
3. A process according to claim 1, wherein the first hydrocarbon oil fraction comprises at most 10 %wt of material boiling above 540 °C and the second hydrocarbon oil fraction comprises at least 10 %wt of material boiling above 540 °C.
- 25 4. A process according to any one of claims 1-3, wherein the product obtained in step a) is separated by means of distillation into one or more distillates and a residue which residue is subsequently subjected together with the second hydrocarbon oil fraction to the catalytic cracking in step b).
- 30 5. A process according to any one of claims 1-3, wherein the product obtained in step a) is separated by means of distillation into one or more distillates and a residue which residue is subsequently subjected together with the residue obtained in step b) and the first hydrocarbon oil fraction to the hydrocracking in step a).
- 35 6. A process according to any one of claims 1-5, wherein step a) is carried out at a temperature of 350-450 °C and a pressure of 10-300 bar.
- 40 7. A process according to any one of claims 1-6, wherein in step a) a catalyst system is used which comprises at least a catalyst comprising one metal of the group consisting of Ni, Mo and Co on alumina as carrier.
8. A process according to any one of claims 1-7, wherein step b) is carried out at a temperature of 400-900 °C and a pressure of 1-10 bar.
- 45 9. A process according to any one of claims 1-8, wherein in step b) a zeolitic catalyst is used.
10. Light hydrocarbon oil distillates whenever prepared by a process as described in any one of claims 1-9.
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## EUROPEAN SEARCH REPORT

Application Number

EP 90 20 3477

| DOCUMENTS CONSIDERED TO BE RELEVANT                                                                                                                                                                                                                                                                  |                                                                                              |                                                                                                                                                                                                                               |                                               |
|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------------------------------|
| Category                                                                                                                                                                                                                                                                                             | Citation of document with indication, where appropriate, of relevant passages                | Relevant to claim                                                                                                                                                                                                             | CLASSIFICATION OF THE APPLICATION (Int. Cl.5) |
| X                                                                                                                                                                                                                                                                                                    | US-A-3 726 789 (KOVACH)<br>* Figure; column 4, lines 64-73; column 5, lines 12-17 *<br>- - - | 1,3-10                                                                                                                                                                                                                        | C 10 G<br>69/00                               |
| Y                                                                                                                                                                                                                                                                                                    |                                                                                              | 2                                                                                                                                                                                                                             |                                               |
| Y                                                                                                                                                                                                                                                                                                    | EP-A-0 317 028 (SHELL)<br>* Claims *<br>- - -                                                | 2                                                                                                                                                                                                                             |                                               |
| X                                                                                                                                                                                                                                                                                                    | US-A-2 360 622 (ROETHEL)<br>* Figure 1; claim 1 *<br>- - -                                   | 1,2                                                                                                                                                                                                                           |                                               |
| X                                                                                                                                                                                                                                                                                                    | US-A-3 245 900 (PATERSON)<br>* Figure *<br>- - -                                             | 1                                                                                                                                                                                                                             |                                               |
| X                                                                                                                                                                                                                                                                                                    | GB-A-1 001 449 (CALIFORNIA RESEARCH)<br>* Figure; claims *<br>- - -                          | 1,2,6-10                                                                                                                                                                                                                      |                                               |
| A                                                                                                                                                                                                                                                                                                    | US-A-3 755 141 (YOUNGBLOOD et al.)<br>* Figure; claims *<br>- - - - -                        | 1-10                                                                                                                                                                                                                          |                                               |
|                                                                                                                                                                                                                                                                                                      |                                                                                              |                                                                                                                                                                                                                               | TECHNICAL FIELDS<br>SEARCHED (Int. Cl.5)      |
|                                                                                                                                                                                                                                                                                                      |                                                                                              |                                                                                                                                                                                                                               | C 10 G                                        |
| The present search report has been drawn up for all claims                                                                                                                                                                                                                                           |                                                                                              |                                                                                                                                                                                                                               |                                               |
| Place of search<br>The Hague                                                                                                                                                                                                                                                                         |                                                                                              | Date of completion of search<br>19 March 91                                                                                                                                                                                   | Examiner<br>MICHIELS P.                       |
| CATEGORY OF CITED DOCUMENTS<br>X: particularly relevant if taken alone<br>Y: particularly relevant if combined with another document of the same category<br>A: technological background<br>O: non-written disclosure<br>P: intermediate document<br>T: theory or principle underlying the invention |                                                                                              | E: earlier patent document, but published on, or after the filing date<br>D: document cited in the application<br>L: document cited for other reasons<br>.....<br>&: member of the same patent family, corresponding document |                                               |