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# **EUROPEAN PATENT APPLICATION**

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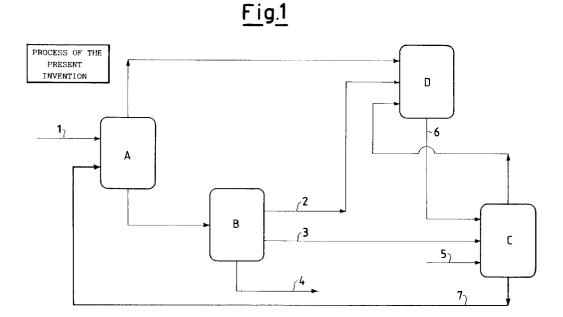
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# (54) Process for reducing the viscosity of heavy oil residues

- (57) Process for reducing the viscosity of heavy oil residues, which comprises a first step for the visbreaking of heavy oil residues and a second step for the thermal cracking (II) of the heavy gas oil formed in the visbreaking process, the above thermal cracking producing a thermal residue as well as lighter products, said process being characterized in that:
- (a) the thermal residue obtained in the thermal cracking step is almost totally recovered;
- (b) a composition consisting of fresh heavy oil residues diluted with the thermal residue recovered in step (a) is refed to the visbreaking step.



### Description

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The present invention relates to a process for reducing the viscosity of heavy oil residues.

To obtain less viscous oil products starting from extremely viscous heavy oil residues, visbreaking processes are widely used, described for example in Beuther et al. "Thermal Visbreaking of Heavy Residues", The Oil and Gas Journal", 57:46, Nov.9, 1959, pages 151-175; or described in Rhoe et al. "Visbreaking: A Flexible Process", Hydrocarbon Processing, January 1979, pages 131-136.

The above processes can be applied to various refinery streams, such as atmospheric or vacuum residues, furfural-extracts, propane-deasphalted tars, catalytic cracking bottoms.

Visbreaking processes are thermal processes, carried out under comparatively mild conditions, which produce lighter hydrocarbon fractions. Visbreaking processes typically produce gases, l.p.g., naphtha and gas oil, heavy distillates.

Visbreaking processes are often accompanied by thermal cracking processes in which the heavy vacuum gas oil coming from visbreaking, is subjected to thermal cracking under more drastic conditions than the previous visbreaking step. In this way other lighter fractions are recovered.

These combined processes (visbreaking + thermal cracking) have the disadvantage however of producing considerable quantities of residues which, owing to their physico-chemical characteristics (for example density, viscosity and distillation curve), can only be used as fuel oil, after possible fluxing with gas oil.

The necessity was therefore felt of finding new thermal processes which were just as effective but which produced smaller quantities of the above residues.

A process has now been found which reduces the viscosity of heavy oil residues and which overcomes the disadvantages of the combined processes described above, as it not only reduces but almost totally eliminates thermal cracking residues.

In accordance with this, the present invention relates to a process for reducing the viscosity of heavy oil residues, which comprises a first step for the visbreaking (I) of heavy oil residues and a second step for the thermal cracking (II) of the heavy gas oil formed during the visbreaking process, the above thermal cracking producing a thermal residue as well as lighter products, said process being characterized in that:

- (a) the thermal residue obtained in the thermal cracking step is almost totally recovered;
- (b) a composition consisting of fresh heavy oil residues diluted with the thermal residue recovered in step (a) is refed to the visbreaking step.

The term visbreaking means the process, well known in the prior art, for reducing the viscosity of heavy oil fractions. The above visbreaking processes can be carried out, as is known, on the heavy oil residue without or in the presence of hydrogen (hydrovisbreaking), or in the presence of so-called hydrogen donor solvents (see for example US-A-2.953.513), or in the presence of hydrogen and donor solvent (see US-A-4.292.168) and also in the presence of catalysts (see for example US-A-5.057.204).

In the preferred form of embodiment, the visbreaking process (I) is carried out without hydrogen, catalysts and hydrogen donor solvents. It consists in feeding the heavy oil residue into an oven heated to the desired temperature for a preset time.

As in most oil processes, there is a correlation between reaction temperature and residence time of the reagents. One visbreaking process will therefore be more rigid than another if, at the same temperature, the residence time is greater.

The visbreaking process can usually be carried out with one or more ovens, but in any case the temperature of the visbreaking oven or ovens is between 350 and 525°C, preferably between 380 and 500°C, with a residence time of between 2 and 20 minutes, preferably between 3 and 10.

As mentioned above, the heavy oil residues to be subjected to the visbreaking step (I) can come from various refinery streams.

The visbreaking process can therefore be applied to a variety of heavy oil fractions, such as vacuum residues, atmospheric residues, furfural-extracts, propane-deasphalted tars, catalytic cracking bottoms, asphalts. Generally at least 75% by weight of the components of the heavy oil residue has a boiling point which is higher than 370°C. The above heavy oil residues can also contain impurities due to heteroatoms, for example nitrogen or sulphur, and metals, particularly Vanadium.

In the preferred form of embodiment, the heavy oil residue fed to the visbreaking step (I) basically consists of atmospheric residue. Atmospheric residues usually have the following characteristics: density of between 0.940 and 1,000 g/cm<sup>3</sup>; initial distillation point (according to ASTM D 1160 method), of between 180 and 220°C; temperature at which 5% in volume distills from 330 to 370°C; temperature at which 10% in volume distills from 380 to 410°C; temperature at which 50% in volume distills from 490 to 520°C.

The visbreaking step (I) produces numerous hydrocarbon fractions. The following fractions are normally recovered:
a) gases and I.p.g., b) naphtha, c) gas oil, d) heavy vacuum distillate, e) vacuum residue + fuel oil and/or tar.

For the embodiment of the process of the present invention, the separation of the visbreaking products into the above fractions is irrelevant. It is preferably however to recover the fractions with a high additional value such as naphtha and gas oil.

It is essential on the other hand to recover part or all of the heavy vacuum gas oil, otherwise known as HVGO (high vacuum gas oil). This is a hydrocarbon fraction having a density at 15°C of between 0.880 and 0.980 g/cm<sup>3</sup>, an initial distillation point (ASTMD 1160) of between 240 and 290°C and a final distillation point of between 530 and 590°C.

This heavy vacuum gas oil is usually recovered, at least mostly, by distillation under vacuum, normally at about 20-40 mm Hg.

Other heavy vacuum gas oil can be recovered as a column bottom from a distillation column at atmospheric pressure, or at pressures slightly higher than atmospheric pressure, usually at pressures of 2-4 bars. The characteristics of this fraction (i.e. column residue at atmospheric pressure) fall within the above range for heavy vacuum gas oil. As a result, reference to heavy vacuum gas oil obtained downstream of the vis-breaking process (I), means both that which is recovered by distillation at reduced pressure, and that recovered as an atmospheric residue.

Part or all of the heavy vacuum gas oil thus separated is fed to the thermal cracking step (II).

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If only a part of the above heavy vacuum gas oil is fed to the thermal cracking step, the remaining part can be any other oil fraction having the same physico-chemical characteristics mentioned above for the heavy vacuum gas oil. The vacuum residue of the topping is a typical fraction which can possibly be used in the feeding of the thermal cracking (II) together with the heavy vacuum gas oil recovered downstream of the visbreaking process.

It is preferably however for the thermal cracking step to be fed with all the heavy vacuum gas oil fraction recovered after the visbreaking.

It is obvious that, when the thermal cracking oven has dimensions for operating with quantities of heavy vacuum gas oil which are greater than those coming from the visbreaking, it is necessary to also use other oil fractions having the characteristics of the heavy vacuum gas oil.

If, on the other hand, the thermal cracking oven has dimensions for operating with quantities of heavy vacuum gas oil which are smaller than the isolated quantities after the visbreaking step, it will be necessary to bleed part of the heavy vacuum gas oil or separate only the desired quantity.

The thermal cracking step (II) is carried out under more severe conditions than the visbreaking step (I), and therefore either at higher temperatures, with the same residence time, or with greater residence times, at the same temperature.

The temperature of the thermal cracking step (II) is usually between 450 and 510°C and the residence times are between 20 and 60 minutes.

At the end of the thermal cracking step the fraction called thermal residue is recovered, which consists of what results from the thermal cracking after removing the light fractions (350°C-).

The stream leaving the thermal cracking is normally fed into a separator where the lighter fractions, those at 350°C-, are separated. The remaining product consists of the thermal residue, which has a density at 15°C of between 1.00 and 1.07, a P value (determined by the Shell method Nr. 1600 of 1983) of between 1.4 and 2.3, an initial distillation point (according to the regulation ASTM D 1160), of between 180 and 220°C, the temperature at which 50% distills of between 440 and 490°C, the temperature at which 90% distills of between 570 and 610°C.

The thermal residue thus recovered is mixed with another heavy oil residue, the same or different from the initial charge, and the mixture thus obtained is refed to the visbreaking step (I).

The mixture of heavy oil residue and thermal residue preferably consists of 5-50% by weight, more preferably from 10 to 40% by weight, even more preferably from 20 to 30% by weight, of thermal residue, the complement to 100 consisting of the heavy oil fraction.

The process of the present invention allows almost all the thermal residue to be eliminated in a combined visbreaking + thermal cracking plant.

Figure 1 represents the process scheme of the present invention.

In the above figure, (A) represents the vis-breaking plant, (B) the distillation unit under vacuum, (C) the Thermal Cracking unit, (D) the atmospheric distillation unit.

With respect to the streams of figure 1, (1) is the heavy oil residue, (2) is the light Vacuum Gas oil, (3) is the heavy Vacuum Gas oil, (4) is the Visbreaking Residue, (5) is the external heavy vacuum Gas oil, (6) is the residue recycled from the fractionation unit, (7) is the thermal Residue.

Figure 1 shows the Visbreaker plant (A), fed by the heavy oil residue (1). From this plant a light stream is obtained, which is sent to an atmospheric distillation unit (D), and a heavy stream, which is sent to a distillation unit under vacuum (B). From this unit a light vacuum gas oil fraction is obtained (2), which is fed to the atmospheric distillation unit (D), together with the heavy vacuum gas oil fraction (3), and a visbreaking residue, which will be used as a component for fuel oils. The heavy vacuum gas oil fraction (3) forms the charge for the Thermal Cracker plant (C), together with the

heavy gas oil obtained as residue (6) of the atmospheric fractionation unit (D), and together with possible charges of a similar composition, of a different origin. A light fraction is obtained from the Thermal Cracker plant (C), which is fed to the atmospheric distillation unit (D), and a thermal residue, which is recycled to the Visbreaker plant.

Figure 2 shows, for comparative purposes, a conventional process of the prior art, in which, there is no recycling of the thermal residue at the end of the thermal cracking step.

The following examples provide a better illustration of the present invention.

# **EXAMPLES**

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Two runs are carried out in the refinery feeding in both cases an atmospheric residue having the following characteristics:

15	Density at 15°C	:	0.981
	P Value	:	2.10
	Conradson carbonaceous residue	:	9.70%
20	Viscosity at 50°C	:	49.3 cSt
	Total sulphur	:	2.82%
25	Distillation ASTM D1160		
30	Initial boiling point		: 197°C
	5% Volume evaporated		: 343°C
35	10% Volume evaporated		: 393°C
	20% Volume evaporated		: 429°C
	30% Volume evaporated		: 455°C
40	40% Volume evaporated		: 480°C
	50% Volume evaporated		: 512°C
45	60% Volume evaporated		: 552°C
	70% Volume evaporated		: 609°C
50	80% Volume evaporated		: 655°C
	90% Volume evaporated		: 711°C
55	95% Volume evaporated		: 822°C
	Final point		: 850°C

The feeding to the Thermal Cracking (II) had the following characteristics:

5	Density at 15°C	: 0.975
	Conradson carbonaceous residue	: 1.04%
	Distillation ASTM D1160	
10	Initial boiling point	: 275°C
	5% Volume evaporated	: 325°C
15	10% Volume evaporated	: 348°C
	20% Volume evaporated	: 375°C
20	30% Volume evaporated	: 398°C
	40% Volume evaporated	: 414°C
25	50% Volume evaporated	: 436°C
	60% Volume evaporated	: 448°C
30	70% Volume evaporated	: 468°C
	80% Volume evaporated	: 485°C
35	90% Volume evaporated	: 510°C
	95% Volume evaporated	: 535°C
40	Final point	: 587°C

With reference to figure 1, the feeding to the Thermal Cracking consists (in both tests 1 and 2) of 60% of HVGO from the distillation unit under vacuum (B), 30% from the bottom of the atmospheric fractionation unit (D), and the remaining 10% of heavy gas oil ex vacuum pot of the topping, the latter fraction obviously coming from other parts of the refinery.

The thermal residue, after elimination of the light products, had the following characteristics:

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	Density at 15°C	:	1.053
5	P Value	:	2.00
	Total sulphur	:	3.68%
10	Distillation ASTM D1160		
10	Initial boiling point	:	205°C
	5% Volume evaporated	:	383°C
15	10% Volume evaporated	:	408°C
	20% Volume evaporated	:	426°C
20	30% Volume evaporated	:	442°C
	40% Volume evaporated	:	456°C
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	50% Volume evaporated	:	474°C
30	60% Volume evaporated	:	490°C
30	70% Volume evaporated	:	520°C
	80% Volume evaporated	:	544°C
35	90% Volume evaporated	:	594°C
	95% Volume evaporated	:	618°C
40	Final point	:	>750°C

In comparative test 2 the thermal residue was fluxed with gas oil to give fuel oil and the subsequent visbreaking step was fed with other fresh heavy oil residue.

In test 1 the thermal residue was mixed with other heavy oil residue, and the whole mixture was sent to the visbreaking step (I). The above composition consisted of 25% of thermal residue and the remaining 75% of fresh heavy oil residue.

The two runs were carried out according to the scheme of figures 1 and 2, i.e. test 1 was carried out recycling almost all of the thermal residue leaving the thermal cracking step, whereas comparative test 2 was carried out according to the scheme of figure 2, i.e. without recycling the thermal residue obtained leaving the thermal cracking step.

In the above experiment the temperature at the bottom of the visbreaking is 485°C, whereas the temperature of the thermal cracking oven is 495°C.

The results of the two tests, both carried out over a period of 20 days, are shown in table 1.

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TABLE 1

FRACTION	YIELD % w/w	
	Test 1	Test 2
Gas	3.8	2.1
L.P.G.	3.7	2.9
C5/C6	2.5	2.1
C7 - 140 °C	8.6	5.8
Gas oils	45.2	35.9
Thermal residue	0.2	16.5
Visbreaking residue	36	34.7

The above yield data, which refer to average values, show how the process of the present invention leads to a decisive improvement in the yields of gas oils (about 9%) and a very small increase (about 2%) in the C7-140°C distillates. The increase of the other distillates is less significant.

A very important result lies in the consistent reduction of residues (visbreaking + thermal cracking) of more than 10 percentage points, and therefore, proportionally, of the quantity of gas oil used as fluxing agent.

# Claims

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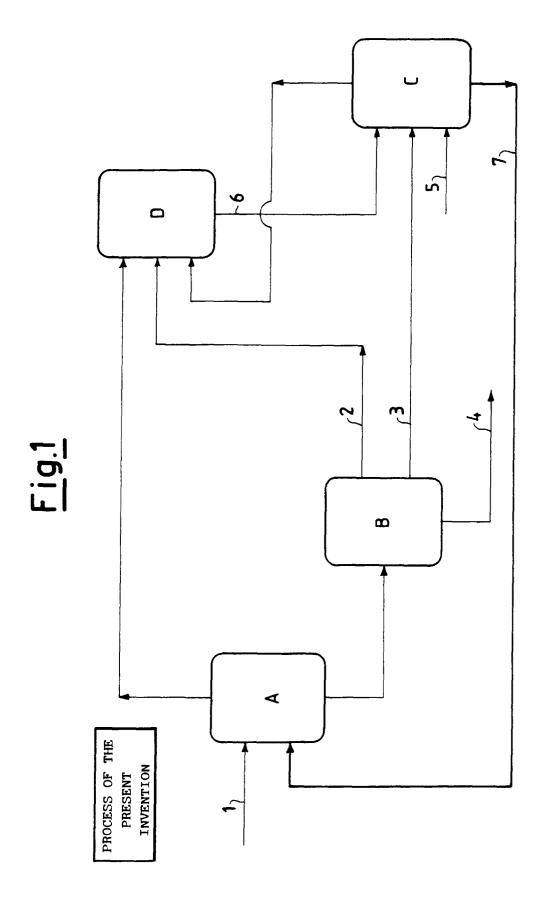
1. Process for reducing the viscosity of heavy oil residues, which comprises a first step for the visbreaking of heavy oil residues and a second step for the thermal cracking of the heavy gas oil formed in the vis-breaking process, the above thermal cracking producing a thermal residue as well as lighter products, said process being characterized in that:

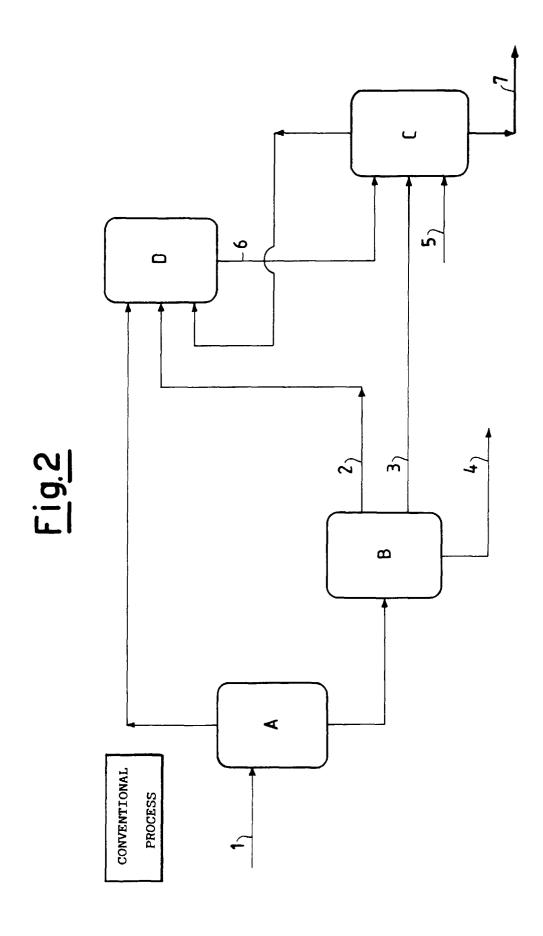
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- (a) the thermal residue obtained in the thermal cracking step is almost totally recovered;
- (b) a composition consisting of fresh heavy oil residues diluted with the thermal residue recovered in step (a) is refed to the vis-breaking step.
- 2. Process according to claim 1, characterized in that the visbreaking process is carried out without hydrogen, catalysts and hydrogen donor solvents.
  - 3. Process according to claim 1, characterized in that the heavy oil residue basically consists of atmospheric residue.
- **4.** Process according to claim 1, characterized in that a mixture of fresh heavy oil residue and thermal residue is refed to the visbreaking step, consisting of 5-50% by weight of thermal residue, the complement to 100 consisting of fresh heavy oil residue.
- 5. Process according to claim 4, characterized in that the composition refed to the visbreaking step consists of 10-40% by weight of thermal residue.
  - **6.** Process according to claim 5, characterized in that the composition refed to the visbreaking step consists of 20-30% by weight of thermal residue.

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# **EUROPEAN SEARCH REPORT**

Application Number EP 96 20 2825

Category	Citation of document with indication, of relevant passages	where appropriate,	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
A	US-A-4 836 909 (RESEARCH RESIDUAL OIL PROCESSING) * the whole document *	ASSOCIATION FOR :	1-6	C10G51/02
A	US-A-4 663 021 (FUJI STAN SUMIMOTO METAL INDUSTRIES			
A	EP-A-0 249 052 (VEB PETRO KOMBINAT SCHWEDT)	CHEMISCHES		
A	DE-A-35 04 941 (LINDE)			
A .	REVUE DE L'ASSOCIATION FR TECHNICIENS DU PETROLE, no. 240, November 1976, pages 27-31, XP002019993 MAZEL: "LES PROCEDES DE PARTIE)" * figure 2 AND 3 *	PARIS,		
				TECHNICAL FIELDS SEARCHED (Int.Cl.6)
				C10G
	The present search report has been drawn	up for all claims		
	Place of search	Date of completion of the search		Examiner
	THE HAGUE	2 December 1996	Mic	chiels, P
X: par Y: par doc	CATEGORY OF CITED DOCUMENTS  ticularly relevant if taken alone ticularly relevant if combined with another sument of the same category hnological background	T : theory or principle E : earlier patent docu after the filing dat D : document cited in L : document cited for	ment, but pub e the application other reasons	lished on, or n