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(54) **METHOD FOR THE RETARDED COKING OF PETROLEUM RESIDUES**

(57) This invention relates to petroleum processing, in particular to producing coke with a delayed coking process and to an assembly for trapping the products formed during the coke steaming and cooling processes.

Petroleum coke deposits in delayed coking reaction drums. When one drum fills up, the flow of feed into that drum is switched off. The temperature in the switched off drum rises to 420-450 °C. To remove coke from the drum, the drum needs to be water-cooled to 60-90 °C, but the petroleum vapour products must be removed first and steamed water steam. Low-quality fractionating of the products formed during the steaming and cooling of coke results in losses of petroleum products and in atmospheric pollution.

DELAYED COKING OF PETROLEUM RESIDUE

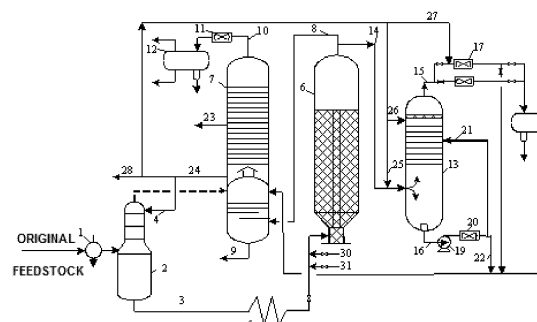


Fig. 1

Description

[0001] This invention relates to petroleum processing, in particular to producing coke with a delayed coking process and to an assembly for trapping the products formed during the coke steaming and cooling processes.

[0002] Petroleum coke deposits in delayed coking reaction drums. When one drum fills up, the flow of feed into that drum is switched off. The temperature in the switched off drum rises to 420-450 °C. To remove coke from the drum, the drum needs to be water-cooled to 60-90 °C, but the petroleum vapour products must be removed first and steamed with water steam. Low-quality fractionating of the products formed during the steaming and cooling of coke results in losses of petroleum products and in atmospheric pollution.

[0003] Table 1 shows a typical composition of the steaming and cooling products of coke produced by delayed-coking.

Table 1.

Steaming and cooling products	Flow rate, kg/hour
1. Gaseous products (C ₁ - C ₄)	300-1000
2. Petroleum products, boiling temperature = 40-350 °C, density 650-950 kg/cm ³	1,000-3,000
3. Petroleum products, boiling temperature >350 °C, density >950 kg/ cm ³	500-1,000
4. Water steam	5,000-50,000

[0004] In existing delayed-coking units, gaseous products are usually transferred-as fuel - to a special burner of technological furnaces. Petroleum products with density under 950 kg/ cm³ separate easily from water by sedimentation and re-enter the technological process. Trapping petroleum products with density > 950 kg/ cm³ is extremely difficult because their density is close or equals that of water. They cannot be separated from water by settling, even using demulsifiers.

[0005] There exists a method for delayed coking of petroleum residue, consisting of fractionating in an evaporation column the primary coking feedstock mixed with a recirculator into light fractions and heavy residue. The residue undergoes a delayed coking process. The vapour coking products formed in the coking drum undergo fractionating in the rectification column into light fractions and bottoms, a part of which is used as a recirculator (Russian Federation Patent No. 2209826, Class C10B 55/00, published in 2003).

[0006] The drawback of this method is using bottoms gasoil from the bottom of the rectification column. Bottoms gasoil forms as a result of condensation of high-boiling temperature fractions of the coking distillate in the bottom section of the rectification column, which are introduced into the rectification column from the coking drums. The coking distillate may contain particles of coke, which get into the furnace with secondary feedstock. Therefore it can coke up the furnace and increase the frequency of required overhauls for the entire unit.

[0007] Another drawback is large losses of petroleum products and pollution of the atmosphere due to the lack of devices for trapping the products of coke steaming and cooling.

[0008] The delayed coking method most similar to the present invention is the one that consists of heating the primary feedstock in a pipe still, mixing it with a recirculator, producing the secondary feed by fractionating of the light fractions in an evaporator, heating the secondary feedstock produced in a reaction pipe still, coking it in coking drums, which produces coke and distillates, fractionating the light fractions produced in the evaporator, mixed with coking distillate products, in a rectification column into vapor products, light and heavy gas oils and bottoms. The primary feedstock is heated at 400°C, while water condensate is introduced into the inlet part of the coil of the pipe still to heat the feedstock. (Patent RU No. 2410409, MPK C01B55/10, published on 27 January 2011.)

[0009] The drawback of this method is the insufficient yield of coke products: hydrocarbon gas, benzene, light gas oil and bottoms. There is room for increasing the yield of that unit.

[0010] The new method improves the yield of the unit, while simultaneously improving the yield of the products of coking.

[0011] To achieve this goals, the new delayed coking method of petroleum residue, which includes the coking of primary feedstock, during which coke deposits in the drum, fractionating of the distillate coking products into vapour products, light and heavy gas oils and heavy bottoms, steaming the coke with water steam, cooling it with water, feeding the products of steaming and cooling into the absorber equipped with mass-exchange devices, fractionating the steaming and cooling products into vapour and liquid phases in the absorber, absorbing the low-volatility petroleum products from the vapour phase by feeding the residue from the bottom section of the absorber into a mass-exchange device, cooling and condensing vapour components in a condenser/refrigerator, and fractionating the products of cooling into a gas, petroleum products, and water. In this invention, the heavy coking gas oil produced is split into several flows, one of which is used as a recirculant and is mixed with the feedstock in the evaporation drum prior to coking, while the other flow is used to dilute the steaming and cooling products prior to feeding them into the absorber. The bottoms are returned

from the bottom section of the absorber to the mass-exchange assembly located in the middle part of the absorber (to the third or fourth mass-exchange plate preferably), while the rest of the bottoms is returned into the bottom section of the rectification column.

[0012] A wash agent, heavy gasoil produced by coking, is also fed into the condenser/refrigerator.

[0013] The figure shows a flow diagram of the unit. This flow diagram illustrates the suggested delayed coking method of petroleum residue.

[0014] The unit includes heat exchangers 1 for heating the primary feedstock, evaporation column 2 for producing secondary feedstock 3 by mixing primary feedstock with recirculant 4 (heavy coking gas oil), heating-reaction oven 5 for heating secondary feedstock, secondary feedstock coking drum 6, rectification column 7 for the fractionating of coking distillate products 8 into heavy bottoms 9 and vapour products 10, condenser/refrigerator 11 for cooling vapour products 10, fractionator 12 for the fractionating of the above-mentioned vapour products into a gas, light petroleum products and water, absorber 13, equipped with an assembly for mass exchange, such as valve plates for example, for the absorption of petrol products from the products 14 separated in the process of steaming and then cooling of the coke produced in the coke coking drum, the vapour phase 15 and the bottoms 16, condenser/refrigerator 17 for cooling and condensing of the vapour phase separated in the absorber, fractionator 18 where the condensed products are fractionated into gas, light petroleum products, and water, pump 19 for removing the bottoms 16 from the absorber, refrigerator 20 for cooling the bottoms, pipelines: 21 for returning the bottoms as an absorber to the mass exchange assembly and 22 for feeding the bottoms into the rectification column respectively.

[0015] It was experimentally established that mass exchange between the rising vapours and absorbent in the absorber takes place when the number of valve plates equals 10.

[0016] Rectification column 7 is equipped in its middle part with a system of pipelines for the removal of light gas oil 23 as a final product and heavy gasoil 24, one flow of which is used as recirculant 4, while the other flow is used to dilute products 14 formed during the steaming and cooling of the coking coke formed in the drum, at the inlet of the absorber where it is introduced via pipeline 25, or it is fed as an absorbent into the top mass-exchanger via pipeline 26, or as the wash agent 27 into condenser/refrigerator 17. Pipeline 28 is used for removing gas oil 24 as a final product.

[0017] Light petroleum products are returned from fractionator 18 to the rectification column via pipeline 29. Pipelines 30 and 31 are used for steaming the coke formed in the coking drum and for cooling it with water, respectively.

[0018] The method operates in the following fashion.

[0019] Primary feedstock for coking is heated in heat-exchanger 1 by the heat of the leaving flows, then directed into evaporator column 2, where it is mixed with recirculant 4 in the form of heavy gas oil, producing secondary feedstock 3. The secondary feedstock is heated in heating/reaction oven 5, then transferred to coking drum 6 where the forming coke deposits. Coking distillate products 8 are transferred to rectification column 7 for fractionating. Gaseous products 10, consisting of a gas, benzene and water steam, leave from the top of column 7, are cooled in the condenser/refrigerator 11 and fractionated in fractionator 12 into a gas, light petroleum products and water. Gas oils - light 23 and heavy 24 - are removed from the middle section of the rectification column. Light gas oil is removed as a final product, while heavy gas oil is split into several flows. One part of it is used as recirculate 4, another part is used as diluent 25 of coke steaming and cooling products 14, while the third part is used as absorbent 26, which is conducted into the upper mass exchanger of absorber 13. Yet another part of heavy gas oil is used as wash product 27 in condenser/refrigerator 17. For this purpose one of the sections of the condenser/ refrigerator is taken off the flows of vapours from the absorber, so that hot heavy gas oil can be pumped through it during that time. All other sections continue their normal operation. When one of the sections has been washed, the next section is switched over to washing. The remaining part of the heavy gas oil is removed from the unit. Bottoms 9 are removed from the bottom of the rectification column. It is either mixed with the heavy gasoil removed from the unit or used as a boiler fuel.

[0020] When drum 6 is filled with coke, it is steamed with steam introduced through pipeline 30 and cooled with water introduced through pipeline 31. Steaming and cooling products 14 are conducted into absorber 13, equipped with 10 valve-plates. The high viscosity steaming and cooling products are diluted at the inlet of the absorber with heavy gas oil 25. The vapour steaming and cooling products rise into the top part of the absorber, where petroleum products are absorbed on the plates by bottoms 21 transferred from the bottom of the absorber to the fourth plate from the top, and by heavy gasoil 26, introduced onto the top plate of the absorber.

[0021] The liquid phase of the steaming and cooling products flows down into the bottom part of the absorber, from where it is removed with pump 19 and, via refrigerator 20, is transferred in the form of two flows: flow 21, as an absorber, is introduced onto the fourth plate of the absorber, while the other flow is conducted into rectification column 7.

[0022] Vapour phase 15, consisting of steam, hydrocarbon gases and light petroleum products, enters condenser/refrigerator 17, from where it is sent to fractionator 18. The gases, light petroleum products and water are separated. The gases go to the flare system, the light petroleum products 29, mixed with the bottoms from the absorber, are returned into the lower part of rectification column 7, while water is sent to purification.

[0023] Diluting coke steaming and cooling products with heavy gasoil prior to their introduction into the absorber reduces concentration of low-volatility bottoms, which are removed from the bottom of the absorber and is introduced

as an absorbent. This suggests that the quality of fractionating has improved.

[0024] When heavy gas oil is introduced onto the top plate, low-volatility components are diluted and washed off the plates located above the plates to which the absorbent has been introduced from the bottoms part of the absorber. This reduces significantly the quantity of low-volatility components carried out through the top of the absorber.

[0025] Introducing absorbent to a plate in the middle part of the absorber (the 3rd-4th one from the top, preferably) improves absorption and reduces the quantity of low-volatility components carried out through the top of the absorber. This suggests that the quality of the fractionating of trapped products has improved.

[0026] Having the condenser/refrigerator continuously washed with heavy gas oil improves heat exchange. Having a washing sequence of this kind lets the condenser/refrigerator operate for a very long time without requiring to have it closed down for cleaning.

[0027] Returning the bottoms from the absorber and the separated petroleum products from the fractionator into the rectification column results better trapping of products, while preliminarily mixing the feedstock with heavy gas oil in the evaporator column, which produces secondary feedstock, keeps the feeding of the feedstock heating oven at a constant rate, while keeping up the high yield of this delayed coking method with an assembly for trapping coke steaming and cooling products. (in comparison, in the method that is our prototype, returning the bottoms from the absorber and the separated petroleum products from the fractionator into the rectification column resulted in keeping the feeding rate of the furnace constant, the yield of the method with respect to the primary feedstock would have to come down by the mass of the trapped products).

Examples Supporting this Explanation

Example 1 (using the suggested method)

[0028] Primary feedstock (West-Siberian tar) was introduced into the evaporator column, where it is mixed with a recirculant to produce secondary feedstock. Secondary feedstock was heated in the oven and transferred into the coking drum, where coke was produced and deposited. The petroleum products produced in the coking process and steam were removed from the top of the drum and transferred to the rectification column to be fractionated into distillate, light and heavy gas oils and bottoms. Heavy gas oil served as a recirculant.

[0029] When coke filled up the coking drum, it was steamed with water steam and water-cooled.

[0030] The products of coke steaming and cooling, which include water, gas-phase products, petroleum products boiling at 40-350 °C and with density of 650-950 kg/ m³, and petroleum products boiling above 350 °C and with density of above 950 kg/ m³ are transferred from the coking drums to the absorber. As they are entering the absorber, they are mixed with heavy coking gas oil with boiling temperature of 250 °C. The vapour phase rises into the top part of the absorber and contacts with the absorbent in the mass-exchange devices. The bottoms from the bottom part of the absorber are used as an absorbent. The bottoms are introduced onto the 4th valve plate from the top. Heavy gas oil is introduced onto the top plate of the absorber as a reflux. Its temperature is 120-150 °C. The vapour phase is transferred to the condenser/refrigerator, cooled and moved to the fractionator for fractionating. Heavy coking gas oil of 200-250 °C is introduced as a wash liquid into one of the sections of the condenser/refrigerator, taken off the technological process. Gaseous products are removed through the top of the fractionator, while water and the petroleum product are removed from the bottom. The excess quantity of bottoms in the bottom part of the absorber is returned into the rectification column. The water flushed into the canalisation system.

[0031] Example 2 (using the prototype method). The prototype coking method was used on the same feedstock for comparison.

[0032] Table 2 shows the material balance of the process and technological conditions of coking, using the method suggested here in comparison with the prototype method.

[0033] As can be seen from the data in Table 2, the new method of delayed coking of petroleum residues improves the performance of the unit as a whole, while simultaneously increasing the yield of the coking products: carbon dioxide, benzene, light gas oil and bottoms gas oil.

Table 2

Technological Conditions and Material Balance of Coking		
Characteristics	Examples	
Technological conditions	New method	Patent 2410409 method
1. Unit performance in relation to primary feedstock, T/h	150	150
2. Quantity of recirculate (heavy gasoil), T/h	12	12

(continued)

Technological Conditions and Material Balance of Coking		
Characteristics	Examples	
3. Unit performance in relation to secondary feedstock, T/h	162	162
4. Feedstock temperature after heating in heat-exchanger, °C	250	250
5. Feedstock temperature when entering the furnace, °C	-	250
6. Consumption of water condensate at the inlet of furnace coil, T/h	-	1.0
7. Primary feedstock temperature at furnace outlet, °C	-	400
8. Secondary feedstock temperature at furnace outlet, °C	500	500
Material Balance of Coking, T/h		
Consumed:		
- primary feedstock	150	150
- trapped products of coke steaming and cooling	5	5
Produced:		
- carbon dioxide calculated on C ₅ basis	13	12
- benzene (C ₅ fraction: 180 °C)	16.5	15
- light gas oil (180-350 °C fraction)	46.5	45
- heavy gas oil (350 °C - coking coke)	28.0	28.4
- bottoms gas oil	7.0	5.0
- coke	43.5	43.5
- losses	0.5	1.1
Total involved in coking process, T/h	150+5	150

Claims

1. A method of delayed coking of petroleum residues, which includes coking the feedstock, having coke deposited in the coke drum, fractionating distillate products in a rectification column into vapour products, light and heavy gas oils and heavy bottoms, steaming coke with water steam, water cooling the coke, introducing the products of coke steaming and cooling into an absorber equipped with mass-exchange assemblies, fractionating the steaming and cooling products into vapour and liquid phases in the absorber, having low-volatility petroleum products from the vapour phase by introducing the bottoms from the bottom part of the absorber into the mass-exchange assembly, cooling and condensation of vapour components in a condenser/refrigerator and fractionating the cooling products in a fractionator into gas, petroleum products and water, different in that the produced heavy gas oil is split into several flows, one of which is used as a recirculate and is mixed with the feedstock in the evaporator column prior to coking, the second flow is used to dilute the products of coke steaming and cooling prior to introducing it into the absorber, the third flow is introduced into the top mass-exchange assembly of the absorber, while the bottoms are returned from the bottom part of the absorber into the mass-exchange assembly located in the middle part of the absorber, into the 3rd or 4th mass-exchange assembly preferably, while the left-over part of the bottoms from the absorber as well as the separated petroleum products from the fractionator are returned into the bottom part of the rectification column.
2. A method as described in 1, different in that a wash product, such as heavy coking gasoil for example

DELAYED COKING OF PETROLEUM RESIDUE

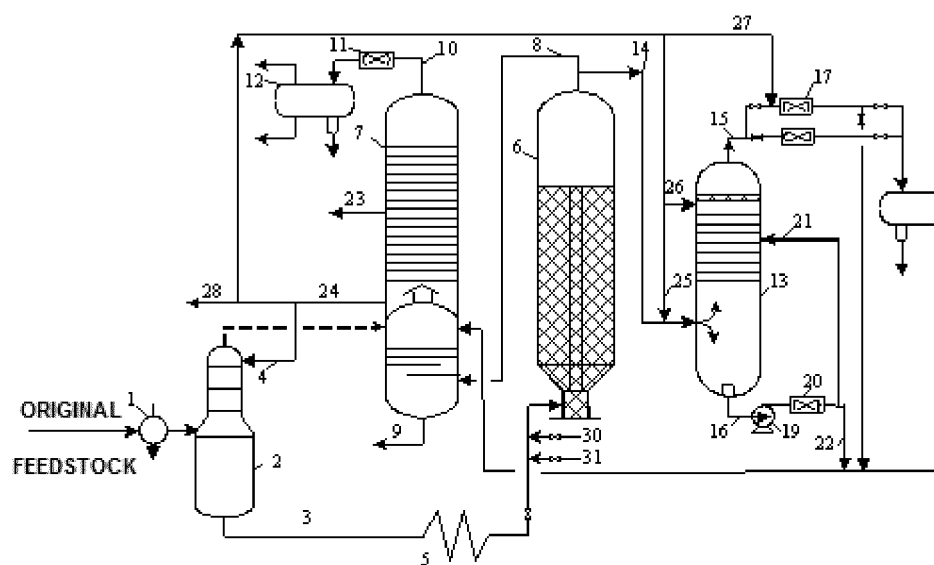


Fig. 1

INTERNATIONAL SEARCH REPORT

International application No.
PCT/RU 2012/000710

5	A. CLASSIFICATION OF SUBJECT MATTER	
	C01B 55/00 (2006.01)	
	According to International Patent Classification (IPC) or to both national classification and IPC	
	B. FIELDS SEARCHED	
10	Minimum documentation searched (classification system followed by classification symbols) C10B 55/00-55/10, B01D 53/00, 53/14, 53/18, 3/00-3/42, C07C 7/00, 7/11	
	Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched	
15	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	
20	Category*	Relevant to claim No.
		Citation of document, with indication, where appropriate, of the relevant passages
	Y	RU 86948 U1 (OBSCHESTVO S OGRANICHENNOI OTVETSTVENNOSTIU "INFORM-TEKHNLOGIJA") 20.09.2009, claims 1-2, p. 4, line 17 - p. 7, line 11, fig.
25	Y	RU 2256687 C1 (GOSUDARSTVENNOE UNITARNOE PREDPRIATIE "INSTITUT NEFTEKHIMPERERABOTKI RESPUBLIKI BASHKORTOSTAN") 20.07.2005, claim 1, table, p. 5, lines 3-7
30	A	RU 2410409 C1 (OBSCHESTVO S OGRANICHENNOI OTVETSTVENNOSTIU "LUKOIL-PERMNEFTEORGSIINTEZ") 27.01.2011
35	A	RU 2458098 C1 (OBSCHESTVO S OGRANICHENNOI OTVETSTVENNOSTIU "PROMINTEKH") 10.08.2012
	A	SU 1263706 A1 (FRIAZINOV V.V. et al.) 15.10.1986
	A	EP 0186955 A2 (MOBIL OIL CORPORATION) 09.07.1986
40	☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.	
45	* 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	
50	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/ Facsimile No.	Authorized officer Telephone No.

REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- RU 2209826 [0005]
- RU 2410409 [0008]
- WO 2410409 A [0033]