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(54) Method and additive to increase yield in thermal conversion operations within petroleum plants

(57) A method and composition of additive to increase yield in medium distillates or to obtain a TAR with a higher level of stability in thermal conversion operations, in particular in Visbreaking, in petroleum plants used to refine crude products with a high paraffin content, where a catechol derivative-based additive is continuously added during the process.

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Description

The present invention relates to a method and to a composition of additive to be used in a thermal conversion operation in petroleum plants, starting from a charge made up of a residue of crude petroleum with a high paraffin component level.

In petroleum plants thermal conversion processes are used to split the largest hydrocarbon molecules, in particular hydrocarbons with a boiling temperature that exceeds 350°C, into smaller hydrocarbon molecules with a lower boiling point. The conversion processes transform the heavy residues obtained in the petrol refining industry into intermediate or light products that are more easily commercialised.

The conversion operation can follow a variety of distinct technologies, which are known by a number of technical names, such as Visbreaking, Coking, Hydrocracking, Thermal Cracking.

Visbreaking (VSB) in particular has gained a certain level of importance in Europe and other industrialised countries because of the contraction of the fuel oil market and the expansion of the consumption of medium distillates, in particular gasoline for vehicles.

The VSB plant is essentially made up of the following parts: a train of exchangers into which the fed charge enters for initial pre-heating, followed by a furnace in which thermal cracking takes place, then a fractionating column, from the base of which flows the residue (TAR), which passes through the exchangers, transferring part of its heat to the charge. It is also possible to foresee a "soaker" between the furnace and the fractionating column.

The operating conditions of a thermal cracking plant of this kind are basically speaking the following: a charge made up of a primary distillation residue or of a vacuum is introduced into the furnace, which operates at a temperature of 420-500 °C (in the presence or in the absence of "soaker", respectively) at a pressure of between 3 and 20 bar.

The charge treated in this manner then goes to a fractionating column, from which light distillates (from 3 to approximately 10% by weight), medium distillates (15-20% by weight) and a residue (TAR 65-75% by weight with respect to the weight of the original charge).

The plant is sized in such a way as to give a permanence at the cracking temperature sufficient to achieve the conversions required by the process.

The term "conversion yield" is used to indicate the percentage of light and medium distillates (gas + petrol + gas oil) with respect to the total charge. The products obtained in this manner from the fractionating column are transferred to the following final destinations:

a) gas and LPG are usually transferred to the refinery network;
b) the petrol (usually high octane) is sent to the petrol "pool" for hydrogenation and de-sulphurization;
c) unstable gas oils, which have a marked tendency to polymerise, are used as much as possible, after adequate hydrogenation, as components in the finished gas oils or as flux oil; and,
d) the residue (TAR), which is present in greater quantities, is unstable due to the presence of unsaturated compounds and secondary cracking products (coke and asphaltenes), and is transformed into fuel oil.

The VSB process is managed with the aim of obtaining maximum transformation into medium and light distillates, in order to satisfy market requests.

It must be pointed out that an increase in conversion of even as little as 1% of the treated charge is to be considered extremely satisfactory in terms of economic yield.

The factor limiting the production of high conversion yields is the need to obtain a residue (TAR) of a quality capable of conforming with the specifications set down by the markets for the resulting fuel oil.

The quality of the TAR is evaluated with reference to specifications relating to the following parameters: stability, percentage of asphaltenes, viscosity.

In effect, if the cracking temperature in the VSB process were to be increased it would certainly be possible to obtain a higher level of conversion into medium and light distillates, but this would produce a much more unstable TAR requiring the addition of a larger amount of flux (generally gas oil) to transform it into fuel.

The stability of the gas oil and the TAR is measured according to the tendency of its polymeric or asphaltene components to separate from the paraffin components over a period of time.

In fact, the composition of these distillation products includes a paraffin, and therefore an aliphatic portion, and an asphaltene, and therefore an essentially aromatic portion. As the asphaltenes are by definition macromolecular aggregates of naphthenic type with a low hydrogen content, which are insoluble in N-hexane, that is to say in paraffin, it will be clearly understood that over a period of time there is a tendency for the two types of component to separate from each other. In this respect it is also found that the ratio between the paraffin portion and the naphthene portion is clearly influenced by the source of the crude oil treated in the plant.

Furthermore, the percentage of asphaltene compounds is another parameter that is controlled when determining the quality of the fuel oil produced.

Asphaltenes take on particular importance as the paraffin content of the charge increases. This is due to the fact that cracking of the long paraffin molecules results in a subsequent cyclization of the radicals formed and a consequent generation of asphaltenes. In effect it has been seen in practice that from the cracking of paraffin charges residues are obtained that have a percentage of asphaltenes that is higher than that of the original charge, and not justified by the concentration effect caused by extraction of the light distillates.

The viscosity is another parameter that has a direct influence on the conversion yield in the plant, as a lower viscosity in the residue requires lower amounts of flux in order to reach commercially required viscosity levels.

Variation in the viscosity depends not only on extraction of the light products, but also on the ability of the radicals formed during cracking to polymerise. This ability is greater the richer the charge is in paraffin.

The polymers formed have a direct influence on the viscosity, increasing it and making it necessary to use a larger amount of flux in order to reach standards. This results in a reduction in net yield for an equivalent viscosity.

In the patent number 1.211.979 to the same Applicant a method and a composition are given to increase the thermal conversion yield, in which an additive based on alkylsuccinimides is added in a continuous manner during the process, particularly during an VSB process. The addition of this additive makes it possible to increase the conversion yield either in the form of an increase in the medium distillate fraction or in the form of an improvement in the quality of the TAR obtained.

The process described in the above mentioned patent has given good results for a process charge having a prevalence of naphthenic hydrocarbons. However, when the charge contains a prevalence of paraffinic hydrocarbons, the process according to patent 1,211,979 does not give satisfactory results.

It has now been surprisingly found, and forms the object of the present invention, that a noticeable increase in the yield of petroleum conversion plants, with particular reference to the working of residues deriving from crude oil with a high paraffin content, can be obtained by means of a process in which one stage foresees the continuous addition of an additive as defined in the continuation of the present description.

The present invention therefore provides a satisfactory completion of the general state of the art as described in the above mentioned patent 1,211,979, extending it to the whole range of raw petroleum products, both those defined as paraffinic crude oil and those defined as naphthenic crude oil.

Residues of crude petroleum with a high level of paraffin components are intended to mean residue deriving from crude oil that has a low sulphur level, not exceeding 1% by weight, a pour point not lower than -5°C and a TBP distillation product not exceeding 50% by weight at 350°C. In this regard it should be noted that it is not necessary for all three of the parameters indicated above to satisfy the prescribed conditions, but it is sufficient for two of the parameters to satisfy those conditions in order for the process and the additive according to the present invention to give effective results.

It is important to note that in the case of the present invention also, the "increase in yield" can be considered both in terms of an increase in conversion of medium and light distillates, and as an improvement in the TAR quality.

However, in the present invention it is advisable to distinguish TAR quality in terms of stability and asphaltene content from TAR quality in terms of viscosity.

In effect, the additive according to the present invention has proved that: a) at the same furnace temperature it is possible to increase the yield due to the reduction of TAR viscosity, accompanied by an improvement in TAR quality in terms of stability and asphaltene content, whereas b) following an increase in the furnace temperature it is possible to produce an increase in yield due to reduction in the viscosity, accompanied by a further increase in the conversion yield of the medium distillates.

The continuous addition of additive can take place in the charge feed upstream of the furnace, on the quench, at the bottom of the fractionating column, or at the outlet from the bottom of the column itself, preferably on the charge upstream of the furnace.

Preferably, in the method according to the present invention, reference parameters are determined for the quality of the TAR at the outlet from the thermal conversion plant fractionating column, in order to determine the amount of additive to be used. A fresh check is carried out on the new reference parameters for the quality of the TAR at the moment in which the system reaches normal operation after introduction of the amount of additive and, optionally, after increasing the temperature of the furnace in the thermal conversion plant, until the TAR quality reference parameters return to the initial value, if the aim is to obtain an increase in the level of medium distillate.

The object of the present invention is therefore a method to increase the yield in a thermal conversion operation in petroleum plants, starting from a charge formed by a residue deriving from crude oil with a high level of paraffin components, having a low sulphur content, not exceeding 1% by weight and/or a pour point not lower than -5°C and/or a TBP distillation product not exceeding 50% by weight at 350°C, in which

there is continuous addition into the conversion plant of an additive, in a proportion of from 100 to 1000 ppm with respect to the charge in the plant, said additive comprising

one or more active principles in a proportion of from 5 to 95% by weight with respect to the total weight of said

additive, and
per se known solvents,
in which said active principles are chosen from the group comprising:

a) sterically hindered phenols,
b) catechol derivatives,
c) bisphenols.

A further object of the present invention is an additive for use in the method described above, in which said additive has the composition indicated above.

The additive to be used in the present invention, in combination with per se known solvents, is essentially made up of one or more active ingredients. Among these active ingredients, catechol derivatives are preferred. Among the latter particular mention is made to 4-tert.butyl-catechol and pyrocatechin.

Among the phenolic type ingredients those in which at least one tert.butyl substituent group is in an ortho position with respect to the hydroxyl in the phenol group. Among these, particular mention is made of 2,6-di-tert.butyl-phenol, 2,6-di-tert.butyl-4-methylphenol and 2,4-dimethyl-6-tert.butylphenol.

As bisphenols to be used as active ingredient in the additive according to the present invention, particular mention can be made of 4,4'-methylene-bis(2,6-di-tert.butylphenol), 4,4'-thio-bis(6-tert.butyl-m-cresol), 2,2'-methylene-bis (4-methyl-6-nonylphenol), 2,2'-methylene-bis(4-methyl-6-tert.butylphenol).

In the choice of active ingredients to be used in the additive,- catecholic derivatives must be present, whereas the phenols and bisphenols can be used either in alternative to each other or simultaneously. Subject to this condition, the proportions of the active ingredients indicated above can be of any kind.

As a further active ingredient in the additive it is also possible to add alkylsuccinimides of the type used in the method described in the patent No. 2,211,979 mentioned above. However, addition of the succinimides is not essential to the effects of the present invention. The above alkylsuccinimides are the ones with a nitrogen content of from 1 to 8% and a total basic number of 20-200 mg/KOH/g, and optionally containing atoms of an element chosen from the class made up of boron and phosphor. The alkylsuccinimides can be added up to a proportion of 30% by weight with respect to the total weight of the additive.

In particular this proportion can be limited to less than 5% by weight.

The proportion of active principles with respect to the total weight of the additive amounts to a percentage of from 5 to 95% by weight, so that the proportion of solvents is between 95 and 5%.

The additive may also optionally include metal deactivators in a proportion by weight not exceeding 5% of the total weight of active ingredients in the additive.

The following are some examples of experimental tests carried out in a Visbreaking plant.

The additive of a known kind is an additive as described in the patent No. 1,211 979, comprising as active ingredients succinimides and phenolic antioxidants in a ratio of 3:1.

The additive according to the invention does not comprise succinimides and includes as active ingredients sterically impeded phenols with tert.butyl groups in an orthic position, catechol derivatives and bisphenols.

Example 1

To compare the effect produced by the action of an additive according to patent No. 1,211,979 and an additive according to the present invention, with a situation in which no additives are used, the residue from VSB (ANMA crude oil) was additioned at 100°C and stored in a muffle, in a closed container at 200°C for 24 hours with a dose of 150 ppm of additive.

The viscosity was measured at zero hour (T0) and again after a period of 24 hours, for a sample without additive (S.A.), using an additive according to the patent No. 1,221, 979 (A.V.) and using an additive according to the invention (A.N.), respectively. The results are indicated in table 1, with the viscosity indicated in centipoise. The viscosity was determined according to Brookfield (TL 6-vel.60) at 100°C.

Table 1

	T0	T 24 hours
No additive S.A.	126 cPs →	310 cPs
Known additive A.V.	129 cPs →	298 cPs
New additive A.N.	128 cPs →	235 cPs

As can be seen the test without additive produces an increased viscosity in the residue. The test using the known additive produces an increase in viscosity not very different from the viscosity without additive, whereas the use of the additive according to the invention produces a definite drop in the increase in viscosity. In this tests the asphaltenes and the stability were not analysed.

Example 2

A high paraffin residue was treated in a Visbreaking plant with Soaker. The charge included 85% of paraffin residues and 15% of asphaltene residues from a vacuum fractionating tower. A comparison test was carried out in the absence of additives (B1) and with the addition of a known additive (A.V.) according to the patent 1.211.979.

The results are indicated in table 2 below.

Table 2

	cPs 100°C Charge viscosity	cPs 100°C Residue viscosity	ton/h Charge rate	ton/h Residue rate	% Raw yield	% isov. yield	°C T cracking
B1 A.V.	700 763	247 265	143.8 145.8	139.7 141.2	2.85 3.16	12.02 12.1	433.5 433.7
Δ = approx. 0							

As can be seen, the percentage isoviscous yield, i.e. at an equivalent viscosity of TAR produced, does not show a significant difference when the known additive is used with a paraffin residue.

Example 3

In a plant like the one described in example 2 above, using the same charge and with a time of residence approximately 20% shorter according to the rate of charge, a comparison test is carried out on a sample without additives (B2) and using an additive according to the present invention (A.N.). The results are shown in Table 3 below.

Table 3

	cPs 100°C Charge viscosity	cPs 100°C Residue viscosity	ton/h Charge rate	ton/h Residue rate	% Raw yield	% isov. yield	°C T cracking
B2 A.N.	1010 1029	406 384	178.4 178.5	172.5 171.5	3.31 3.92	10.5 12.3	436.8 436.9
Δ = approx. 1.8%							

As can be seen in this case the isoviscous yield increases by approximately 20% with respect to the test performed without additive (B2).

This proves that the additive according to the invention has an effect surprisingly superior in the same conditions of use when compared with the additive according to the patent No. 1,211,979, in the case of paraffin charges.

Example 4

A mixed charge of AMNA-SARIR 60 : 40, with a very high paraffin content was treated in a Visbreaking plant with Soaker. A comparison test was carried out without additive (B3) and with an additive according to the present invention (A.N.). The additive was dosed upstream of the cracking furnace. The two tests were carried out at the same furnace temperature.

The results are shown in Table 4 below.

Table 4

	cPs100°C Charge visc.	cPs100°C Residue visc.	% weight charge asphalt.	% weight residue asphalt.	ton/h Charge rate
B3	405	227	3.8	10.9	98.1

Table 4 (continued)

	cPs100°C Charge visc.	cPs100°C Residue visc.	% weight charge asphalt.	% weight residue asphalt.	ton/h Charge rate
A.N.	405	204	3.8	9.1	98.9
	ton/h residual rate	°C Cracking temp.	% Yield	% Yield isovisc.	
B3	86.7	440	11.6	16.7	
A.N.	87.5	440	11.5	17.8	
Δ isoviscous yield = + 1.1% Δ asphaltenes = + 1.8% (-16.5%) Δ viscosity = 23 cPs 100°C = (-10%)					

The results of the tests show in the case of the present invention an improvement in the yield and isoviscosity (+1.1%) due to the reduction in viscosity of the residue (-10%) and at the same time a reduction in the asphaltenes (-16.5%) in the residue, which translates into an improvement in the quality of the TAR.

Claims

1. A method to increase the yield in a thermal conversion operation in petroleum plants, starting from a charge formed by a residue deriving from crude oil with a high level of paraffin components, having a low sulphur content, not exceeding 1% by weight and/or a pour point not lower than -5°C and/or a TBP distillation product not exceeding 50% by weight at 350°C,
characterised by the fact that;

there is continuous addition into the conversion plant of an additive, in a proportion of from 100 to 1000 ppm with respect to the charge in the plant, said additive comprising
one or more active principles in a proportion of from 5 to 95% by weight with respect to the total weight of said additive, and
per se known solvents,
in which said active principles are chosen from the group comprising:

a) sterically hindered phenols,
b) catechol derivatives,
c) bisphenols.

2. A method according to claim 1, in which said active principles comprise said catechol derivatives b) alone, or together with said sterically hindered phenols a), or together with said bisphenols c), or together with both.

3. A method according to claim 1, in which said sterically impeded phenols a) have at least one tert.butyl substituent group in at least one ortho position with respect to the hydroxyl.

4. A method according to claim 3, in which said phenols a) are chosen from the group comprising:

2,6-di-tert.butyl-phenol,
2,6-di-tert.butyl-4-methyl-phenol,
2,4-dimethyl-6-tert.butylphenol.

5. A method according to claim 1, in which said catechol derivatives are chosen from among 4-tert.butyl-catechol and pyrocatechin.

6. A method according to claim 1, in which said bisphenols are chosen from the group comprising: 4,4'-methylene-bis(2,6-di-tert.butylphenol), 4,4'-thio-bis(6-tert.butyl-m.cresol), 2,2'-methylene-bis(4-methyl-6-nonylphenol), 2,2'-methylene-bis(4-methyl-6-tert.butylphenol).

7. A method according to any one of the preceding claims, in which said additive further comprises as an additional active principle one or more alkylsuccinimides with a nitrogen content of from 1 to 8% and a total basic number of from 20 to 200 mg/KOH/g, in a proportion of up to 30% by weight with respect to the total weight of said active principles in said additive.

8. A method according to claim 7, in which said succinimides contain atoms of boron or phosphor.

9. A method according to claim 7 or 8, in which the proportion by weight of said succinimides is less than 5% by weight with respect to the total weight of said active principles in said additive.

10. A method according to any one of the preceding claims, in which said additive further comprises metal deactivators in a proportion by weight not exceeding 5% of the total weight of said active principles in said additive.

11. A method according to any one of the preceding claims, in which said thermal conversion operation is a Visbreaking operation in a plant essentially comprising a furnace and a fractionating column, and in which said additive is added continuously to the charge in the furnace and/or at the outlet from the furnace and/or at the bottom of the column and/or at the outlet from the bottom of the column.

12. A method according to claim 11, in which said additive is added to the charge in the furnace.

13. An additive for use in a method as defined in any one of the preceding claims, comprising:

one or more active principles in a proportion of from 5 to 95% by weight with respect to the total weight of said additive, and
per se known solvents,
in which said active principles are chosen from the group comprising:

a) sterically hindered phenols,
b) catechol derivatives,
c) bisphenols.

14. An additive according to claim 13, in which said active principles comprise said catechol derivatives b) alone, or together with said sterically impeded phenols a), or together with said bisphenols c), or together with both.

15. An additive according to claim 13, in which said sterically hindered phenols a) have at least one tert.butyl substituent group in at least one ortho position with respect to the hydroxyl.

16. An additive according to claim 15, in which said phenols a) are chosen from the group comprising:

2,6-di-tert.butyl-phenol,
2,6-di-tert.butyl-4-methyl-phenol,
2,4-dimethyl-6-tert.butylphenol.

17. An additive according to claim 13, in which said catechol derivatives are chosen from among 4-tert.butyl-catechol and pyrocatechin.

18. An additive according to claim 13, in which said bisphenols are chosen from the group comprising:

4,4'-methylene-bis(2,6-di-tert.butylphenol),
4,4'-thio-bis(6-tert.butyl-m.cresol),
2,2'-methylene-bis(4-methyl-6-nonylphenol),
2,2'-methylene-bis(4-methyl-6-tert.butylphenol).

19. An additive according to any one of claims 13 to 18, in which said additive further comprises as an additional active principle one or more alkylsuccinimides with a nitrogen content of from 1 to 8% and a total basic number of from 20 to 200 mg/KOH/g, in a proportion of up to 30% by weight with respect to the total weight of said active principles in said additive.

20. An additive according to claim 19, in which said succinimides contain atoms of boron or phosphor.

21. An additive according to claim 19 or 20, in which the proportion by weight of said succinimides is less than 5% by weight with respect to the total weight of said active principles in said additive.

22. An additive according to any one of the preceding claims, in which said additive further comprises metal deactivators in a proportion by weight not exceeding 5% of the total weight of said active principles in said additive.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 97 83 0333

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.6)
X	EP 0 321 424 A (CHIMEC) * the whole document *	13-16, 19,20,22	C10G9/00 C10L1/18 C10L1/14 C10L1/24
X	WO 95 20637 A (MEG S.N.C. DI SCOPELLITI SOFIA & C.) * page 23, line 11 - line 33; claims 1-4,6-9,24,38,45-52 * * page 26, line 4 - line 5 *	1,2,5, 13,14,17	
X	US 4 877 513 A (HAIRE ET AL.) * claims 14,16,17 *	13,14,17	
X	US 3 342 723 A (GODARD) * claims 3,6 *	13,14,17	
X	US 3 192 910 A (COFFIELD ET AL.) * table 4 *	13,18	
X	US 4 456 526 A (MILLER ET AL.) * column 2, line 45 - line 50 * * column 3, line 19 - line 26 *	13,14,17	**TECHNICAL FIELDS SEARCHED (Int.Cl.6)**
X	US 5 039 391 A (REID ET AL.) * claims 10,11 *	13,14,17	C10G C10L
X	US 2 638 412 A (BROWDER) * claims 1-4 *	13,15,16	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	26 November 1997	De La Morinerie, B

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
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P : intermediate document

T : theory or principle underlying the invention
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& : member of the same patent family, corresponding document