

(87) International publication number:
WO 2014/035279 (06.03.2014 Gazette 2014/10)

(74) Representative: **Spengler, Robert**
Küfergasse 11
89073 Ulm (DE)

The exploitation of many delayed coking installations, particularly in the reprocessing of oil residues, from which coke with high sulfur content is obtained in the



Description

[0001] The invention relates to the oil-refining industry, in particular to the process of delayed coking with the purpose of obtaining oil coke and gas oil fractions.

[0002] The exploitation of many delayed coking installations, particularly in the reprocessing of oil residues, from which coke with high sulfur content is obtained in the process of coking, is oriented to obtaining the maximum possible quantity of distilled fractions: gasoline, light and heavy coking gas oil. Further on, high quality motor fuels are produced from the obtained distillates by using hydro-catalytic processes - hydraulic cleaning, catalytic cracking, and hydrocracking. Thereby the obtained coking products must correspond to certain quality requirements. The coking gasoline (fraction initial boiling point 180 °C) is sent for hydraulic cleaning and is then subjected to reforming with obtaining a high-octane component of commercial gasoline. The light coking gas oil (fraction 180-350 °C) is subjected to hydraulic cleaning with obtaining diesel fuel. That is why there are requirements to the light gas oil with respect to the end boiling point because the high content of high-boiling fractions in it contributes to the carburization of the hydraulic cleaning catalyst and its premature regeneration. The heavy coking gas oil (fraction >350 °C) is subjected to hydraulic cleaning in the course of the coking of the sulfur feed stock and then to catalytic cracking with obtaining high-octane gasoline or to hydrocracking with obtaining diesel fuel. That is why there are strict requirements also to the heavy gas oil with respect to the end boiling point because the high-boiling fractions in it, which determine the high level of the coking capacity, lead also to premature carburization of the used catalysts. There are requirements to the heavy gas oil also with respect to the bubble-point temperature because, first, the low-boiling fractions, which are boiling off at temperature of up to 350 °C, diminish the yield of the light gas oil which is used for the production of diesel fuel; second, these low-boiling fractions are a ballast in the hydro-catalytic processes, they overload the installation and reduce the end products yield. There are particularly strict requirements to the heavy gas oil and the bottom liquid with respect to the content of coke particles, the so-called carboides, which are deposited on the surface of the catalysts of the hydro-catalytic processes. If the carboides content is high (for example > 0.1 %), then such product is not usable for hydro-catalytic processing and can be used only as a component of boiler fuel.

[0003] In order to increase the production of distillates, the installations for delayed coking are exploited with the minimum possible (sometimes even with a zero) recirculation ratio and at the minimum possible pressure in the coking chamber. The operation of the installations for delayed coking at such technological parameters significantly contributes to increasing the yield of the heavy coking gas oil (fractions boiling off at temperatures above 350 °C). However, along with that, the end boiling point temperature increases significantly, the coking capability, as well as the content of high molecular weight polycyclic aromatic hydrocarbons, resins, asphaltenes and metal-organic compounds also increase. These high molecular hydrocarbons contained in the tail fractions of the heavy coking gas oil determine the quick deactivation of the catalysts used for hydraulic cleaning and hydrocracking.

[0004] A method for delayed coking of oil residues is known, according to which it is proposed to increase the amount of the fed "cold" heavy gas oil in the bottom portion of the column as reflux for the purpose of regulation of the end boiling point temperature of the heavy coking gas oil obtained from the rectification column and as a result of that for improvement of its quality [G.M.Sieli, A.Faegh, S.Shimoda, "Fine regulation of the coking behavior". - Oil-Gas Technologies, 2008, No. 1, p. 74-77]. As a result, the highest boiling fractions contained in the heavy gas oil are condensed, form recirculate and along with the fresh (primary) raw material at the bottom of the rectification column are fed through the furnace as secondary raw material into the coking chamber. In this way, a portion of the highest boiling fractions is removed from the heavy coking gas oil, which leads to improvement of its quality and has a favorable effect of the subsequent hydro-catalytic processing for obtaining motor fuels.

[0005] An essential shortcoming of this method is the circumstance that despite the fact that when the amount of cold reflux is fed into the bottom part (cube) of the rectification column, the end boiling point temperature of the heavy coking gas oil decreases, at the same time the recirculation ratio increases, which leads to higher energy consumption, reduces the fresh raw material productivity and decreases the yield of heavy gas oil. In addition to that, the coke particles, which are introduced into the rectification column from the coking chambers, are dragged into the secondary raw material and after getting into the furnace they cause its premature carburization.

[0006] The closest method to the object of the application is the method for delayed coking of oil residues, including heating of the source raw material, its division into light fraction and heavy residue in the vaporizer, fractioning of the light fractions in the rectification column together with the vapor-liquid products of the coking process, mixing of the heavy residue from the vaporizer with the recirculate - bottom liquid, obtained during the functioning of the rectification column with subsequent coking of the preheated mixture. The quantity and quality of the bottom liquid is regulated by changing the amount of the fed cold heavy gas oil as a reflux for watering the mass-exchange devices at the bottom part of the rectification column, whereby the bottom liquid is fed into the upper portion of the vaporizer equipped with mass-exchange devices (Patent of the Russian Federation RF No. 2209826 from August 10, 2003 MPK C10B55/00).

[0007] This method is oriented in the first place towards regulation of the quality (with respect to density, coking capability and fractional composition) of the bottom liquid extracted from the bottom of the rectification column and sent

to the vaporizer for mixing with the source raw material as a recirculate. In this method, the bottom liquid, which is formed in the main rectification column, is taken out from the bottom of the column and is fed to the vaporizer as recirculate for mixing with the source raw material with the formation of secondary raw material, its heating in the furnace and its feeding into the coking chambers for coking. The organization of the dosed feeding of the cooling gas oil to the mass-exchange devices in the bottom part of the rectification column, the feeding of the bottom liquid from the bottom of the rectification column into the upper portion of the vaporizer, and the organization of the dosed feeding of steam into the bottom portion of the vaporizer lead to increasing the weight of the residue from the bottom of the vaporizer (the secondary raw material) and as a consequence to increasing the production of coke and reducing the power consumption.

[0008] This method has a shortcoming in the sense that in the case of foam transfer from the working coking chambers the bottom liquid from the bottom of the rectification column may contain coke particles which will be deposited on the mass-exchange devices in the vaporizer and infringe upon their operation, whereby the coke particles get in the furnace together with the secondary raw material, which leads to their carburization and, therefore, to a shorter time between the overhauls of the delayed coking installation. This method does not provide regulation of the quantity and quality of the light gas oil extracted from the installation. The change in the amount of the cooling gas oil in this method leads to a change in the recirculation ratio.

[0009] The objective of the proposed method is to increase the time between the overhauls of the installation for delayed coking of oil residues by decreasing the carburization of the mass-exchange devices of the vaporizer and the coils of the reaction furnace by excluding the entry of coke particles in them as well as to obtain two kinds of heavy gas oil with a possibility for regulation of the quality of the obtained gas oil fractions (light gas oil and two kinds of heavy gas oil) independently of the recirculation ratio.

[0010] In the method for delayed coking of oil residues, according to the invention, including heating the source raw material for coking, its feeding into the vaporizer for its mixing with the recirculate and forming a secondary raw material, heating the secondary raw material and its feeding into the coking chamber, feeding the products of the coking from the coking chamber into the rectification column for fractioning with obtaining gas, gasoline, light and heavy coking gas oil as well as bottom liquid, feeding the cooled heavy gas oil to the mass-exchange devices in the lower part of the rectification column with this achieved by feeding cooled light gas oil to the gas-exchange devices in the bottom portion of the rectification column.

[0011] The quantity of the fed cooled light and heavy gas oil is changed depending on the required quantity and quality of the obtained light and heavy gas oil and bottom liquid.

[0012] Heavy coking gas oil is used as recirculate.

[0013] In particular, cooled heavy coking gas oil is used as reflux for regulation of the end boiling point of the heavy gas oil, and cooled light coking gas oil is used for regulation of the bubble-point temperature of the heavy gas oil.

[0014] The principle diagram of the installation for delayed coking for implementation of the proposed method is shown in the drawing.

[0015] The installation comprises a tube-type furnace 1 for heating the source raw material, vaporizer 2 with mass-exchange devices, rectification column 3, tube-type furnace 4, coking chamber 5, strippings 6, coolers 7.

[0016] The method is realized as follows. The source raw material is heated in the tube-type furnace 1 and/or in the heat exchangers and is fed into the vaporizer 2, the upper part of which receives as recirculate heavy coking gas oil from the main rectification column 3. The obtained secondary raw material - a mixture of the source raw material with the recirculate is heated in the tube-type furnace 4 and is fed into one of the alternately operating coking chambers 5. The distillate products formed as result of the coking are fed through the overhead gas line into the rectification column 3 for fractioning. Gas and unstable gasoline are extracted from the top of the column. In order to regulate the quality of the gasoline, a portion of the unstable gasoline is sent to the first tray in the form of live reflux. Light and heavy coking gas oil is extracted in the form of off-stream from the main rectification columns through the strippings 6. The major part of the heavy gas oil from the stripping 6 and after the cooler 7 is extracted from the installation in the form of a finished product, and a portion of it is fed into the overhead gas line as coolant. Cooled-off heavy gas oil from the accumulator of the column 3 is fed into the first mass-exchange device in the bottom part of the rectification column as flush liquid and for regulation of the end boiling point of the heavy coking gas oil. A regulated amount of the cooled-off light coking gas oil is fed to the mass-exchange devices of the upper part of the rectification column 3 for regulation of the bubble-point temperature of the heavy gas oil and, consequently, the end boiling point of the light coking gas oil.

[0017] The quantity of the fed cooled light and heavy gas oil as reflux is changed depending on the required quantity and quality of the obtained light and heavy gas oil and bottom liquid.

[0018] After the cooling, the bottom liquid is extracted from the bottom of the rectification column 3 as a commercial product.

[0019] In this way, the proposed method permits to obtain and to regulate the quality of two heavy gas oil fractions at the same time: the heavy coking gas oil, which can be sent for hydrocracking or hydraulic cleaning and further for catalytic cracking, and the bottom liquid which, depending on its quality, can be used either as raw material for the hydro-catalytic processes or as a component of boiler fuel. Thereby the recirculation ratio does not change.

[0020] The increase in the reflux amount in the bottom part of the rectification column promotes the condensation of the heaviest boiling fractions from the coking distillate coming from the coking chambers. As a result of that, the end boiling point temperature of the heavy gas oil falls down and its density, coking capability and the content of polycyclic aromatic hydrocarbons decrease. Along with that, as a result of the dilution of the heavy gas oil, a relief takes place in the functional composition of the bottom liquid extracted from the bottom of the column, whose density, coking capability and the carboides content are also decreased.

[0021] The organization of the feed of the regulated amount of the cooled light gas oil to the mass-exchange devices of the upper part of the rectification column permits to regulate the bubble-point temperature of the heavy coking gas oil and, respectively, the end boiling point of the light gas oil.

[0022] Thereby the regulation of the qualitative characteristics of the fed coking gas oils is not connected with a change of the recirculation ration because the quantity of the recirculating fractions drawn into the coking is strictly regulated by the amount of the heavy coking gas oil fed into the vaporizer.

[0023] The method is illustrated by the following examples.

Example 1 (based on a prototype).

[0024] In an industrial installation, raw material was coked, whose characteristics are presented in table 1. The raw material is heated in heat exchangers up to a temperature of 270 °C and is then fed into the bottom portion of the vaporizer. Here, in the upper part of the vaporizer, bottom liquid as recirculate is fed from the main rectification column in a quantity of 10% with respect to the raw material. The secondary raw material formed in such a way in the vaporizer is heated in the furnace to a temperature of 500 °C and is fed into one of the coking chamber for coking. The products of the coking in the coking chambers are fed through the overhead gas line into the lower part of the main rectification column. For the condensation of the heaviest boiling products of the coking in the top mass-exchange device in the lower part of the rectification column, the feeding of cold heavy coking gas oil is organized as lower reflux in the amount of 10% with respect to the source raw material. All condensed heavy boiling products of the coking (bottom liquid) are sent to the vaporizer as recirculate for mixing with the source raw material, and the non-condensed light boiling products are fed into the upper part of the rectification column for fractioning with obtaining of gas, gasoline, light and heavy coking gas oils. The time between the overhauls was 275 days. The yield and the quality of the gas oil fractions obtained in the process of coking as well as the length of time between the overhauls are provided in table 2.

[0025] As result of the coking, the yield of the heavy gas oil was 28.2%; it has low density and low level of coking capability, but it contains 37 vol. % fractions boiling off up to 350 °C, which had a negative effect on the yield of the light gas oil (27.1 mass %) used as raw material for the production of diesel fuel.

[0026] Example 2 (based on the proposed method). According to the technological diagram shown in the drawing, coking of oil raw material, whose characteristics are shown in table 1, was performed. The given raw material is heated in heat exchanges to a temperature of 270 °C and then it is fed into the vaporizer, on whose top tray heavy coking gas oil as recirculate is fed in amount of 10% with respect to the source raw material. The obtained secondary raw material from the bottom of the vaporizer is heated in the furnace to a temperature of 500 °C and is then fed into one of the coking chambers for coking. The products of the coking are fed into the bottom part of the rectification column through the overhead gas line. For regulation of the end boiling point temperature of the heavy coking gas oil extracted from the installation, feeding of cooled heavy gas oil as lower reflux in the amount of 10 % with respect to the source raw material is organized to the first mass-exchange device of the bottom part of the rectification column. For regulation of the bubble-point temperature of the heavy coking gas oil in the mass-exchange devices in the upper part of the rectification column, feeding of cooled light coking gas oil in the amount of 20 % with respect to the source raw material (top reflux) was organized. The yield and the quality of the gas oil fractions obtained thereby as well as the length of time between the overhauls are provided in table 2.

[0027] As it can be seen from the table, the yield of heavy gas oil compared to the prototype (example 1) has decreased a little bit, but the organization of the feeding of top reflux has led to reducing the content of the fractions in it, which are boiling off to a temperature of up to 350 °C, from 37 vol. % to 20 vol. %. Such heavy gas oil can be used as a raw material for obtaining motor fuels by means of hydrocracking.

[0028] In addition to that, the yield of the light gas oil has increased compared to the prototype.

[0029] From the bottom part of the rectification column, bottom liquid in the amount of 7 % with respect to the source raw material is extracted, which, taking into account the insignificant content of carboide particles in it, can be used for obtaining diesel fuel by means of hydrocracking.

[0030] In this way, the given example shows that the proposed method permits to increase not only the yield of light gas oil, but also the total yield of heavy gas oils (heavy coking gas oil and bottom liquid) up to 30.4 % (in the prototype, the heavy gas oil yield is 28.2 %) with guaranteed quality characteristics.

[0031] Example 3 (based on the proposed method). In this case, the task was to increase the yield of heavy gas oil compared to example 2, which, due to its quality, could be used as raw material for the hydrocracking.

[0032] To this purpose, coking of the source raw material, analogical to example 2, was performed, but the amount of heavy gas oil, which was fed for refluxing the mass-exchange device in the bottom part of the rectification column of up to 5 vol. %, was reduced, whereby the light gas oil amount, which was fed for refluxing the mass-exchange device in the upper part of the rectification column has remained the same as in example 2.

[0033] The results of the coking are presented in table 2.

[0034] As one can see from example 3, the reduction of the lower reflux quantity compared to example 2, i.e. the reflux fed to the first mass-exchange device in the bottom part of the rectification column leads to increasing the weight of the fractional composition of then fed heavy coking gas oil, which is due to the lower condensation of the high-boiling fractions from the coking distillate: If in the case of feeding 10 % of lower reflux the content of the fractions boiling off at a temperature higher than 500 °C was 10 vol. %, then when 5 % lower reflux is fed, the content of the fractions boiling off at a temperature higher than 500 °C, has increased up to 14 %. However, at the same time, when the amount of the fed top reflux is unchanged, the content in the heavy gas oil, according to example 3, of the fractions boiling off at a temperature up to 350 °C was reduced by 20 vol. % (example 3) up to 16 vol. %, which increases the yield of heavy coking gas oil. Thereby, at the same time, the weight of the bottom liquid has increased and its yield has decreased. The fairly high carboide content in the bottom liquid (0.12 %) does not permit to use it in a pure form as raw material for the hydro-catalytic processes due to the possible deactivation of the catalysts. That is why it can be used either as a component of the boiler fuel or as raw material for the cracking after its preliminary mixing with the heavy gas oil, extracted from the side portion of the column, for decreasing the concentration of the carboides.

[0035] Example 4 (based on the proposed method). The task was to increase the yield of the light gas oil compared to example 2 by preserving the quality of the heavy gas oil for its use as raw material for the hydrocracking. The same raw material as in the examples 1-3 was subjected to coking in a similar manner as in example 2. The amount of the heavy gas oil added as reflux to the mass-exchange device in the bottom part of the rectification column has remained the same as in example 2, but at that the quantity of the fed top reflux (of the light gas oil) was 15 %.

[0036] The results of the coking are presented in table 2.

[0037] As it can be seen, by decreasing the quantity of the top reflux we increased the yield of the light gas oil by 1.6 % with respect to the source raw material, increasing its weight by density and end boiling point. Thereby, at the same time, the yield of the heavy gas oil has decreased and, naturally, its quality has changed: the density has increased by 0.9517 g/cm³ up to 0.9541 g/cm³, the coking capability has increased from 0.31 to 0.49, the content of the fractions boiling off at up to 350 °C has decreased from 20 vol. % to 9 vol. %.

[0038] In this way, it follows from the data in table 2 that the organization of the two refluxes: with heavy gas oil in the bottom part of the rectification column and with light gas oil in the upper part of the column permits to regulate, depending on the production needs, both the yield and the quality of the products extracted from the column. Therefore, when it is required to increase the generation of heavy coking gas oil, for example as raw material for the installation for catalytic cracking, and at the same time for reducing the generation of bottom liquid used as a component of the furnace oil, it is necessary to decrease the quantity of the bottom reflux of the heavy gas oil (examples 2 and 3). Thereby, at the same time, the quality of the heavy gas oil and the bottom liquid extracted from the rectification column change: in the heavy gas oil within the limits of the requirements that are admissible for the raw material of the catalytic cracking, the density and the coking capability increase, the fraction composition becomes heavier (the content of the fractions boiling off at temperatures above 500 °C), the density and the coking capability of the bottom liquid also increase and its fraction composition becomes heavier.

[0039] On the other hand, when it is required, for example, to increase the yield of light coking gas oil used for the production of diesel fuel and at the same time to reduce in the heavy coking gas oil the content of the fractions boiling off at temperatures of up to 350 °C (i.e. namely the diesel fuel fraction), it is necessary to decrease the amount of the top reflux (examples 2 and 4). Thereby the yield of light coking gas oil will increase from 29.9 % to 31.4 % with some weight increase on density, fractional composition, and at the same time the content of the fractions boiling off at temperatures up to 350 °C in the heavy gas oil was reduced from 20 vol. % to 9 vol. %.

[0040] In this way, the use of the proposed method will permit, compared to the prototype, to increase the time between the overhauls of the installation for implementation of the delayed coking of oil residues due to the fact that the use of the heavy coking gas oil as recirculate and the extraction of the bottom liquid from the bottom part of the rectification column, containing coke particles, as a commercial product excludes the involvement of the bottom liquid in the coking process, prevents the probability for penetrating of coke particles (carboides) into the mass-exchange trays of the vaporizer and in the reaction furnace and their carburization.

[0041] In addition, the proposed method for delayed coking ensures the obtaining of two kinds of heavy coking gas oils which differ in their physico-chemical quality characteristics and have concrete areas of use: of the heavy coking gas oil extracted from the side part of the rectification column, from which one can obtain motor fuels by means of hydrocracking or hydrofinishing, with subsequent catalytic cracking, and bottom liquid which, depending on its quality, can be used either as raw material in the hydrocatalytic processes or as a component of the boiler fuel.

[0042] In addition, the total yield of the heavy coking gas oils in the proposed method is higher than in the method

according to the prototype. This is due to the fact that in the method according to the prototype the bottom liquid is involved in the coking in a mixture with the source raw material with the formation of additional amount of coke, gas and gasoline, while in the proposed method the bottom liquid is extracted from the installation in the form of a finished product.

[0043] In addition, the proposed method will permit to regulate both the quality and the quantity of the obtained light gas oil, heavy gas oil and bottom liquid, whereby the said regulation is not connected with any change of the recirculation ratio, whereby, in the method according to the prototype, when the amount of the cooling gas oil fed to the mass-exchange devices in the bottom part of the rectification column changes, the recirculation ratio also changes.

Table 1

Characteristics of the source raw material for the coking (oil tar mixture of West-Siberian and Arlansk oils)		
No.	Parameter name	Parameter value
1	Density, ρ_4^{20}	1.0360
2	Sulfur content, mass %:	3.9
3	Coking capacity, mass %	18.2
4	Funnel viscosity, °E	
	at 80°C	952.4
	at 100°C	202
5	Fractional composition:	
	- up to 460 °C boils off, mass %	1.0
	- up to 500 °C boils off, mass %	4.72
	- above 500 °C boils off, mass %	95.28

Table 2

Yield and characteristics of the gas oil fractions extracted from the rectification column

Parameter name	Example based on a prototype		Proposed method examples											
	1		2			3			4					
	Light gas oil of coking	Heavy gas oil of coking	Light gas oil of coking	Heavy gas oil of coking	Bottom liquid	Light gas oil of coking	Heavy gas oil of coking	Bottom liquid	Light gas oil of coking	Heavy gas oil of coking	Bottom liquid	Light gas oil of coking	Heavy gas oil of coking	Bottom liquid
1. Lower reflux duty, raw material %	-	-	-	-	20	-	-	20	-	-	15	-	-	-
2. Lower reflux duty, raw material %	10	10	10	10	10	10	10	5	10	10	10	10	10	10
3. Product yield of the fresh raw material from the coking, mass %	27.1	28.2	29.8	23.4	7.0	29.8	27.4	3.0	31.4	21.8	7.0	31.4	21.8	7.0
4. Density, g/cm ³	0.8509	0.9414	0.8636	0.9517	0.9731	0.8670	0.9583	0.9809	0.8652	0.9541	0.9731	0.8652	0.9541	0.9731
5. Coking capacity, mass %	-	0.15	-	0.31	0.81	-	0.53	1.03	-	0.49	0.86	-	0.49	0.86
6. Fractional composition:	162	208	172	258	350	179	270	390	176	268	360	176	268	360
- Start of boiling temperature. °C	215	316	226	327	386	234	336	400	231	351	391	231	351	391
- 10% vol. boils off at temperature. °C														
- 90% vol. boils off at														

5

10

15

20

25

30

35

40

45

50

55

temperature. °C	309	420	343	481	505	350	495	-	347	487	507
- End of boiling temperature. °C	340	512	363	520	-	371	-	-	368	520	-
- Up to 350 °C boils off. % vol.	-	37	93	20	-	90	16	-	91	9	-
- Above 500 °C boils off. % vol.	-	8	-	10	18	-	14	20	-	11	18
7. Carboides content, mass %	-	-	-	-	0.05	-	-	0.12	-	-	0.05
8. Run life of the installation, days	275		350		350		350		350		350

Claims

1. A method for delayed coking of oil residues, including heating the source raw material for coking, its feeding into the vaporizer for its mixing with the recirculate and forming a secondary raw material for coking, heating the secondary raw material and its feeding into the coking chamber, feeding the products of the coking from the coking chamber into the rectification column for fractioning with obtaining gas, gasoline, light and heavy coking gas oil as well as bottom liquid, feeding the cooled heavy gas oil to the mass-exchange devices in the lower part of the rectification column, **characterized in that** the cooled light gas oil is fed to the gas-exchange devices in the upper portion of the rectification column.
2. The method from Claim 1, **characterized in that** the quantity of the fed cooled light and heavy gas oil is changed depending on the required quantity and quality of the obtained light and heavy gas oils and bottom liquid.
3. The method according to claims 1 or 2, **characterized in that** heavy coking gas oil is used as recirculate.

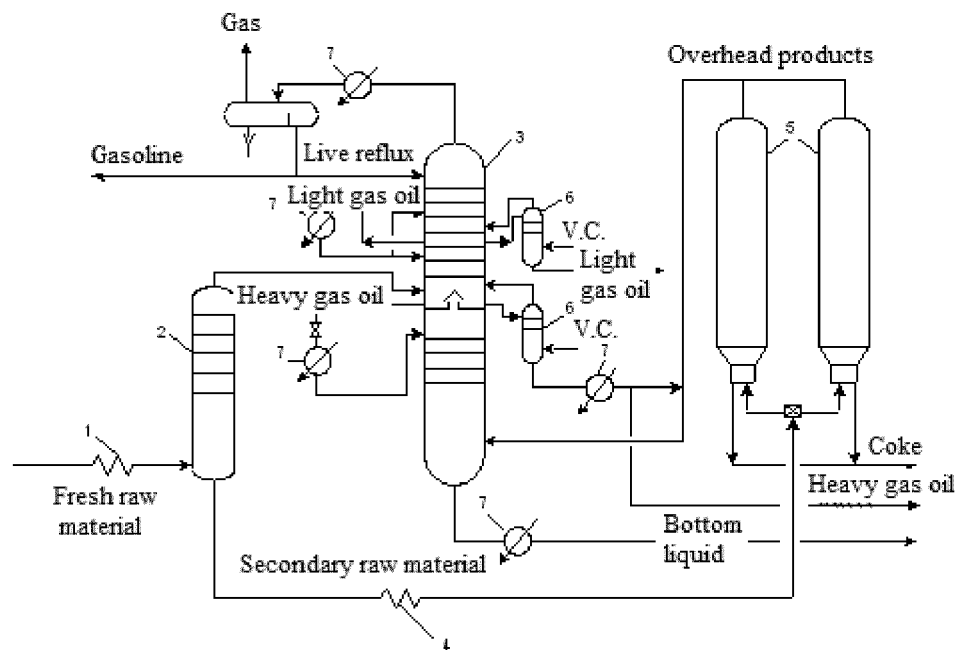


FIG.1

INTERNATIONAL SEARCH REPORT

International application No.

PCT/RU 2012/000709

A. CLASSIFICATION OF SUBJECT MATTER

C10B 55/00 (2006.01)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C10B 55/00-55/10, C07C 7/00, 7/04-7/06, B01D 3/00-3/42

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

Esp@cenet, DWPI

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	RU 2458098 C1 (OBShCHESTVO S OGRANICHENNOI OTVETSTVENNOSTIU "PROMINTEKH") 10.08.2012, claims 1-3	1-3
A	RU 2410409 C1 (OBShCHESTVO S OGRANICHENNOI OTVETSTVENNOSTIU "LUKOIL-PERMNEFTEORGSIINTEZ") 27.01.2011	1-3
A	RU 2256687 C1 (GOSUDARSTVENNOE UNITARNOE PREDPRIATIE "INSTITUT NEFTEKHIMPERERABOTKI RESPUBLIKI BASHKORTOSTAN") 20.07.2005	1-3
A	EP 186955 A2 (MOBIL OIL CORPORATION) 09.07.1986	1-3

☐ Further documents are listed in the continuation of Box C.

☐ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

22 April 2013 (22.04.2013)

Date of mailing of the international search report

06 June 2013 (06.06.2013)

Name and mailing address of the ISA/

Authorized officer

Facsimile No.

Telephone No.

REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- RU 2209826 [0006]

Non-patent literature cited in the description

- **G.M.SIELI ; A.FAEGH ; S.SHIMODA.** Fine regulation of the coking behavior. *Oil-Gas Technologies*, 2008, 74-77 [0004]