

(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets

(11)

Publication number:

**0 372 652
A1**

(12)

EUROPEAN PATENT APPLICATION

(21)

Application number: **89203073.5**

(51)

Int. Cl.⁵: **C10G 55/04**

(22)

Date of filing: **04.12.89**

(30)

Priority: **05.12.88 GB 8828335**

(43)

Date of publication of application:
13.06.90 Bulletin 90/24

(84)

Designated Contracting States:
BE DE ES FR GB IT NL SE

(71)

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Process for the conversion of a heavy hydrocarbonaceous feedstock.

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Process for the conversion of a heavy asphaltenes-containing hydrocarbonaceous feedstock comprising at least 25 %wt of hydrocarbons with a boiling point of at least 520 °C into products with a lower boiling point, which process comprises preheating the hydrocarbonaceous feedstock, passing the preheated feedstock through a thermal cracking zone so that a conversion of the hydrocarbons with a boiling point of 520 °C and above of at least 35 %wt is obtained, separating the effluent from the cracking zone into one or more distillate fractions and a residual fraction, and deasphalting the residual fraction to obtain an asphalt and a deasphalted oil.

EP 0 372 652 A1

PROCESS FOR THE CONVERSION OF A HEAVY HYDROCARBONACEOUS FEEDSTOCK

The present invention relates to a process for the conversion of a heavy asphaltenes-containing hydrocarbonaceous feedstock comprising at least 25 %wt of hydrocarbons with a boiling point of at least 520 °C into products with a lower boiling point.

Thermal cracking is a suitable process for the conversion of heavy asphaltenes-containing hydrocarbonaceous feedstocks into products with a lower average boiling point. Thermal cracking is a fairly simple process and comprises preheating the feedstock to the appropriate temperature and sending the preheated feedstock to a thermal cracking zone. There the cracking takes place. At the outlet of the thermal cracking zone the effluent is usually quenched to stop the cracking reactions and the effluent is fractionated to yield one or more distillate fractions and a residue. The residue contains virtually all asphaltenes present in the cracked product and is normally not treated any further but disposed of as refinery or commercial fuel.

An important aspect of the process relates to the stability of the cracked residue after blending with suitable diluents to give the resulting fuel the desired product specifications such as viscosity, sulphur content, density and Conradson Carbon Number. It is known that if the cracking is too severe, the character of the asphaltenes and the oils changes such that sludge formation occurs. Sludge formation especially occurs in the thermal cracking of asphaltenes-containing feedstocks. If the feedstock has been deasphalted and the deasphalted oil is thermally cracked, only at extremely high conversions some sludge is formed. The sludge basically comprises coke particles that are not soluble in the cracked oil and/or in the fuel when the cracked residue has been blended to yield a fuel. If the sludge formation is above a certain specified limit, the fuel does not comply with commercial fuel specifications.

A way to prevent sludge residues in the moderation of the severity of the thermal cracking process. Therefore, dependent on the type of feedstock the severity of the thermal cracking is selected such that the conversion of the heavy hydrocarbons, i.e. the hydrocarbons with a boiling point of 520 °C and above, is below about 30 %wt. The problem of sludge formation will be avoided at this conversion level. It will be evident that then the yield on distillates is not optimal. Another way to prevent sludge formation is to deasphalt the feedstock prior to the thermal cracking process. Conversion levels higher than 30 %wt are then attainable. However, the asphaltenes that have been removed can no longer contribute to the production of distillates and hence also in this case the yield on distillates is not optimal.

A batch process in which it is attempted to maximise the yield on distillates is delayed coking. In this process the feedstock is allowed to stay in so-called coker drums to crack and yield distillates and coke. Heavy products are recycled and when the coker drum is filled with coke, the process continues in another coke drum. Hence, the coker drums are filled/emptied batchwise. It will be evident that the facts that delayed coking is operated batchwise and that more or less solid coke has to be handled form drawbacks of this process.

The present invention provides a process in which the conversion can be increased without incurring the problems of an unstable residue and a batchwise operation, whilst the yield of distillates is enhanced.

Accordingly, the present invention provides a process for the conversion of a heavy asphaltenes-containing hydrocarbonaceous feedstock comprising at least 25 %wt of hydrocarbons with a boiling point of at least 520 °C into products with a lower boiling point, which process comprises preheating the hydrocarbonaceous feedstock, passing the preheated feedstock through a thermal cracking zone so that a conversion of the hydrocarbons with a boiling point of 520 °C and above of at least 35 %wt is obtained, separating the effluent from the cracking zone into one or more distillate fractions and a residual fraction, and deasphalting the residual fraction to obtain an asphalt and a deasphalted oil.

The asphalt obtained contains the solid coke particles that may have formed during the cracking reactions, and the deasphalted oil contains virtually no asphaltenes and has a lower viscosity, a lower density and a lower Conradson Carbon Number than the residual fraction obtained in the separation of the effluent from the thermal cracking zone. The deasphalted oil does not have any stability problems and can be used directly as blending component in the preparation of a commercial fuel, or be used for different purposes.

The heavy hydrocarbonaceous feedstock that is used in the process according to the present invention comprises at least 25 %wt of hydrocarbons with a boiling point of at least 520 °C (520 °C⁺ hydrocarbons). When the percentage of 520 °C⁺ hydrocarbons is lower the stability problem is less likely to occur. Convenient feedstocks include atmospheric residues of crude oils, so-called long residues. Suitably, the feedstock comprises more than 37.5 %wt of 520 °C⁺ hydrocarbons, more preferably more than 75 %wt and most advantageously more than 90 %wt. A very convenient feedstock is a vacuum residue of a crude oil, a so-called short residue.

Of course, also atmospheric or vacuum residues of different origin, e.g. obtained in the preparation of synthetic crudes from synthesis gas, may be used in the present process. If desired, the heavy feedstock may comprise a cycle oil obtained by catalytic cracking and/or residual oils obtained from tar sands and shale oils.

5 The feedstock contains asphaltenes. Unless indicated otherwise, the term asphaltenes in this specification refers to C_5 -asphaltenes, determined analogous to the method of IP 143 but using C_5 hydrocarbons. Another way to express the asphaltenes content is by using C_7 -asphaltenes in accordance with IP 143. It is appreciated that the number for C_5 -asphaltenes will be higher than for C_7 -asphaltenes.

10 Although the process can be carried out with a feedstock that does not contain asphaltenes, it is observed that thermal cracking of feedstocks without asphaltenes is less prone to causing stability problems and/or sludge formation. The asphaltenes content of a typical deasphalted oil is less than 5 %wt. The asphaltenes content in the feedstock of the present process may vary, dependent on the source from which it originates. Suitably, the C_5 -asphaltenes content in the feedstock ranges from 5 to 50 %wt, determined according to the modified IP 143 method.

15 Before being passed into the thermal cracking zone the feedstock is preheated. Usually this is done in one or more furnaces or furnace sections, provided with heat exchange tubes or coils through which the feedstock to be preheated is passed. The temperature to which the feedstock is preheated is preferably from 350 to 600 °C.

20 The thus preheated feedstock is passed through the thermal cracking zone. The feedstock may be passed in an upward or a downward direction through the cracking zone. Preferably, the flow is upward. The feedstock may be passed through a cracking zone that is constituted as an empty vessel, e.g. as described in US-A 1,899,889. Preferably the thermal cracking zone is situated in a soaking vessel containing internals. The internals are preferably in the form of perforated plates. In such a soaking vessel the internals provide compartments by means of which the occurrence of back-mixing is decreased. A very suitable soaking vessel is described in EP-A 7656. For more detailed information on the internals reference to this specification is made.

25 The present invention provides a high conversion of the 520 °C⁺ hydrocarbons. That means that the yield on distillate fractions will be high. The conversion of the 520 °C⁺ hydrocarbons is preferably from 35 to 70 %wt. At a conversion below 30 %wt hardly any stability problem will occur, whereas at a conversion above 70 %wt the residual fraction will be so viscous and rich of coke that handling thereof will be very cumbersome. Very good results have been obtained at a conversion of 520 °C⁺ hydrocarbons from 40 to 60 %wt.

30 The thermal cracking is generally carried out in the absence of reducing gases, such as hydrogen. The cracking can be carried out in the presence of steam. The conditions at which the thermal cracking may be carried out can be varied. One might adjust the temperature, pressure and residence time at will in such a way that the desired conversion occurs. It will be evident to a person skilled in the art that the same conversion can be obtained at a high temperature and a short residence time on the one hand and at a lower temperature but at a longer residence time at the other hand. Further, the cracking reactions are endothermic and therefore the temperature tends to decrease over the cracking zone in the case of soaker cracking. Hence, the person skilled in the art will be able to select the conditions in the cracking zone such that the desired conversion level will be obtained. Suitable cracking conditions include a temperature of 350 to 600 °C, a pressure of 1 to 100 bar and a residence time of 0.5 to 60 min. The residence time relates to the cold feedstock.

35 It may be useful to subject the effluent from the thermal cracking zone to quenching prior to its separation into one or more distillate fractions and a residual fraction. Quenching may be carried out by contacting the effluent with a colder quench fluid. Suitable quench fluids include relatively light hydrocarbon oils, such as gasoline or a recycled cool residual fraction obtained from the effluent.

40 After the optional quench of the effluent, the effluent is separated into one or more distillate fractions and a residual fraction. The distillate fractions comprise e.g. gas (C_{1-4} hydrocarbons), gasoline, middle distillates and optionally one or more vacuum distillates. The residual fraction obtained will contain the heavy 520 °C⁺ hydrocarbons.

45 As described above the residual fraction obtained may be very viscous. If desired, the residual fraction may be blended with a diluent to facilitate handling of the resulting mixture. Suitable diluents include cutter oils, such as gasoline, gasoil and other hydrocarbon streams from both straight run and catalytic cracking origin. Although the handling of the mixture will be made easier, a drawback of this addition of the diluent resides in an increased volume that has to be subjected to the deasphalting step. Economic motives may be decisive in assessing whether addition of a diluent is advantageous or not.

50 The deasphalting of the residual fraction may be carried out in a conventional manner. Solvent

deasphalting is known in the art. In this step the residual fraction is treated countercurrently with the extracting medium which is usually a light hydrocarbon solvent containing paraffinic compounds, preferably C₃₋₈ paraffinic hydrocarbons, more preferably butane, pentane and/or hexane, in particular pentane. A rotating disc contactor or a plate column can be used with the residual fraction entering at the top and the extracting medium entering at the bottom. The paraffinic compounds dissolve in the extracting medium and are withdrawn at the top of the apparatus. The asphaltenes that are insoluble in the extracting medium are withdrawn at the bottom of the apparatus. The conditions at the deasphalting are suitably a total solvent to residual fraction ratio of 1.5 to 8.0 wt/wt, a pressure from 1 to 50 bar and a temperature from 160 to 230 °C. These conditions allow the production of very heavy asphalts. To enable the handling of such heavy asphalts the addition of cutter oils to the asphalt may be desirable.

The deasphalting will suitably be carried out such that more than 35 %wt of the asphaltenes of the residual fraction are removed therefrom. Preferably more than 50 %wt of the asphaltenes are removed, more preferably more than 80 %wt.

Preferably, more than 15 %wt of the residual fraction is recovered as asphalt. That ensures a complete removal of all solid particles and a removal of the vast majority of the asphaltenes. The resulting deasphalted oil will then have excellent properties as to the density, Conradson Carbon number and viscosity, and therefore will not incur any problem when used in the preparation of a fuel. Dependent on the type of feedstock and the conversion level of the thermal cracking conveniently from 15 to 50 %wt, preferably from 20 to 45 %wt of the residual fraction is separated as asphalt.

As indicated above, the deasphalted oil resulting from the deasphalting step can be used as residual fuel or can be used as a blending component for a residual fuel. The specifications for a fuel may be such that the deasphalted oil is preferably blended with a so-called cutter oil to bring the resulting mixture on the desired product specifications. The specifications relate not only to the stability, but also to other characteristics such as the Conradson Carbon content, viscosity and density.

Other useful uses for the deasphalted oil include the use of the oil as feed for a hydrotreatment or a hydrocracking process, for a catalytic cracking process or for a thermal cracking process.

The asphalt can suitably be combusted, e.g. in a fluid bed combustion unit, or in the form of an emulsified fuel. Another useful outlet for the asphalt is the use as feed for a gasification unit to yield synthesis gas or fuel gas.

The invention will be further illustrated by means of the following Examples.

EXAMPLES

The thermal cracking experiments were carried out in a pilot plant apparatus comprising a coil which was heated while the feedstock was passed through it, and a soaking vessel. The feed rate of the feedstock was selected such that the residence time (based on the cold feedstock) in the heating coil was 2 min. and the residence time in the soaking vessel was 38 min. In the experiments the temperature was varied in accordance with the desired conversion. After the soaking vessel a heat exchanger was arranged and a fractionator to cool the effluent from the soaking vessel and subsequently to separate the effluent into a gaseous (C₁₋₄) fraction, a gasoline (C₅ - 165 °C) fraction, a gasoil (165 -350 °C) fraction and a residual (350 °C+) fraction.

The deasphalting experiments were carried out in a rotating disc contactor operating at a pentane:residual fraction weight ratio of 2.0-2.2, a feed rate of about 2.0 kg of residual fraction/h, and at a pressure of 40 bar. The temperature in the contactor was varied between 170 and 210 °C.

In the experiments different feedstocks were used: a Middle East short residue (Feedstock I), a Venezuela short residue (Feedstock II) and a North Sea short residue (Feedstock III). Some characteristics of the feedstocks are indicated in Table I below.

TABLE I

Feedstock	I	II	III
Viscosity at 100 °C, mm ² /s	2347	-	555
Viscosity at 150 °C, mm ² /s	-	1224	61.8
Conradson Carbon No. %wt	21.7	26.7	13.5
C ₅ -asphaltenes (IP 143 mod.), %wt	19.9	31.9	8.0
Toluene insolubles (ASTM D 593) %wt	<0.01	<0.01	<0.01
1-Methyl naphthalene insolubles (ASTM D 593), %wt	<0.01	<0.01	<0.01
350-520 °C fraction, %wt	7.0	4.6	5.0
520 °C ⁺ fraction, %wt	93.0	95.4	95.0

EXAMPLE 1

With the above feedstock I thermal cracking experiments were carried out. The thermal cracking conditions and the results of the experiments are indicated in table II.

TABLE II

Experiment No.	1	2	3	4
Feedstock No.	I	I	I	I
Pressure, bar gauge	5	5	5	5
Coil outlet temperature, °C	450	465	475	481
Product distribution, %wt				
C ₁₋₄ ,	1.3	2.6	2.8	3.6
C ₅ -165 °C,	2.4	5.1	6.7	7.5
165-350 °C,	6.0	12.7	16.5	16.4
350-520 °C,	19.3	22.2	22.4	22.8
520 °C ⁺ ,	71.0	57.4	51.6	49.7
520 °C ⁺ conversion, %wt	23.7	38.2	44.4	46.5
Properties of 350 °C ⁺ residual fraction				
Density 25/25 g/ml	1.037	1.053	1.063	1.069
Viscosity at 150 °C, mm ² /s	98.7	108.0	105.3	126.3
Conradson Carbon No., %wt	21.3	28.2	28.5	29.6
C ₅ -asphaltenes, %wt	24.0	27.8	31.8	31.5
Toluene insolubles, %wt	<0.01	0.52	0.54	0.48
520 °C ⁺ content, %wt	78.6	70.2	67.6	66.2

When the 350 °C⁺ residual fractions obtained are subjected to a deasphalting step at a feedstock rate of 2.0 kg/h, a pentane/350 °C⁺ residual fraction ratio weight of 2.0, at a pressure of 40 bar and at an average temperature of 180 °C, deasphalted oils (DAO's) and asphalts (ASP's) are obtained in the following yields and having the properties as indicated in Table III.

TABLE III

	Experiment No.	5	6	7	8
5	350 °C ⁺ fraction from Experiment No.	1	2	3	4
	Yield DAO, %wt of total fraction,	78	78	78	78
	Yield ASP, %wt of total fraction,	22	22	22	22
	Properties DAO				
10	Density 25/25 g/ml	0.977	0.992	1.002	1.007
	Viscosity at 100 °C, mm ² /s	64.4	68.8	67.5	77.4
	Conradson Carbon No., %wt	6.82	9.02	9.12	9.47
	C ₅ -asphaltenes, %wt	3.1	3.6	4.1	4.1
	Toluene insolubles, %wt	<0.01	<0.01	<0.01	<0.01
15	Properties ASP				
	Toluene insolubles, %wt	<0.01	2.33	2.42	2.15

EXAMPLE 2

With other feedstocks thermal cracking experiments were carried out giving the results of the Table IV below.

TABLE IV

30	Experiment No.	9	10	11	12	13	14
	Feedstock No.	II	II	II	III	III	III
	Pressure, bar gauge	5	5	5	5	5	5
	Coil outlet temperature, °C	440	471	480	470	500	510
35	Product distribution, %wt						
	C ₁₋₄ ,	1.7	3.7	5.3	1.1	3.0	3.3
	C ₅ -165 °C,	2.9	6.5	8.2	2.8	7.7	10.1
	165-350 °C,	7.8	14.1	17.4	7.2	17.1	23.4
	350-520 °C,	14.7	18.2	15.4	17.8	22.9	26.1
40	520 °C ⁺ ,	72.9	57.5	53.7	71.1	49.3	37.1
	520 °C ⁺ conversion, %wt	23.6	39.6	43.7	25.0	48.1	61.0
	Properties of 350 °C ⁺ residual fraction						
45	Viscosity at 150 °C, mm ² /s	839	1744	13000	35.5	30.4	29.3
	Conradson Carbon No., %wt	31.5	34.3	38.9	16.0	20.8	22.6
	C ₅ -asphaltenes, %wt	36.0	36.9	35.8	12.4	19.8	27.0
	1-methyl naphthalene insolubles %wt	0.12	1.08	1.12	-	-	-
	Toluene insolubles, %wt	-	-	-	<0.01	0.34	0.84
50	520 °C ⁺ content, %wt	82.9	74.0	77.1	79.6	64.6	55.0

When the 350 °C⁺ residual fractions obtained in experiments according to the present invention, i.e. experiment nos. 10, 11, 13 and 14, respectively, are subjected to a deasphalting step at a feedstock rate of 2.0 kg/h, a pentane/350 °C⁺ fraction ratio weight of 2.0, at a pressure of 40 bar and at an average temperature of 185 °C, deasphalted oils (DAO's) and asphalts (ASP's) are obtained in the following yields and having the properties as indicated in Table V.

TABLE V

	Experiment No.	15	16	17	18
5	350 °C* fraction from Experiment No.	10	11	13	14
	Yield DAO, %wt of total fraction,	75	75	76	76
	Yield ASP, %wt of total fraction,	25	25	24	24
	Properties DAO				
10	Density 25/25 g/ml	1.030	1.004	0.937	0.941
	Viscosity at 150 °C, mm ² /s	55.6	134.1	24.0	27.6
	Conradson Carbon No., %wt	11.3	12.8	6.7	7.2
	aC ₅ -asphaltenes, %wt	4.76	4.62	2.53	3.46
15	1-Methyl naphthalene insolubles, %wt	<0.01	<0.01	-	-
	Toluene insolubles, %wt	-	-	<0.01	<0.01
	Properties ASP				
	Insolubles				
20	- 1-methyl naphthalene %wt	4.29	4.45	-	-
	- toluene %wt	-	-	1.39	3.47

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Claims

1. Process for the conversion of a heavy asphaltenes-containing hydrocarbonaceous feedstock comprising at least 25 %wt of hydrocarbons with a boiling point of at least 520 °C into products with a lower boiling point, which process comprises preheating the hydrocarbonaceous feedstock, passing the preheated feedstock through a thermal cracking zone so that a conversion of the hydrocarbons with a boiling point of 520 °C and above of at least 35 %wt is obtained, separating the effluent from the cracking zone into one or more distillate fractions and a residual fraction, and deasphalting the residual fraction to obtain an asphalt and a deasphalted oil.
2. Process according to claim 1, in which the hydrocarbonaceous feedstock is a vacuum residue of a crude oil.
3. Process according to claim 1 or 2, in which the feedstock is preheated to a temperature of from 350 to 600 °C.
4. Process according to any one of claims 1 to 3, in which the preheated feedstock is passed upwards through the thermal cracking zone.
5. Process according to any one of claims 1 to 4, in which the thermal cracking zone is situated in a soaking vessel containing internals.
6. Process according to claim 5, in which the internals comprise perforated plates.
7. Process according to any one of claims 1 to 6, in which the conditions prevailing in the thermal cracking zone are a temperature of 350 to 600 °C, a pressure of 1 to 100 bar, and an average residence time of 0.5 to 60 min.
8. Process according to any one of claims 1 to 7, in which the conversion of the hydrocarbons with a boiling point of at least 520 °C in the thermal cracking zone is from 35 to 70 %wt, in particular from 40 to 60 %wt.
9. Process according to any one of claims 1 to 8, in which the residual fraction is deasphalted using C₃₋₈ paraffinic hydrocarbons.
10. Process according to claim 9, in which the paraffinic hydrocarbons comprise butane, pentane and/or hexane, in particular pentane.
11. Process according to any one of claims 1 to 10, in which the deasphalting is carried out at a total solvent to residual fraction ratio of 1.5 to 8 wt/wt, a pressure of 1 to 50 bar and a temperature of 160 to 230 °C.
12. Process according to any one of claims 1 to 11, in which the deasphalted oil is blended with a cutter oil.

13. Process according to any one of claims 1 to 11, in which the deasphalted oil is catalytically cracked.

14. Process according to any one of claims 1 to 11, in which the deasphalted oil is hydrotreated or hydrocracked.

15. Process according to any one of claims 1 to 11, in which the deasphalted oil is thermally cracked.

5 16. Process according to any one of claims 1 to 15, in which the asphalt is combusted in a fluid bed combustion unit.

17. Process according to any one of claims 1 to 15, in which the asphalt is gasified to obtain synthesis gas.

10 18. Process according to any one of claims 1 to 15, in which the asphalt is used in the preparation of emulsified fuels

19. Process according to claim 1, substantially as described hereinbefore with reference to the examples.

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DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	EP-A-0 202 099 (TOYO ENGINEERING) * Claims 1,5; example; page 3, line 22 - page 4, line 14; page 7, line 18 - page 8, line 10 * ----	1,2,3,5 ,6,7,8, 9,10	C 10 G 55/04
P,A	EP-A-0 328 216 (SHELL) * Claims 1-6,9,10,11; examples 1,2; page 3, lines 27-32 * ----	1,2,7,9 ,10,11, 17	
A	GB-A- 731 721 (STANDARD OIL) * Claims 1,4,5,6,7 * -----	1,2,7,9 ,10,11, 13	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			C 10 G
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 05-03-1990	Examiner DE HERDT O.C.E.
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			