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(71) Applicant: **MOBIL OIL CORPORATION**
150 East 42nd Street
New York New York 10017(US)

(72) Inventor: **Choi, Byung Chang**
1933 Lark Lane
Cherry Hill New Jersey 08003(US)
Inventor: **Karsner, Grant George**
114 William Feather Drive
Voorhees Township New Jersey 08043(US)
Inventor: **Lee, Chang-Kuei**
213 Hillary Lane
Sewell New Jersey 08080(US)
Inventor: **Malladi, Madhava**
40 Tattersall Drive
Mantua New Jersey 08051(US)
Inventor: **Milstein, Donald**
1568 Applewood Circle
Yardley Pennsylvania 19067(US)

(74) Representative: **Cooper, John Anthony et al**
Mobil Court 3 Clements Inn
London WC2A 2EB(GB)

(54) Hydrocarbon solvent extraction process.

(57) A solvent extract obtained from a conventional hydrocarbon solvent extraction process, for example one employing furfural as the extraction solvent, is cooled and separated by decantation to provide a pseudo-raffinate containing most of the non-aromatics and a pseudo-extract having a hydro-aromatic content of H_{alpha}hydrogen of at least 20 percent of the total hydrogen content. The pseudo-extract is ideally suited as a hydrogen-donor for a variety of refinery operations such as visbreaking.

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HYDROCARBON SOLVENT EXTRACTION PROCESS

This invention relates to a process for the selective solvent extraction of hydrocarbon mixtures, and in particular to a process for the solvent extraction of lubricating oils using furfural. The invention related also to the processing of residual petroleum stocks by visbreaking in the presence of certain highly aromatic hydrogen-donor materials obtained from the solvent extraction process.

Solvent extraction is a well known procedure for the separation of aromatic hydrocarbons from mixtures with nonaromatic hydrocarbons of similar boiling range. Furfural has been found to be an excellent selective solvent in the separation of hydrocarbons of relatively high boiling point, for example hydrocarbons useful in the manufacture of lubricating oils and catalytic cracking feed stocks. Furfural extraction has also been found useful in the manufacture of kerosine and low boiling gas oil products where a raffinate of low aromatic content is produced.

In a typical furfural extraction process, a liquid hydrocarbon mixture containing aromatic and non-aromatic hydrocarbons is contacted with liquid furfural in an extraction column effecting formation of a raffinate phase, which is withdrawn from the top of the column and which contains a major portion of the non-aromatic hydrocarbons, and an extract phase which is withdrawn from the bottom of the column and which contains most of the furfural containing dissolved hydrocarbons including a major portion of the aromatic hydrocarbons and the remaining non-aromatic hydrocarbons. The two phases can then be separated into their constituents by distillation. U.S. Patent 3,205,167 proposes to treat the extract phase by cooling thus separating it into one phase comprising a naphthenic oil known as a pseudo-raffinate and containing a little solvent and the other phase comprising the so-called "extract proper" containing the more aromatic and sulfurized components of the oil and a large quantity of solvent. However, U.S. Patent 3,205,167 is silent regarding the specific temperature range within which this cooling operation is to be carried out and says nothing of the composition or properties of the "extract proper".

Visbreaking, or viscosity breaking, is a well known petroleum refining process in which reduced crudes are pyrolyzed, or cracked, under comparatively mild conditions to provide products having lower viscosities and pour points, thus reducing the amounts of less viscous and more valuable blending oils, so-called "cutter stock", required to make the residual stocks useful as fuel oils. The visbreaker feed stock usually consists of a mixture of two or more refinery streams derived from sources such as atmospheric residuum, vacuum residuum, furfural-extract, propane-deasphalted tar and catalytic cracker bottoms. Most of these feed stock components, except the heavy aromatic oils, behave independently in the visbreaking operation. Consequently, the severity of the operation for a mixed feed is limited greatly by the least desirable - (highest coke-forming) components. In a typical visbreaking process, the crude or resid feed is passed through a heater and heated to 425 to 525°C at 450 to 7000 kPa. Light gas-oil may be recycled to lower the temperature of the effluent. Cracked products from the reaction are flash distilled with the vapor overhead being fractionated into a light distillate overhead product, for example gasoline and light gas-oil bottoms, and the liquid bottoms are vacuum fractionated into heavy gas-oil distillate and residual tar. Examples of such visbreaking methods are described in Beuther et al., "Thermal Visbreaking of Heavy Residues," The Oil and Gas Journal, 57:46, November 9, 1959, pp. 151-157; Rhoe et al., "Visbreaking: A Flexible Process," Hydrocarbon Processing, January 1979, pp. 131-136; and U.S. Patent 4,233,138.

European Patent Application 133,774 describes a process for visbreaking a heavy petroleum residual oil which comprises subjecting the oil to an elevated temperature for a period of time corresponding to an equivalent reaction time of 250 to 1500 ERT seconds at 427°C in the presence of from 0.1 to 50 weight percent, based on the residual oil, of a hydro-aromatic solvent having a content of H_{Ar} hydrogen (protons which are attached directly to aromatic rings and which constitute a measure of aromaticity of a material) and H_{alpha} hydrogen (protons which are attached to non-aromatic carbon atoms themselves attached directly to an aromatic ring, for example alkyl groups and naphthenic ring structures) each of at least 20 percent of the total hydrogen content, and recovering a fuel oil product having a viscosity lower than that of the starting residual oil. The hydro-aromatic solvent used in this process is a thermally stable, polycyclic, aromatic/hydroaromatic distillate hydrogen donor material, preferably one which results from one or more petroleum refining operations. The hydrogen-donor solvent nominally has an average boiling point of 200 to 500°C, and a density of 0.85 to 1.1 g/cc. Examples of such suitable hydrogen donor materials are highly aromatic petroleum refinery streams, such as fluidized catalytic cracker "main column" bottoms which are highly preferred, fluidized catalytic cracker "light cycle oil," and thermofor catalytic cracker "syntower" bottoms, all of which contain a substantial proportion of polycyclic aromatic hydrocarbon constituents such as naphthalene, dimethylnaphthalene, anthracene, phenanthrene, fluorene, chrysene, pyrene, perylene,

diphenyl, benzothiophene, tetralin and dihydronaphthalene, for example. Such refractory petroleum materials are resistant to conversion to lighter (lower molecular weight) products by conventional non-hydrogenative procedures. Typically, these petroleum refinery residual and recycle fractions are hydrocarbonaceous mixtures having an average carbon to hydrogen ratio above 1:1, and an average boiling point above 230°C.

In accordance with the invention, there is provided a solvent extraction process which comprises the steps of:

(a) contacting a liquid hydrocarbon feed containing aromatic and non-aromatic hydrocarbon components with an extraction solvent at an elevated temperature to provide a raffinate phase containing the major portion of the non-aromatic components of the feed and a minor portion of the extraction solvent and an extract phase containing the major portion of the aromatic hydrocarbon components and a minor portion of the non-aromatic hydrocarbon components of the feed and a major portion of the extraction solvent;

(b) cooling the extract phase; and

(c) separating the cooled extract phase by decantation into a pseudo-raffinate containing most of the non-aromatic components of the extract phase and a pseudo-extract containing most of the aromatic components of the extract phase and most of the extraction solvent, the degree of the cooling being such that the pseudo-extract has a hydro-aromatic content of H_{alpha} hydrogen of at least 20 percent of the total hydrogen.

The pseudo-extract resulting from the process, referred to herein as a "double decantation" process, is well-suited for use in processes employing a hydrogen-donor, for example in the visbreaking process described in European Patent Application 133,774. The pseudo-raffinate is advantageously used as feedstock in an otherwise conventional catalytic cracking processes, the operational parameters of which are well known in the art. The pseudo-raffinate can also be recycled to the first extraction step of the process to produce additional lube stock.

The invention is described below in greater detail by way of example only with reference to the accompanying drawings, in which

Fig. 1 is a schematic representation of the solvent extraction process of the invention carried out with the preferred solvent, furfural; and

Fig. 2 is a schematic representation of a visbreaking process employing as hydrogen donor the pseudo-extract obtained in accordance with the solvent extraction process.

Referring first to Fig. 1 of the drawings, a liquid hydrocarbon charge stock containing both aromatic and non-aromatic hydrocarbon components, for example Arab medium crude, is introduced into an extraction column together with a quantity of a suitable extraction solvent, in this case the preferred solvent, furfural. The amount of extraction solvent can vary widely and will frequently range from 100 to 300 volume percent of the charge stock. The extraction process of the invention contemplates the use of a conventional solvent extraction unit operated under conventional conditions. For example, in a typical lube oil facility, the extraction column is operated within a predetermined temperature profile so as to provide a raffinate phase which, following dewaxing, will provide a lube oil product meeting specifications taking into account the properties of the charge stock. The extraction column is commonly operated at 65 to 150°C, and preferably 80 to 120°C, at the bottom, the temperature at the top of the column being some 10 to 35°C, and preferably from 15 to 30°C, higher than this. Such a temperature profile is entirely suitable for practicing the extraction process of the invention. Under these conditions, the extract phase will usually contain a relatively minor amount of non-aromatic components, for example from 10 to 25 weight percent of the non-aromatic content of the original feed. Although more of these non-aromatics can be shifted to the raffinate phase by lowering the bottom temperature of the extraction unit, this may be achieved only at the expense of lube stock quality. Of course, where lube stock quality is not a compelling consideration, the extraction column can be operated within a different temperature profile.

Following its withdrawal from the bottom of the furfural extractor, the extract phase is passed through a heat exchanger where it is cooled to a temperature resulting in the separation of the stream into a pseudo-raffinate containing most of the non-aromatic components and a pseudo-extract containing most of the aromatic components. The greater the degree of cooling, the more aromatics will be shifted to the pseudo-extract. Such cooling must, at a minimum, be sufficient to provide a pseudo extract possessing a hydro-aromatic content of H_{alpha} hydrogen of at least 20 percent, and preferably up to 50 percent, based on total hydrogen content. In general, cooling the extract phase to a temperature of from 30 to 70°C, and preferably from 38 to 50°C., is sufficient to provide such a pseudo-extract. The cooled two-phase stream is then separated in a decanter to provide the pseudo-extract which, after removal of furfural (or other extraction solvent as the case might be), for example by distillation, is ready to be employed as a hydrogen-donor.

The pseudo-raffinate resulting from the double decantation process, with its enriched non-aromatic hydrocarbon content, is advantageously employed as co-feed in a catalytic cracking operation, for example an FCC or TCC process. Alternatively, the pseudo-raffinate can be recycled to the initial extraction unit to produce more lube oil.

The use of the pseudo-extract as a hydrogen-donor in visbreaking is advantageously carried out in a facility of the type shown schematically in Fig. 2 in which a viscous hydrocarbon oil feed, typified by a 496°C+ Arab Heavy resid, is supplied by line 22 to visbreaking heater 25. The feed is blended with the pseudo-extract as the hydrogen-donor material supplied through line 50 in an amount of 0.1 to 50 weight percent, preferably 0.1 to 20 weight percent, based on the resid charge, (a weight ratio of hydrogen-donor to resid of 0.001 to 0.5, preferably 0.001 to 0.2). Mild thermal cracking of the resid under visbreaking conditions occurs in visbreaker 25 and produces a visbreaker effluent stream carried by line 28.

Visbreaking process conditions can vary widely based on the nature of the heavy oil material, the hydrogen-donor pseudo-extract and other factors. In general, the process is carried out at temperatures ranging from 350 to 485°C, preferably 425 to 455°C, at residence times ranging from 1 to 60 minutes, preferably 7 to 20 minutes. The expression "Equivalent Reaction Time", also referred to as "ERT", refers to the severity of the visbreaking operation expressed as seconds of residence time in a reactor operating at 427°C. In very general terms, the reaction rate doubles for every 12 to 13°C increase in temperature. Thus 50 seconds of residence at 427°C is equivalent to 50 ERT, and increasing the temperature to 456°C would make the operation five times as severe, that is 300 ERT. Expressed as ERT, the visbreaking process operates at an Equivalent Reaction Time of 250 to 1500 ERT seconds, and preferably 400 to 1200 ERT seconds and more preferably 500 to 800 ERT seconds, at 427°C. The pressure employed in the visbreaker will usually be sufficient to maintain most of the material in the reactor coil and/or soaker drum in the liquid phase. Normally the pressure is not considered as a control variable, although attempts should be made to keep the pressure high enough to maintain most of the material in the visbreaker in the liquid phase. Some vapor formation in the visbreaker is not harmful, and is frequently inevitable because of the production of some light ends in the visbreaking process. Some visbreaker units operate with 20-40 percent vaporization material at the visbreaker coil outlet. Lighter solvent will vaporize more and the vapor will not do much good towards improving the cracking of the liquid phase material. Accordingly, liquid phase operation is preferred, but significant amounts of vaporization can be tolerated. The pressures commonly encountered in visbreakers range from 170 to 10450 kPa, with a vast majority of units operating with pressures of 1480 to 7000 kPa. Such pressures will usually be sufficient to maintain liquid phase conditions and the desired degree of conversion.

The visbreaker effluent stream carried by line 28 is cooled by admixture with a quench stream from line 31, and the visbreaker effluent continued through line 29 to distillation column 30 where it is fractionated to obtain C_5-gases (C_3, C_4 and lower) and a C_5 -135°C naptha fraction from the top through line 34. A 220 to 370°C gas oil fraction is taken off as a bottoms stream through line 33 where portions may be recycled as a quench stream through line 31, recovered as heavy fuel oil 32 or, via line 33, blended with cutter stock to meet fuel oil product specifications.

The overhead fraction removed from the distillation column in line 34 is passed through a cooler separator 36 which is operated under conditions effective to separate the incoming liquid into a C_5-off-gas stream 38, mainly C_3 or C_4 and lower, and a C_5 -135°C naptha fraction which is taken off via line 40. Because of the boiling range and quality of the hydrogen-donor, it can simply be allowed to remain with the bottom fraction and used directly as heavy fuel oil, this avoiding the need for separation.

The use of the pseudo-extract as hydrogen-donor in visbreaking is not limited to the visbreaker/distillation arrangement described above. Any visbreaker scheme can be used, ranging from a tubular reactor which is entirely in the heater, to a soaking drum reactor wherein most of the visbreaking reaction occurs in the soaking drum. Any combination of the two processes can also be used, for example much of the visbreaking reaction can be accomplished in a coil while the remainder of the visbreaking can be made to occur in a soaking drum down-stream of the coil. Similarly, any distillation scheme known in the art can be used to process the visbreaker reactor effluent. In conventional visbreaking operations, it is preferred to quench the visbreaker effluent with a quench stream as shown in the drawing, but it is also possible to use heat exchange, fin/fan coolers, or some other conventional means of cooling the visbreaker effluent. However, since there is a risk of coking up the heat exchanger tubes in such an arrangement, use of a quench stream is preferred.

The following Examples illustrate the double decantation process of this invention (Examples 1 to 3), the use of pseudo-extract as hydrogen donor in visbreaking (Example 4) and the use of pseudo-raffinate in a thermofor catalytic cracking operation (Example 5).

EXAMPLES 1-3

In the data set forth in TABLE I below, the conditions of operation of a furfural extraction column and decanter and the properties of the resulting pseudo-raffinate and pseudo-extract are given:

TABLE I: Double Decantation of Furfural Extracts

Charge Stock	Example 1 100 SUS Light Neutral	Example 2 100 SUS Light Neutral	Example 3 Bright Stock
Crude Type:			
% Arab Medium	100	0	100
% Arab Light	0	100	0
Furfural Extraction Conditions			
Dosage, %	175	175	260
Temperature, °C	84	90	120
Raffinate Phase (Vol.%)	53	53	72
Extract Phase (Vol.%)	47	47	28
Furfural Column Extract Phase Properties			
API	12.5	15	13.4
Sulfur, Wt.%	4.77	4.02	4.14
Total N, Wt.%	0.13	0.09	0.17
RI at 70°C	1.5356	1.5263	1.5269
CCR, Wt.%	0.23	0.04	3.38
H_{alpha}, Wt.%	18	17	12
Aromatics, Wt.%	-	76.2	-
Double Decantation Conditions			
Temperature, °C	50	38	50
Solvent Dosage, Vol.%	240	350	240
Pseudo-Raffinate, Vol.%	38.3	45.9	88.9
Pseudo-Extract, Vol.%	61.7	54.1	11.1
Pseudo-Raffinate Properties			
API	20	25.7	14.8
Sulfur, Wt.%	3.6	1.95	4.2
Total N, Wt.%	0.04	0.012	0.09
RI at 70°C	1.501	1.4807	1.5233
CCR, Wt.%	0.01	less than 0.01	3.33
Aromatics, Wt.%	-	58.3	-
Pseudo-Extract Properties			
API	8.2	7	3.1
RI at 70°C	1.557	1.5608	1.605
H_{alpha}, Wt.%	22	26	greater than 22

EXAMPLE 4

Visbreaking was carried out upon an Arab Heavy Resid base stock (580°C+) both with and without the pseudo-extract of Example 1 as hydrogen donor. Use of the pseudo-extract permitted the visbreaking unit to be operated under more severe conditions as expressed in terms of "equivalent reaction time" (ERT), as explained above. The operating conditions and the results of visbreaking were as follows:

TABLE II: Visbreaking Conditions and Product Stream

Feed Rate (m^3/day)	Base Stock (without pseudo-extract)	Base Stock (with added pseudo-extract)	
Base Stock	2300	2300	
Pseudo-Extract (Example 1)	-	250	
Visbreaking Conditions			
Inlet Pressure, kPa	4200	4200	
Outlet Pressure, kPa	2850-3200	2850-3200	
Reactor Temp., °C	454	454	
Residence Time, seconds	130	150	
Equivalent Reaction Time	700	800	
Visbreaking Products Stream (m^3/Day)			**Difference**
Gasoline	312	331	+ 19
Distillate	53	176	+123
External Cutter Stock (required to meet heavy fuel oil specifications)	1428	914	-514

As these data indicate, the more severe visbreaker conditions made possible by the addition of pseudo-extract as a hydrogen donor resulted in greater yields of gasoline and distillate and a sharp reduction in the amount of cutter stock required to provide a heavy fuel oil (HFO) meeting specifications.

EXAMPLE 5

Thermofor catalytic cracking was carried out upon a virgin gas oil (VGO) both with and without the addition of the pseudo-raffinate of Example 2. The reactor conditions and results were as follows:

TABLE III: Thermofor Catalytic Cracking and Product Stream

Feed Rate (m^3/Day)	VGO without pseudo-raffinate	VGO with pseudo-raffinate	
VGO	2655	2655	
Psuedo Raffinate, Example 2	-	397	
Reactor Conditions			
Catalyst Circulation Rate, tonne/h	670	670	
Catalyst/Oil, wt. ratio	3.59	4.24	
LHSV	3.03	2.61	
Reactor Temperature, °C	488	496	
Catalyst Activity	47.5	47.5	
Product Stream (m^3/Day)			Difference
Gasoline	1436	1570	+134
Distillate	480	540	+160
Heavy Fuel Oil	120	350	+230

The significant advantages resulting from the use of pseudo-raffinate obtained in accordance with the invention in a TCC operation is apparent from these data. The increase in operation severity made possible by the use of pseudo-raffinate resulted in greater levels of production of gasoline, distillate and heavy fuel oil.

Claims

1. A solvent extraction process which comprises the steps of:

(a) contacting a liquid hydrocarbon feed containing aromatic and non-aromatic hydrocarbon components with an extraction solvent at an elevated temperature to provide a raffinate phase containing the major portion of the non-aromatic components of the feed and a minor portion of the extraction solvent and an extract phase containing the major portion of the aromatic hydrocarbon components and a minor portion of the non-aromatic hydrocarbon components of the feed and a major portion of the extraction solvent;

(b) cooling the extract phase; and

(c) separating the cooled extract phase by decantation into a pseudo-raffinate containing most of the non-aromatic components of the extract phase and a pseudo-extract containing most of the aromatic components of the extract phase and most of the extraction solvent, the degree of the cooling being such that the pseudo-extract has a hydro-aromatic content of H_{alpha} hydrogen of at least 20 percent of the total hydrogen.

2. A process according to claim 1, wherein the solvent is furfural.

3. A process according to claim 1 or claim 2, wherein the extraction step (a) is carried out in a column, is operated with a bottom temperature of from 65 to 150°C and a top temperature of from 10 to 35°C higher than the bottom temperature.

4. The process according to claim 3, wherein the extraction column is operated with a bottom temperature of 80 to 120°C and a top temperature of 15 to 30°C higher than the bottom temperature.

5. A process according to any one of claims 1 to 4, wherein the extract phase is cooled in step (b) to a temperature of 30 to 70°C.

6. A process according to claim 5, wherein the extract phase is cooled in step (b) to a temperature of 38 to 50°C.

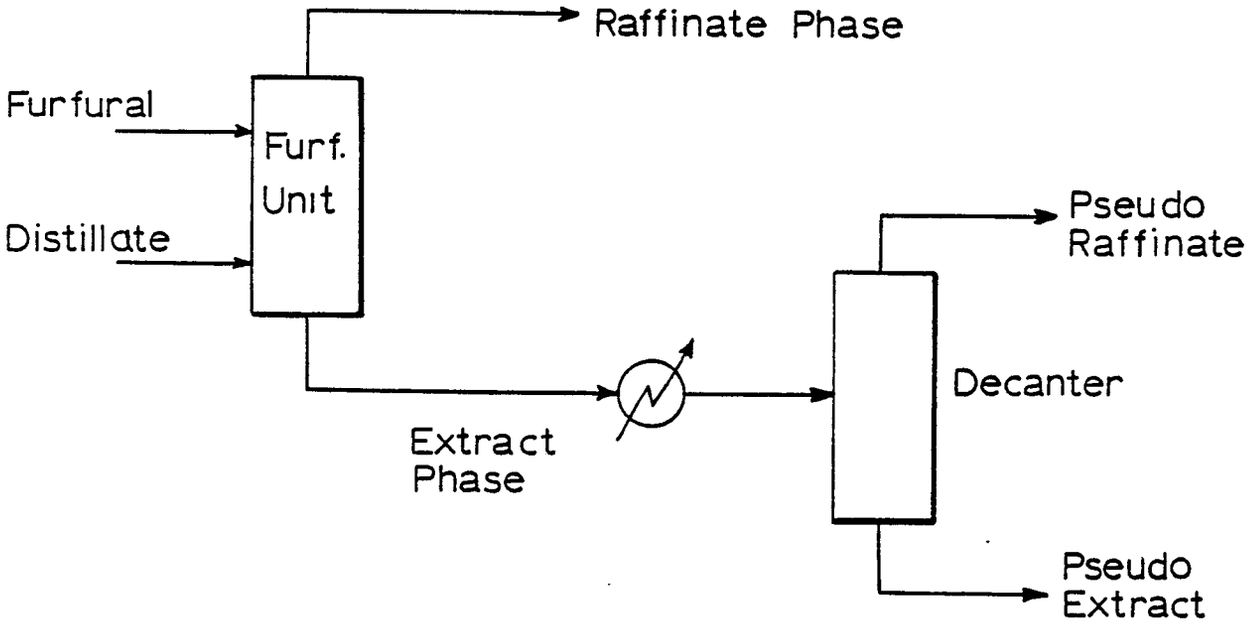
7. A process for visbreaking a heavy petroleum residual oil which comprises subjecting the oil to an elevated temperature for a period of time corresponding to an equivalent reaction time of 250 to 1500 ERT seconds at 427°C, in the presence of from 0.1 to 50 weight percent, based on the residual oil, of a hydro-aromatic solvent having a content of H_{alpha} hydrogen of at least 20 percent of its total hydrogen content, the hydroaromatic solvent being the pseudo-extract resulting from the process of any one of claims 1 to 6 from which the extraction solvent has been substantially removed, and recovering a fuel oil product having a viscosity lower than that of the starting residual oil.

8. A process according to claim 7, wherein visbreaking is carried out at 350 to 485°C for 1 to 60 minutes.

9. A process according to claim 7 or claim 8, wherein visbreaking is carried out in the presence of 0.1 to 20 weight percent, based on the residual oil, of the hydro-aromatic solvent.

10. A process according to claim 9, wherein the amount of hydro-aromatic solvent is 10 to 20 weight percent.

FIG.1


Raffinate Phase
Furfural
Furf.
Unit
Distillate
Pseudo
Raffinate
Decanter
Extract
Phase
Pseudo
Extract

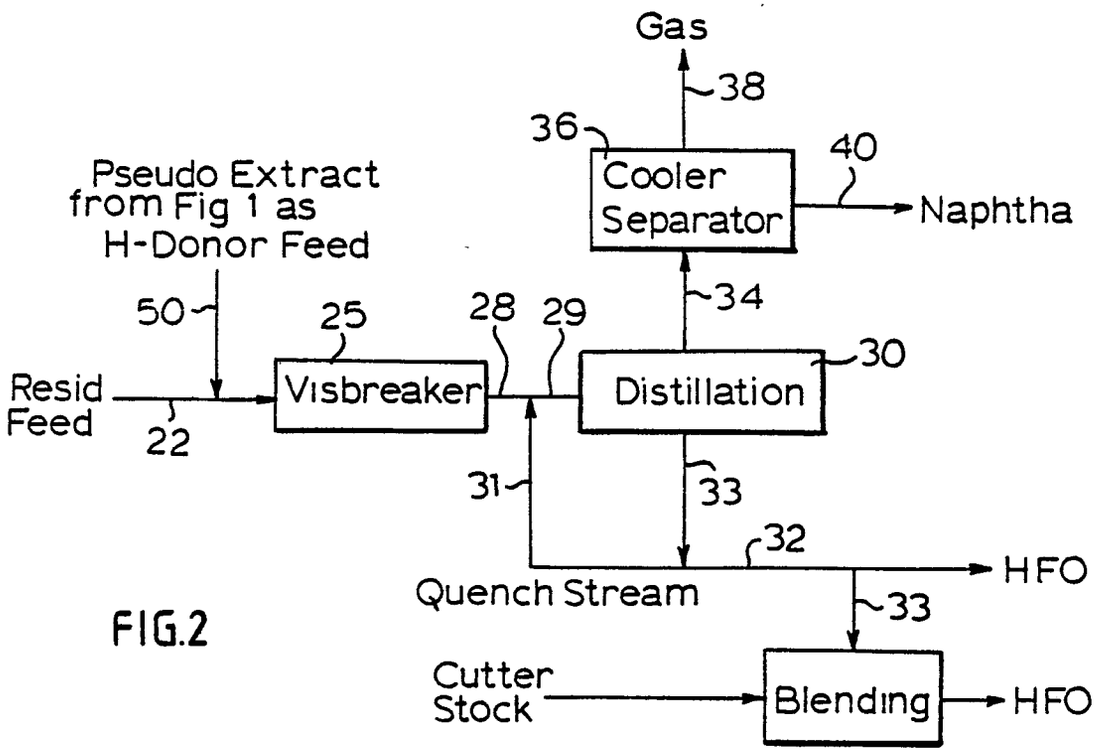

Gas
38
36
40
Cooler
Separator
Naphtha
Pseudo Extract
from Fig 1 as
H-Donor Feed
50
25
28
29
34
30
Resid
Feed
22
Visbreaker
Distillation
31
33
32
HFO
Quench Stream
33
Cutter
Stock
Blending
HFO

FIG.2

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EUROPEAN SEARCH REPORT

. Application number

EP 86308408.3

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.4)
A	EP - A1 - 0 128 047 (EXXON RESEARCH AND ENGINEERING COMPANY) * Claims; page 10, line 22; abstract * --	1	C 10 G 21/16 C 10 G 45/58
A	US - A - 4 498 980 (FORTE) * Claims; column 5, lines 29-68 * --	1	
A	GB - A - 993 927 (THE BRITISH PETROLEUM COMPANY) * Claims; page 1, line 49 - page 2, line 32 * ----	1	

TECHNICAL FIELDS SEARCHED (Int. Cl.4)

C 10 G 21/00

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
VIENNA	03-04-1987	STÖCKLMAYER

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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