

Description

This invention relates to the processing of residual petroleum stocks by visbreaking in the presence of certain highly aromatic hydrogen-donor materials.

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 required to make the residual stocks useful as fuel oils. The visbreaker feedstock 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 feedstock 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 about 425 to about 525°C at about 450 to about 7000 kPa. Light gas-oil may be recycled to lower the temperature of the effluent to about 260 to about 370°F. 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.

Various visbreaking processes have been proposed in which residual oils are added at the visbreaking stage with or without added hydrogen or hydrogen-donors. For example, U.S. Patent 3,691,058 describes the production of single ring aromatic hydrocarbons (70—220°C) by hydrocracking a heavy hydrocarbon feed (565°C-) and recycling 32—70°C and 220°C+ product fractions to extinction. This is integrated with visbreaking of residua in the presence of 1 to 28 weight% free radical acceptor at 370—480°C in the presence or absence of hydrogen (to enhance residua depolymerization). U.S. Patent 4,067,757 describes a process which involves passing a resid up through a bed of inert solids (packed bed reactor) in the absence of hydrogen or presence of 9—1800 Nm³ hydrogen per m³ resid at 400—540°C to enhance production of middle distillate (175—345°C).

U.S. Patent 2,953,513, proposes the production of hydrogen-donors by partial hydrogenation of certain distillate thermal and catalytic tars, boiling above 370°C, containing a minimum of 40 weight% aromatics, to contain H/C ratios of 0.7—1.6. The resid feed is then mixed with 9—83 volume% of hydrogen donor and thermally cracked at 427—482°C to produce low boiling products. U.S. Patent 4,090,947 describes a thermal cracking process (425—540°C) for converting residu to lighter products in the presence of 10—500 volume% hydrogen-donor. The hydrogen-donor is produced by hydrotreating premium coker gas oil (345—480°C) alone or blended with gas oil produced in the thermal cracker. U.S. Patent 4,292,168 proposes upgrading heavy hydrocarbon oils without substantial formation of char by heating the oil with hydrogen and a hydrogen transfer solvent without a catalyst at temperatures of about 320 to 500°C and a pressure of 2200 to 18000 kPa for a time of about 3 to 30 minutes. Examples of hydrogen-donor transfer solvents include pyrene, fluoranthene, anthracene and benzantracene. U.S. Patent 4,292,686 describes a process for contacting a resid with a hydrogen-donor at 350 to 500°C and a pressure of 2 to 7 MPa with liquid hourly space velocities ranging from 0.5 to 10.

In U.S. Patent 4,428,828, there is described a process for visbreaking a deasphalted oil, and subsequently reblending it with the asphaltic fraction to produce a product of low viscosity and pour point. This process reduces the amount of cutter stock required to make relatively low viscosity products. The reduction in cutter stock requirement is achieved by minimizing coke formation in the visbreaker, by excluding the worst coke formers, permitting more severe operation of the visbreaker. Although this approach helps, it does not provide a complete solution, moreover, it requires a solvent deasphalting unit.

The present invention is based on the observation that by visbreaking heavy petroleum residu in the presence of certain hydrogen-donor solvents, visbreaking severity can be greatly increased without significant coke or sediment formation.

Accordingly, the present invention provides 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_A and H_o hydrogen 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 the process of the invention 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 suitable hydrogen-donors are highly aromatic petroleum refinery streams, such as fluidized catalytic cracker (FCC) "main column" bottoms, FCC "light cycle oil," and thermofor catalytic cracker (TCC) "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 about 1:1, and an average boiling point above 230°C.

An FCC main column bottoms refinery fraction is a highly preferred hydrogen donor solvent for use in the process of the invention. A typical FCC main column bottoms (or FCC clarified slurry oil (CSO)) contains a mixture of constituents as represented in the following mass spectrometric analysis:

Compounds	Aromatics	Naphthenic/ Aromatics	Labile H ₂ %
Alkyl-Benzene	0.4	—	0.00
Naphthene-Benzenes	—	1.0	0.03
Dinaphthene-Benzenes	—	3.7	0.16
Naphthalenes	0.1	—	0.00
Acenaphthenes (biphenyls)	—	7.4	0.08
Fluorenes	—	10.1	0.11
Phenanthrenes	13.1	—	—
Naphthene-phenanthrenes	—	11.0	0.18
Pyrenes, fluoranthenes	20.5	—	0.00
Chrysenes	10.4	—	0.00
Benzofluoranthenes	6.9	—	0.00
Perylenes	5.2	—	0.00
Benzothiophenes	2.4	—	—
Dibenzothiophenes	2.4	—	—
Naphthobenzothiophenes	—	2.4	—
Total	64.4	35.6	0.60

A typical FCC main column bottoms or clarified slurry oil has the following analysis and properties:

Elemental Analysis, Weight%	
C	89.93
H	7.35
O	0.99
N	0.44
S	1.09
Total	99.80
Pour Point, °C: 10	
CCR, %: 9.96	
Distillation:	
IBP, °C:	254
5% °C:	338
95%, °C:	485

Another preferred hydrogen-donor material is a light cycle oil (LCO) taken from the main tower fractionator of a FCC operation of the riser type in which the LCO results from a distillation cut point not

(13)

substantially above about 370°C.

A typical FCC LCO has the following analysis and properties:

	Boiling Point Distribution, weight%	FCC LCO
5	215°F	4.8
	215—343°F	87.9
10	343—427°F	7.3
	427—538°F	—
	538°F+	—
15	H, weight%	10.64
	S, weight%	1.01
20	N, weight%	0.24
	Ni + V, PPM by weight	—
	CCR, weight%	—
25	Paraffins, weight%	12.7
	Mononaphthenes	11.7
30	Polynaphthenes	12.8
	Monoaromatics	24.7
	Diaromatics	21.7
35	Polyaromatics	14.3
	Aromatic sulfur type	2.1
40	Total hydrogen, weight%	9.0—9.5

FCC main tower bottoms and light cycle oils are obtained by the catalytic cracking of gas oil in the presence of a solid porous catalyst. More complete descriptions of the production of these petroleum fractions are described in U.S. Patents 3,725,240 and 4,302,323, for example.

A process closely related to FCC is TCC, or thermoform catalytic cracking. Thermoform catalytic cracking is roughly analogous to FCC; both processes operate without addition of hydrogen, both operate at relatively low pressure, and both require frequent regeneration of catalyst. The products of thermoform catalytic cracking will have hydrogen contents and distribution very similar to those obtained as a result of FCC. Accordingly, light cycle oils obtained as product streams from a TCC process, or main column bottoms streams obtained as a result of a TCC process, are also suitable for use in the process of the invention.

Another source hydrogen donor solvent for use in the process of the invention is the heavy fraction normally associated with lubricating oil. The lubricating oil may be either a paraffin based oil or a naphthenic based oil. Preferably the lubricating oil is first subjected to aromatics extraction, so that the extract will have more ideal properties.

It is also possible to use the aromatic extract from a lube oil plant. By itself, this material will be too highly aromatic and will not be a very good hydrogen-donor; however, it may be subjected to conventional hydrogenation to produce a hydrogen-donor diluent with the right hydrogen content and distribution.

Hydrotreating the aromatic extract from a lube oil plant is a very expensive operation but this may be justified when the total cost of using hydrotreated-aromatic extract is less than the cost of using lubricating oil base stock.

Diluents or solvents with the right hydrogen content and distribution are produced also by the catalytic dewaxing of lubricating oil stocks and the catalytic dewaxing of fuels.

Another suitable hydrogen donor solvent source is the highly aromatic tars produced in olefin crackers.

Further sources of suitable hydrogen donor solvents are the various coal liquifaction processes.

Particularly preferred hydrogen-donor solvents are those which are recovered from liquified coal extract, hydrogenated and recycled back to the coal liquifaction step. Coal liquifaction processes are, of course, exceedingly expensive, and a coal liquifaction plant would not normally be constructed merely to generate solvent for addition to a visbreaker. Coal liquifaction plants may, however, be operated adjacent to a convention refinery with a visbreaker, and in these special situations a solvent stream derived from coal liquifaction may be used with good effect.

Normally it will be most economic to use whatever solvents can be found in a refinery, without hydrotreating, for use in the process of the invention. It is also possible, although usually more expensive, to take a hydrogen-donor solvent which is not entirely satisfactory, and subject it to conventional hydrogenation treatments to increase its hydrogen content and/or alter its hydrogen distribution. If such a charge stock is very highly aromatic, quite a substantial amount of hydrogen must be added to make the hydrogen-donor solvent suitable for use in the process of the invention. Excessive hydrogenation should be avoided, however, since it is not beneficial to saturate all of the aromatic rings in the hydrocarbon solvent. The reasons for this will be understood from the following discussion of hydrogen-donor properties.

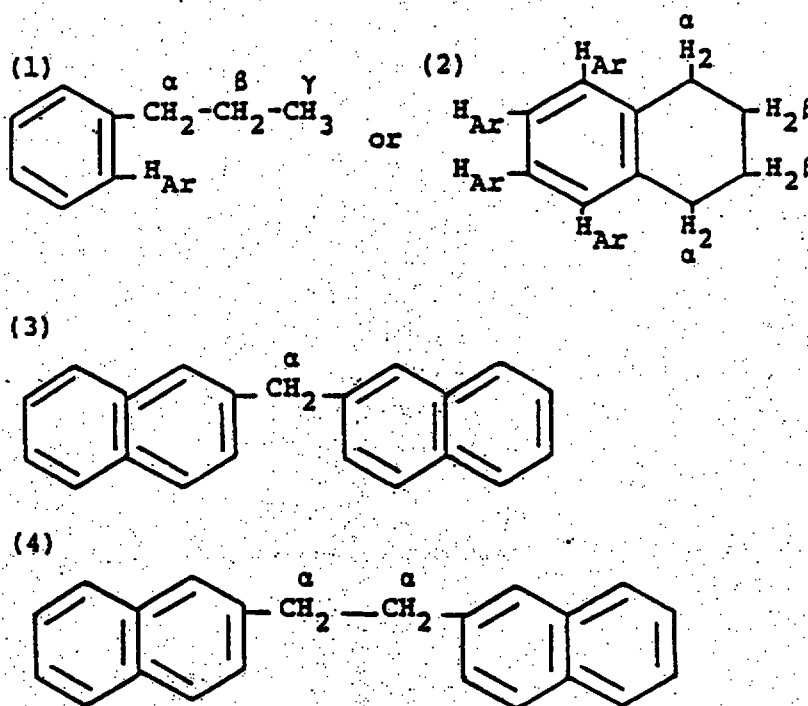
Critical features of the hydrogen-donor solvent are its particular proportions of aromatic, naphthenic and paraffinic moieties and the type and quantity of hydrogen associated therewith. A high content of aromatic and naphthenic structures together with a high content of alpha hydrogen provides a superior hydrogen-donor material.

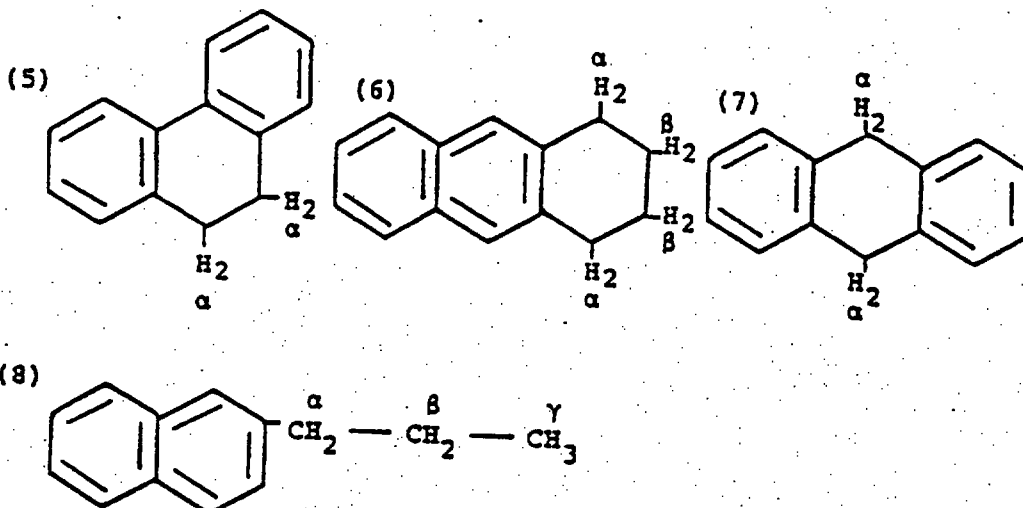
All solvents used according to the invention are hydro-aromatic solvents.

The hydrogen transfer ability of a donor material can be expressed in terms of specific types of hydrogen content as determined by proton nuclear magnetic resonance spectral analysis. Nuclear magnetic resonance characterization of heavy hydrocarbon oils is well developed. The spectra are divided into four bands (H_a , H_b , H_γ and H_{Ar}) according to the following frequencies in Hertz (Hz) and chemical shift (δ):

	H_a	H_b	H_γ	H_{Ar}
Hz	0—60	60—100	120—200	360—560
δ	0—1.0	1.0—1.8	2.0—3.3	6.0—9.2

The H_{Ar} protons are attached directly to aromatic rings and are a measure of aromaticity of a material. H_a protons are attached to non-aromatic carbon atoms themselves attached directly to an aromatic ring structure, for example alkyl groups and naphthenic ring structures. H_b protons are attached to carbon atoms which are in a second position away from an aromatic ring, and H_γ protons are attached to carbon atoms which are in a third position or more away from an aromatic ring structure. This can be illustrated by the following:





Some alpha hydrogens are not donatable, for example the alpha hydrogen in toluene. The alpha hydrogens shown in compound (8) above, for example, also are not donatable. Compound (8) is not, therefore, a hydro-aromatic solvent.

The H_{Ar} protons are important because of their strong solvency power. A high content of H_{Ar} protons is particularly significant because H_{Ar} protons are labile and are potential hydrogen-donors.

The hydrogen-donor material employed in the process of the invention has a hydrogen content distribution such that the H_{Ar} proton content is at least 20 percent, preferably from 20 to 50 percent, and the H_{Ar} proton content is at least 20 percent, preferably from 20 to 50 percent. For example, in H-donor streams containing 9.5 weight% total hydrogen, the α -hydrogen content should be at least 1.9 weight% (20% of total hydrogen content). The balance of the hydrogen is non- α hydrogen.

Hydrogen-donors possessing the desired hydrogen content distribution may frequently be obtained as a bottoms fraction from the catalytic cracking or hydrocracking of gas oil stocks in the moving bed or fluidized bed reactor processes. In general, depending upon such conditions as temperature, pressure, catalyst-to-oil ratio, space velocity and catalyst nature, a high severity cracking process results in a petroleum residuum solvent having an increased content of H_{Ar} and H_{Ar} protons and a decreased content of the less desirable non- α -hydrogen.

The proton distribution of examples of various highly aromatic hydrocarbon by-product streams are shown below.

16

Example	H _a (weight%)	Non- α -Hydrogen (weight%)	H _{Ar} (weight%)	H Total (weight%)
<u>FCC/LCO</u>				
#1 (used in Table 4)	22.2 (2.07)	57.8	20.0	9.34
#2 (used in Table 5)	34.1 (3.18)	36.8	29.1	9.32
#3	34.3 (3.19)	35.5	30.2	9.30
<u>FCC/CSO</u>				
#1 (used in Table 3)	34.0 (2.43)	33.0	33.0	7.15
#2	30.0 (2.15)	35.0	35.0	7.17
#3	19.4 (1.39)	65.0	5.0	7.16
<u>FCC/MCB</u>				
#1	36.0 (2.65)	32.0	32.0	
#2	36.4 (2.68)	18.8	44.8	
#3	18.5 (1.36)	64.3	17.2	
#4	18.1 (1.33)	67.7	14.2	
<u>TCC/Syntower Bottoms</u>				
#1	29.8 (2.78)	28.8	41.4	
#2	18.2 (1.70)	58.8	23.0	
#3	16.3 (1.52)	68.1	15.6	
<u>SRC Recycle Oil</u>				
	27.1	21.6	46.3	
<u>TCC Distillate</u>				
#1	21.5 (2.39)	58.4	20.1	
#2	20 (2.07)	58	22	
#3	6.9 (0.89)	85.1	8	

All of the values reported above are for non-hydrotreated materials.

From the data given above, it will be seen that hydrocarbons having the same general process derivation may or may not have the desired proton distribution. For example, FCC/MCB #1 and #2 and FCC/CSO #1 and #2 have the desired proton distribution while FCC/MCB #3 and #4 and FCC/CSO #3 do not. Furthermore, although it is preferred that the highly aromatic hydrogen donor component is derived from petroleum, it will be noted that the SRC recycle solvent closely resembles FCC/MCB #1 and #2.

In most hydrocarbon processes, there is a tradeoff between reaction temperature and residence time of reactants. Because visbreaking is a well-known and widely practiced process, however, sophisticated correlations have been developed so that it is possible to express precisely the severity of the visbreaking process.

An expression of the "severity" of a particular visbreaking operation does not mean that a certain degree of conversion can be predicted or obtained or that a certain amount of coke or sediment will be formed; rather it means that it is possible to predict that if all other reaction parameters are unchanged (feed composition, reactor pressure, for example) except for the temperature and residence time in the reactor, two operations can be compared and it can be determined whether one process is more severe than the other.

Fairly elegant equations and tables have been developed for this purpose. Typical of such presentations is the discussion of "soaking factor" in Petroleum Refinery Engineering-Thermocracking and Decomposition Process — Equation 19—23 and Table 19—18, in Nelson — Modern Refining Technology, Chapter 19.

Although that text uses the term "soaking factor", the term "ERT" or "Equivalent Reaction Time" in seconds as measured at 427°C is used herein to express visbreaking severity; numerically, soaking factor is the same as ERT.

ERT refers to the severity of the 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, 60 seconds of residence time at 427°C is equivalent to 60 ERT, and increasing the temperature to 456°C would make the operation five times as severe, i.e. 300 ERT. Expressed in another

way, 300 seconds at 427°C is equivalent to 60 seconds at 456°C, and the same product mix and distribution should be obtained under either set of conditions.

Most visbreakers operate with a coil, some operate with a combination of a coil and a drum, and a few operate primarily with a drum. As far as product distribution is concerned, it is believed that it is of no great significance whether the residence time is obtained in a coil, drum, or combination of both.

Frequently, visbreaker units are built with a coil, and when an expansion of the unit's capacity is desired it is cheaper to add a soaking drum (and increase the oil's residence time) than to build and operate a bigger furnace and achieve a higher reactor temperature.

Typical of the coil/soaking drum combinations is the process described in U.S. Patent 4,247,387.

The process of the invention is advantageously carried out in refinery facilities of the type shown diagrammatically in the accompanying drawing. Referring to the drawing, 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 hydrogen-donor material supplied through line 50 in an amount 0.1 to 50 weight%, preferably 0.1 to 20 weight%, 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. This stream is cooled by admixture with a quench stream from line 31, and the visbreaker effluent continues through line 29 to distillation column 30 where it is fractionated to obtain C₅-gases (C₃, C₄ and lower) and a C₅-135°C naphtha fraction from the top through line 34. A 220—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 C₅- off-gas stream 38, mainly C₃ or C₄ and lower, and a C₅-135°C naphtha 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, thus avoiding the need for separation.

The process of the invention is not, of course, limited to the visbreaker/distillation scheme discussed above. Any visbreaker arrangement 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 may also be used, i.e. much of the visbreaking reaction may be accomplished in a coil, while the remainder of the visbreaking occurs in a soaking drum down-stream of the coil.

Any distillation scheme known in the art may 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 light products which are obtained as by-products in the visbreaking process are not particularly desirable for blending with other refinery streams. Usually, the visbroken product will be processed to produce the maximum amount of fuel oil, and this means that as much of the resulting light ends that can be tolerated in the product, will be left in. Usually the limiting factor on light ends is the flash point of the fuel.

Although a blending operation is shown in the drawing, in which cutter stock is blended with heavy fuel oil from line 33, the process of the invention has the great advantage of minimizing the amount of cutter stock required. Blending is not an expensive or difficult unit operation, but it may be eliminated, in some circumstances, by simply adding the hydrogen-donor and/or cutter stock to the visbreaker feed.

The visbreaker may also be integrated with a deasphalting unit, either upstream or downstream of the unit, as described in U.S. Patent 4,428,824. When a combination of deasphalting and visbreaking is practiced, it will usually be possible to push the visbreaker a little harder than could otherwise be tolerated. In some instances, it may be preferable to subject deasphalted oil to conventional visbreaking, operated without hydrogen-donor solvent, while subjecting the asphaltic fraction to hydrogen-donor visbreaking. Alternatively, the process described in U.S. Patent 4,428,824 may be practiced, wherein the only visbreaking that occurs is on deasphalted oil. In this instance, addition of hydrogen-donor solvent to the visbreaker feed (consisting of a deasphalted oil) will permit improved operation.

The process of the invention is suitable for upgrading a wide variety of heavy liquid hydrocarbon oils at least 75 weight percent of the components of which boil at above 370°C. Included in this class of materials are residual fractions obtained by catalytic cracking of gas oils; solvent extracts obtained during the processing of lube oil stocks, asphalt precipitates obtained from deasphalting operations, high boiling bottoms or resids obtained during vacuum distillation of petroleum oils and tar sand bitumen feedstocks.

Visbreaking process conditions can vary widely based on the nature of the heavy oil material, the hydrogen-donor material 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. Expressed as ERT, the process of the invention operates at and Equivalent Reaction Time at 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 limit of severity is determined primarily by product quality. Visbreaking is a good and inexpensive process, and once a visbreaker has been installed, it does not cost much to run it at high severity in order to achieve the maximum viscosity reduction possible with a given feed stock. However, the two limiting factors in the visbreaker operation are the formation of coke (which tends to plug the coil and/or soaking drum used in the visbreaking operation and also take the product out of specification) and sediment formation in the product.

Sediment formation is a very complex phenomenon. As a generalization, it can be stated that, if the fuel composition is changed enough, the asphaltic materials no longer dissolve in the product and hence settle out as sediment. The problem becomes worse when cutter stocks or blending stocks are added to the visbreaker product; asphaltics or other materials that would remain dissolved in the visbreaker product are no longer soluble upon blending the visbreaker product with other materials.

The pressure employed in a 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 are 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% vaporization material at the visbreaker coil outlet. Lighter solvents 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.

An important aspect of the invention is the improvement of visbreaker performance by optimizing operational severity for heavy oil feedstocks. In general, as severity is increased, increased yields of distillate and gaseous hydrocarbons are obtained with a reduction in the amount of cutter oil required for blending to obtain specification-viscosity residual fuel oil. At high severities, however, there is an increased tendency to form coke deposits which result in plugged heater tubes and/or the production of unstable fuel oils as measured by sediment formation. By means of the process of the invention, the use of certain hydrogen-donors has been found to suppress the formation of sedimentation species and thus permit a higher severity operation than is otherwise possible without adding hydrogen donors, while still producing stable fuel oil. As an example, the visbreaking of a heavy petroleum feed stock conventionally carried out at a severity of 500 ERT seconds may be increased to a higher severity of 800 ERT seconds to obtain a fuel oil product free of sedimenting species. At high severities, the cutter stock requirement is substantially reduced which thus represents a considerable financial saving.

According to a further aspect of the invention, non-hydrotreated solvents derived from thermal and fluidized catalytic cracking processes can also be used with advantage in the thermal cracking of heavy oils at higher severities in order to convert significant quantities of the heavy oil into lighter products.

Thus, the present invention also provides a process for the thermal cracking a heavy oil which comprises subjecting the oil to an elevated temperature for a period of time corresponding to an equivalent reaction time of 1500 to 15,000 ERT seconds at 427°C, in the presence of from 0.1 to 50 weight%, based on the heavy oil, of a non-hydrotreated solvent derived from a thermal or fluidized catalytic cracking process having a content of H_A and H_B hydrogen each of at least 20 percent of the total hydrogen content, and recovering lighter products from the reaction mixture.

The following Examples illustrate the invention.

Examples

A series of visbreaking experiments on heavy residual stocks was carried out at a severity of 800 ERT seconds in the presence of 2.5 and 5.0 weight% of the FCC/CSO #1 hydrogen-donor identified above.

The feed was an Arab Heavy residual stock which had been fractionated to two slightly different cut points. Feed properties were as follows (Table 1):

TABLE 1

	Nominal initial boiling point, °C	454	496
5	Viscosity, mm ² /S at 38°C	1079.4	4789.2
	66°C	89.6	957.4
	Pour point, °C	38	48
10	APT	7.4	5.9
	Specific gravity, 15°C	1.0184	1.0295
	Aromatics sulfur content, weight%	5.16	5.4
15	CCR, weight%	16.3	18.3

The cutter stock used to dilute the product to meet viscosity specifications had the properties given in Table 2.

TABLE 2

25	API	37.4
	Specific gravity, 15°C	0.8377
30	ASTM—D86 Distillation, °C	
	10%	245
	30%	254
	50%	264

Conventional visbreaking of these Arab Heavy feeds is limited by sediment formation. Table 3 below shows the effect of solvent addition upon visbreaking. Viscosity reduction was significantly better for visbreaking in the presence of CSO.

The feed used in this experiment was the 496°C+ Arab Heavy. The experimental apparatus used was a laboratory visbreaker, basically a batch reactor which closely simulated a commercial visbreaker.

The data in Table 3 do not show a simple dilution or thinning effect due to the addition of hydrogen donor. It would be expected that adding a relatively thin solvent to the visbreaker product would reduce somewhat the viscosity of the product. To compensate for this thinning effect, the same amount of hydrogen-donor added to the feed in accordance with the invention, was added to the product of the prior art process. Some small amount of viscosity reduction clearly occurred because of the addition of 2.5% clarified slurry oil, but it was added in both the test illustrating the process of the invention and the test showing the prior art method. Accordingly the viscosity, pour point and sedimentation values reported in Table 3 are all on a uniform basis, i.e., the stated amount of FCC/CSO was added before any viscosity, pour point or sedimentation tests were run.

The viscosity and pour point test were conducted before cutter stock was added. The sedimentation test was conducted after cutter stock was added. Usually enough cutter stock is added to reduce the viscosity and/or pour point of the product to the desired level. A problem encountered with severe visbreaking is that after addition of cutter stock, sediment forms. The sediment is probably asphalt that is soluble in the visbreaker product, but relatively insoluble in the cutter stock. In general, as more cutter stock is added (to meet viscosity requirements of the product) more asphalt or other sediment will precipitate. Refiners would like to achieve product specifications without any cutter stock addition, but frequently addition of 10, 20 or even 30 weight% cutter stock to visbreaker products is necessary to meet viscosity specifications, or occasionally, density specifications. Addition of 10 and 20 weight% cutter stock is believed representative of amounts of cutter stock frequently added in refinery installations.

TABLE 3
Clarified Slurry Oil Hydrogen Donor

	Added before visbreaking				Added after visbreaking			
	2.5		5.0		2.5		5.0	
5 Weight% LCO Hydrogen-donor								
Viscosity, mm ² /s at 82°C	757		667		6472		1619	
10 Pour Point, °C	24		18		49		43	
Weight% Cutter Stock added to: Blend of CSO with visbroken resid					10	20	10	20
15 Visbroken blend of CSO and resid	10	20	10	20				
Sediment, volume%*	Tr	Tr	Tr	3.3	.85	16	.9	14.5

20 * Tr = trace.

The benefits of adding, for example 2.5 weight% FCC clarified slurry oil to the visbreaker feed are evident. The viscosity has been profoundly reduced by the addition of only 2.5 weight% hydrogen-donor to the feed, rather than to the product of the visbreaker.

25 The pour point of the product has been significantly reduced also; 2.5 weight% clarified slurry oil reduce the pour point from 49°C to 24°C. Similar results are obtained due to the addition of 5 weight% CSO, reducing the pour point from 43°C to 18°C.

The sediment test used was the centrifuge method used to determine the compatibility of sediment in blended marine fuel oil. This method is used to predict the volume% of incompatible sediment in blended 30 marine fuel oils.

A 100 ml sample of the blended fuel oil is centrifuged in a heated centrifuge (65.5°C ± 1°C) centrifuged for 3 hours at a relative centrifugal force of 700 units. Further details of the centrifuge operation can be taken from ASTM D—96.

35 There is another test method commonly referred to as a hot filtration test, which gives weight% sediment after hot filtration and washing with normal hexane. A fuel with 1 volume% sediment will usually, but not always, have about 0.5 weight% sediment. All testing reported herein uses the hot centrifuge method so results are reported in volume% sediment.

In the sediment test used herein, there is no dilution of the sample with virgin gas oil; rather the sample is charged to the centrifuge without dilution. There is nothing wrong with adding virgin gas oil to achieve 40 the standardized viscosity before running the test, but every addition of a new hydrocarbon species makes it harder to interpret experimental results. The significance of the results shown in Table 3 is the dramatic reduction in sediment formation obtained by adding 2.5 weight% CSO to the visbreaker feed.

Even when blended with 20 weight% cutter stock, the visbroken product of the invention had only a trace, or acceptable, amount of sediment. In contrast, the prior art method, in which 2.5 weight% CSO was 45 added after visbreaking, produced 16 volume% sediment after addition of 20 weight% cutter stock.

The advantages of adding 2.5 weight% CSO to the visbreaker feed may be summarized as follows.

- (i) lower viscosity
- (ii) lower pour point
- (iii) more cutter stock tolerated.

50 Another series of tests was run using the slightly lighter Arab Heavy resid, having a 454°C IBP. In this test, significantly larger amounts of light cycle oil hydrogen-donor were added, namely 10 and 20 weight%; light cycle oil. In this example, both the feed and the hydrogen-donor diluent are slightly lighter, or lower in molecular weight, as compared to the feed and hydrogen-donor used in the examples reported in Table 3. The hydrogen content and distribution of the hydrogen-donor used in this example is given above under 55 the discussion of FCC/LCO #1.

The test procedure used, and a visbreaking severity (800 ERT seconds) were identical to those used for the testing reported in Table 3.

TABLE 4
Light Cycle Oil Hydrogen Donor

	Added before visbreaking		Added after visbreaking	
5				
Weight% LCO hydrogen donor	10	20	10	20
Viscosity, mm ² /s at 54°C	189.9	79.8	259.2	110.9
10				
Pour point, °C	-7	-15	2	-1
Weight% Cutter Stock added to:				
Blend of LCO with visbroken resid			15	15
15				
Visbroken blend of LCO and resid	15	15		
20				
Sediment, volume%	1	0.5	3	5

These data show that a significant reduction in the amount of sediment in the visbreaker product after addition of cutter stock can be obtained by the practice of the invention.

Table 5 below illustrates that an increase in visbreaking severity in the presence of 10 weight% LCO translates into a considerable savings in the cutter stock required to make a 120 mm²/s (50°C) fuel oil product. By visbreaking at 800 ERT seconds in the presence of 10 weight% LCO, a 191 m³/day reduction in cutter stock requirement is achieved, in comparison to conventional visbreaking at 500 ERT seconds.

TABLE 5
454°C + Arab Heavy Resid

	Conventional Visbreaking	H-donor Visbreaking
30		
Severity, ERT seconds	500	800
35		
Feed Rate, m ³ /day		
Resid	2020	2020
H-Donor (LCO)	0	202
40		
Products, weight%		
C ₄ -	1.58	2.3
C ₅ -149°C	3.00	4.6
149°C+ Bottoms	95.42	93.1
45		
Viscosity of 149°C+ Bottoms, mm ² /s at 50°C	1560	160
Cutter Stock required to make 120 mm ² /s heavy fuel oil, m ³ /day	445	52
50		
Total Cutter Stock required including H-Donor, m ³ /day	445	254

Additional testing was carried out on the 496°C+ Arab Heavy resid, and the results obtained are set out in Table 6.

0 133 774

TABLE 6
496 C+ Arab Heavy Resid: 800 ERT seconds

Bottoms	LCO Added to Feed		LCO Added to Visbroken	
Amount LCO Added, weight%	10	20	10	20
Mixture Viscosity, mm ² /s at 82°C	177	53.5	939	246
Sediment, volume%	GT 0.05	GT 0.05	1.6	17.0

Additional tests were conducted on a different feedstock, a heavy Nigerian resid feed. Feed and cutter stock properties were as set out in Table 7, and test results are set out in Table 8.

TABLE 7

	510°C + Nigerian Heavy Resid	Cutter Stock
APT	10.5	24.6
Specific Gravity (15°C)	0.9965	0.9065
Pour Point, °C	100	-7
Viscosity, mm ² /s at 50°C	38	2.2
80°C	1859.8	1.24
100°C	565.9	—
<u>Distillation, °C</u>	<u>D1160—1</u>	<u>D86</u>
5%	500	189
10%	528	198
30%	591	231
50%	598 (@ 33%)	270
95%	—	373

0 133 774

TABLE 8
510°C + Heavy Nigerian Resid

	BASE	20% TCC Distillate #1 Added to Feed
Severity, ERT Seconds	1200	1500
Feed Rate, m ³ /day		
Resid	636	636
H-Donor (TCC Distillate #1)	0	127
Product Yields, weight% (m ³ /day)		
C ₄ -	1.7	2.0
Naphtha (C ₅ -166°C)	4.8 (41)	5.3
Distillate (166—343°C)	11.2 (80)	27.6 (223)
Bottoms (343°C+)	82.4 (512)	65.2 (483)
Viscosity of bottoms, mm ² /s at 50°C	15687	12456
Cutter Stock required for 120 mm ² /s product, m ³ /day	244	222
Overall yields, m ³ /day		
Naphtha	41	47
Distillate	(164)	(126)
Comparison, m ³ /day		
Naphtha	BASE	6
Distillate	"	38

NOTE: In both cases, the viscosity of the bottoms (343°C+) increased at higher severity.

Table 9 below sets out the results of a test conducted using Durban Visbreaker feed.

TABLE 9
Durban Visbreaker Feed

	Base	H-Donor
Severity, ERT Seconds	630	800
Feed Rate, m ³ /day		
Resid	1294	1294
H-Donor (FCC LCO)	0	94
Product Yield, weight%		
C ₄ -	5.8	6.0
C ₅ -132°C	2.7	4.4
132°C+ Bottoms	91.5	89.6
132°C+ Properties:		
Kinematic Viscosity, mm ² /s at 50°C	2739	819
Specific Gravity at 15°C	1.0184	1.0115
Cutter Stock required for 150 mm ² /s product, m ³ /day	532	352
Total Cutter Stock including H-Donor, m ³ /day	532	446
Comparison, m ³ /day	BASE	(86)



Claims

1. 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} and H_a hydrogen 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.
2. A process according to claim 1, wherein visbreaking is carried out at 400 to 1200 ERT seconds.
3. A process according to claim 2, wherein visbreaking is carried out at 500 to 800 ERT seconds.
4. A process according to any one of claims 1 to 3, wherein visbreaking is carried out at 350 to 485°C for 1 to 60 minutes.
5. A process according to claim 4, wherein visbreaking is carried out at 425 to 455°C.
6. A process according to claim 4 or claim 5, wherein visbreaking is carried out for 7 to 20 minutes.
7. A process according to any one of claims 1 to 6, 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.
8. A process according to claim 7, wherein the amount of hydro-aromatic solvent is 10 to 20 weight percent.
9. A process according to any one of claims 1 to 8, wherein the hydro-aromatic solvent has a H_{Ar} content from 20 to 50% and a H_a content from 20 to 50%, based on total hydrogen content.
10. A process according to claim 9, wherein the hydro-aromatic solvent has a H_{Ar} content of at least 2.0 weight percent and a H_a of at least 1.9 weight percent.
11. A process according to any one of claims 1 to 10, wherein the hydro-aromatic solvent is a non-hydrotreated solvent derived from thermal or fluidized catalytic cracking of a petroleum oil.
12. A process according to claim 11, wherein the hydro-aromatic solvent is selected from FCC main column bottoms, TCC syntower bottoms, clarified slurry oil and light cycle oil.
13. A process according to claim 12, wherein the hydro-aromatic solvent is FCC light cycle oil or TCC light cycle oil.
14. A process according to any one of claims 1 to 10, wherein the hydro-aromatic solvent is SRC recycle oil.
15. A process for thermal cracking a heavy oil which comprises subjecting the oil to an elevated temperature for a period of time corresponding to an equivalent reaction time of 1500 to 15,000 ERT seconds at 427°C, in the presence of from 0.1 to 50 weight%, based on the heavy oil, of a non-hydrotreated solvent derived from a thermal or fluidized catalytic cracking process having a content of H_{Ar} and H_a hydrogen each of at least 20 percent of the total hydrogen content, and recovering lighter products from the reaction mixture.

Patentansprüche

1. Verfahren zum Visbreaking eines schweren Erdöl-Rückstandsöls, bei dem dieses Öl während eines Zeitraumes, der einer äquivalenten Reaktionszeit von 250—1500 ERT s bei 427°C entspricht, in Gegenwart von 0,1 bis 50 Gew.-%, bezogen auf das Rückstandsöl, eines hydroaromatischen Lösungsmittels mit einem Gehalt an H_{Ar} - und H_a -Wasserstoff von jeweils mindestens 20% des gesamten Wasserstoffgehaltes einer erhöhten Temperatur unterzogen wird und ein Heizölprodukt mit einer Viskosität zurückgewonnen wird, die geringer als die des Ausgangs-Rückstandsöls ist.
2. Verfahren nach Anspruch 1, worin das Visbreaking bei 400 bis 1200 ERT s durchgeführt wird.
3. Verfahren nach Anspruch 2, worin das Visbreaking bei 500 bis 800 ERT s durchgeführt wird.
4. Verfahren nach einem der Ansprüche 1 bis 3, worin das Visbreaking 1 bis 60 Minuten lang bei 350 bis 485°C durchgeführt wird.
5. Verfahren nach Anspruch 4, worin das Visbreaking bei 425 bis 455°C durchgeführt wird.
6. Verfahren nach Anspruch 4 oder 5, worin das Visbreaking 7 bis 20 Minuten lang durchgeführt wird.
7. Verfahren nach einem der Ansprüche 1 bis 6, worin das Visbreaking in Gegenwart von 0,1 bis 20 Gew.-% an hydroaromatischem Lösungsmittel, bezogen auf das Rückstandsöl, durchgeführt wird.
8. Verfahren nach Anspruch 7, worin die Menge des hydroaromatischen Lösungsmittels 10 bis 20 Gew.-% beträgt.
9. Verfahren nach einem der Ansprüche 1 bis 8, worin das hydroaromatische Lösungsmittel einen H_{Ar} -Gehalt von 20 bis 50% und einen H_a -Gehalt von 20 bis 50%, bezogen auf den gesamten Wasserstoffgehalt, aufweist.
10. Verfahren nach Anspruch 9, worin das hydroaromatische Lösungsmittel einen H_{Ar} -Gehalt von mindestens 2.0 Gew.-% und einen H_a -Gehalt von mindestens 1,9 Gew.-% aufweist.
11. Verfahren nach einem der Ansprüche 1 bis 10, worin das hydroaromatische Lösungsmittel ein nicht mit Wasserstoff behandeltes Lösungsmittel ist, das vom thermischen oder katalytischen Wirbelschichtcracken von Erdöl abgeleitet ist.
12. Verfahren nach Anspruch 11, worin das hydroaromatische Lösungsmittel von Rückständen der Hauptkolonne des FCC, Rückständen vom Syntower, vom TCC, einer geklärten Ölaufschlammung und leichten Kreislaufölen ausgewählt ist.



13. Verfahren nach Anspruch 12, worin das hydroaromatische Lösungsmittel leichtes Kreislauföl vom FCC oder leichtes Kreislauföl vom TCC ist.

14. Verfahren nach einem der Ansprüche 1 bis 10, worin das hydroaromatische Lösungsmittel Kreislauföl vom SRC ist.

15. Verfahren zum thermischen Cracken eines Schweröls, bei dem dieses Öl während eines Zeitraumes, der einer äquivalenten Reaktionszeit von 1500 bis 15.000 ERT s bei 427°C entspricht, in Gegenwart von 0,1 bis 50 Gew.-%, bezogen auf das Schweröl, eines nicht mit Wasserstoff behandelten Lösungsmittels, das vom thermischen oder katalytischen Wirbelschichtcrackverfahren abgeleitet wurde und einen Gehalt an H_{Ar} - und H_a -Wasserstoff von jeweils mindestens 20% des gesamten Wasserstoffgehaltes aufweist, einer erhöhten Temperatur unterzogen wird und die leichteren Produkte aus dieser Reaktionsmischung zurückgewonnen werden.

Revendications

1. Un procédé de réduction de la viscosité d'une huile résiduaire pétrolière lourde, consistant à soumettre cette huile à une température élevée pendant une période de temps correspondant à un temps de réaction équivalent (ERT) de 250 à 1 500 secondes ERT à 427°C, en présence de 0,1 à 50% en poids, exprimé par rapport au poids de l'huile résiduaire, d'un solvant hydro-aromatique présentant des teneurs respectives en hydrogène H_{Ar} et en hydrogène H_a d'au moins 20% de la teneur totale en hydrogène, et à récupérer un fuel traité présentant une viscosité plus faible que celle de l'huile résiduaire de départ.

2. Un procédé selon la revendication 1, dans lequel la réduction de la viscosité est mise en oeuvre dans des conditions correspondant à 400 à 1 200 secondes ERT.

3. Un procédé selon la revendication 2, dans lequel la réduction de la viscosité est effectuée dans les conditions correspondant à 500 à 800 secondes ERT.

4. Un procédé selon l'une quelconque des revendications 1 à 3, dans lequel la réduction de la viscosité est mise en oeuvre à une température de 350 à 485°C pendant 1 à 60 minutes.

5. Un procédé selon la revendication 4, dans lequel la réduction de la viscosité est mise en oeuvre à une température de 425 à 455°C.

6. Un procédé selon la revendication 4 ou la revendication 5, dans lequel la réduction de la viscosité est mise en oeuvre pendant une durée de 7 à 20 minutes.

7. Un procédé selon l'une quelconque des revendications 1 à 6, dans lequel la réduction de viscosité est mise en oeuvre en présence de 0,1 à 20% en poids, exprimé par rapport au poids de l'huile résiduaire, du solvant hydro-aromatique.

8. Un procédé selon la revendication 7, dans lequel la quantité de solvant hydro-aromatique est de 10 à 20% en poids.

9. Un procédé selon l'une quelconque des revendications 1 à 8, dans lequel le solvant hydro-aromatique a une teneur en H_{Ar} de 20 à 50% et une teneur en H_a de 20 à 50% par rapport à la teneur totale en hydrogène.

10. Un procédé selon la revendication 9, dans lequel le solvant hydro-aromatique a une teneur en H_{Ar} d'au moins 2,0% en poids et une teneur en H_a d'au moins 1,9% en poids.

11. Un procédé selon l'une quelconque des revendications 1 à 10, dans lequel le solvant hydro-aromatique est un solvant non hydrotraité provenant du craquage catalytique fluidisé ou du craquage thermique d'une huile de pétrole.

12. Un procédé selon la revendication 11, dans lequel le solvant hydro-aromatique est choisi parmi les produits de cuve de colonne principale FCC, les produits de cuve de "synthower TCC", les huiles de bouillie clarifiées et les huiles de recyclage légères.

13. Un procédé selon la revendication 12, dans lequel le solvant hydro-aromatique est une huile de recyclage légère FCC ou une huile de recyclage légère TCC.

14. Un procédé selon l'une quelconque des revendications 1 à 10, dans lequel le solvant hydro-aromatique est une huile de recyclage SRC.

15. Un procédé de craquage thermique d'une huile lourde qui consiste à soumettre cette huile à une température élevée pendant une période de temps correspondant à un temps de réaction équivalent (ERT) de 1 500 à 15 000 secondes ERT à 427°C, en présence de 0,1 à 50% en poids, exprimé par rapport au poids de l'huile lourde, d'un solvant non hydrotraité provenant d'un procédé de craquage catalytique thermique ou à l'état fluidisé présentant des teneurs respectives en hydrogène H_{Ar} et en hydrogène H_a d'au moins 20% par rapport à la teneur totale en hydrogène, et à récupérer les produits plus légers dans le mélange réactionnel.

