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(54) **DELAYED COKING PROCESS**

(57) This invention relates to oil refining, in particular to producing petroleum coke by delayed coking. It aims at lengthening the periods between two consecutive overhauls of the plant and at producing distillate products to be used in production of engine fuels. The proposed technology includes heating the original mixture at 250-430 °C, feeding the preheated mixture into the evaporator, to have it mixed with the recirculate (heavy coking gasoil), producing a secondary mixture, heating the secondary mixture at the reaction temperature, 460-510 °C,

and then coking it, fractionating the light fractions in the rectification column into a gas, benzene, heavy gasoil, and bottoms. Prior to feeding the preheated secondary mixture into the coking chamber, it is mixed with bottoms, and the quality and quantity of bottoms and heavy gasoil are controlled by varying temperature on the first plate in the lower section of the rectification column by feeding onto it heavy coking gasoil as reflux, while heavy coking gasoil plays the role of the recirculate.

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Description

[0001] This invention relates to oil refining, in particular to producing petroleum coke by delayed coking.

[0002] There is a delayed coking method, in which the original (primary) mixture is heated in a furnace and then fed into the lower part of the rectification column where it mixes with coking products fed from the coking chambers in a vaporous state. When the liquid primary mixture comes into contact with the steam, some of the least volatile fractions of the coking products condense, forming the recirculate. Mixing this with the primary mixture produces a secondary mixture, which is then heated in a furnace and transferred into one of the alternating coking chambers. To control the recirculation coefficient, the primary mixture can be fed into the rectification column via several inlets. When the mixture is fed through the top inlet, the recirculation coefficient reaches its maximum value. When the primary mixture is fed through the bottom inlet, i.e. beneath the inlet for the steam of reaction products from the coking chambers, the recirculation coefficient drops to its lowest value. An alternative method to control the recirculation coefficient is feeding heavy gasoil to the first sieve plate in the lower part of the rectification column. [G. G. Valyavin, B. M. Ezhov and O. M. Salyakhov, "Exploitation of Technological Equipment and How to Extend Working Periods of Delayed Coking Plants Between Overhauls", Topical Review, Moscow: TsNIITE Neftekhim, 1979, pp. 30-33.]

[0003] The drawback of this technology is the high recirculation coefficient due to high energy consumption by heating, cooling and transfer by pumping of a large number of recirculating fractions, which have very little effect on coking.

[0004] In addition, a high recirculation coefficient reduces the efficiency of the plant with respect to the original (primary) mixture. The most important drawback is that the steam of the reaction products, entering the rectification column from the coking chamber, may carry particles of coke, which, coming inside the reaction chamber together with the secondary mixture, erode the furnace pipes and coke them up, which makes frequent overhauls necessary.

[0005] The closest to the proposed invention is the method of producing petroleum coke with delayed coking which includes heating the original mixture to 300-350°C, separating the light fractions and heavy residue with a fractionator, using contact facilitating devices, fractionating the light fractions in a rectification column together with distillate coking products, feeding the bottoms formed in the rectification column as the recirculate into the evaporator to mix it with the heavy residue and form the secondary mixture, coking this mixture, preheated, in the evaporator, producing coke in the coking chambers and distillate products, which are directed to the rectification column. Quantity and quality of the bottoms involved in the mixture as a recirculate, are controlled by feeding a dosed quantity of cooling gasoil to the mass exchangers in the lower part of the rectification column (Russian Federation Patent No. 2209826, C10B 55/00, published 10 August 2003).

The drawback of this method is the low distillate output, considering that producing distillates is the main goal of delayed coking because they are used in engine fuels.

[0006] Moreover, this method predetermines the need for frequent overhauls of a delayed coking plant because using the bottoms from the rectification column, which contain coke particles carried by distillate coking products from the coking chambers, would cause erosion and coking up of the furnace pipes of reaction- heating furnaces.

[0007] The proposed invention aims at boosting up the output of distillates and to reduce the frequency of overhauls at the same time.

[0008] To achieve these goals, the proposed delayed coking method includes heating the primary mixture at 250-430 °C, feeding the preheated mixture into the evaporator to mix it with the recirculate and form a secondary mixture, heating the secondary mixture at 460-510 °C, then coking it in the coking chamber, fractionating the light fractions in the rectification column, producing a gas, benzene, light gasoil and heavy gasoil and bottoms. Prior to sending the heated mixture into the coking chamber, the secondary mixture is mixed with bottoms, the quantity and quality of the latter and of heavy coking gasoil being controlled by controlling temperature on the first plate in the lower part of the rectification column by using heavy coking gasoil as the reflux and heavy coking gasoil as the recirculate.

[0009] Involving bottoms from the rectification column in the coking process by supplying it directly into the coking chamber and also admitting heavy gasoil into the evaporator as the recirculate will boost up the output of distillates (benzene and light gasoil), used in engine oils. Using coking heavy gasoil as the recirculate with no carbon particles, will slow down the coking up of the reaction furnace and reduce erosion of the spiral tubes and pumps of the reaction furnace, which will reduce the frequency of overhauls of the delayed coking plant.

[0010] The option of controlling the quantity and quality of heavy gasoil and bottoms provides an opportunity to optimise the material balance of the plant on distillates output.

[0011] The diagram shows the layout and main parts of the plant for implementation of the proposed delayed coking technology.

[0012] The plant includes the heat-exchanger 1, the heating/reaction furnace 2, the evaporator 3 with mass exchangers, the rectification column 4, the heating/reaction furnace 5, and the coking chambers 6.

[0013] The proposed technology works as follows. The original mixture is heated at 230-270 °C in the heat exchanger 1, using the heat of the outgoing streams of products, heated again, at 350-430 °C, in the furnace 2, and then fed into the lower part of the evaporator 3, equipped with mass exchangers. A strictly controlled quantity of heavy coking gasoil,

used as the recirculate, is delivered from the rectification column 4 onto the first plate in the upper section of the evaporator. Its amount varies from 2% to 100% or more on the original mixture, which is known from the level of the equipment used. The secondary mixture, consisting of the primary mixture and the recirculate, is introduced at the bottom of the evaporator 3. It is heated at 460-510 °C in the heating furnace 5, and then delivered into one of the alternatively working coking chambers 6 to produce coke. The coking distillate products formed are passed on from the coking chambers 6 to the lower part of the rectification column 4 for fractioning, via a dome pipe. Carbon dioxide and benzene are removed from the top part of the rectification column 4.

[0014] Bottoms are removed from the lower part of the rectification column 4. Then they are transferred either into the coking chambers 6, pre-mixed with the secondary mixture heated in furnace 5, or brought out as a final product.

[0015] Light and heavy coking gasoil are discharged as side withdraws. The main part of the heavy gasoil is removed as a final product, while the rest passes into the dome pipes to serve as a coolant to cool down coking products, to prevent the coking up of the dome pipe lines and to cool down the bottoms at the bottom of the rectification column 4. Bottoms, hot or cooled, are passed from the accumulator of the rectification column 4 to the first plate in the lower part of the rectification column as the reflux to keep the temperature right in the lower section of the column 4 and on the plate as the means of controlling the quality of heavy coking gasoil and bottoms.

[0016] Quality and quantity of heavy gasoil and bottoms works as follows.

[0017] When increasing the output of heavy gasoil and increasing its fraction weight with respect to the end boiling point, the reflux rate onto the first plate in the lower part of the column 4 is reduced, so that the temperature on the plate goes up. The output of bottoms removed from the lower section of column 4 goes down simultaneously, and its fraction weight increases (due to the decreased content of volatile fractions).

[0018] Vice versa, when decreasing the output of heavy gasoil and making its fractional composition lighter with respect to its end boiling temperature is required, the reflux rate on the first plate of the rectification column 4 lower section is increased, so that the temperature on the plate decreases. Some volatile fractions condense simultaneously and become part of bottoms - due to the lower temperature on the plate. The result is a greater output of bottoms and a lighter fraction weight.

[0019] The following examples illustrate the proposed method.

EXAMPLE 1 (using the prototype method)

[0020] Tar from West Siberia oil was coked in an industrial delayed coking plant of 1,200,000 tonne/year capacity with respect to the original mixture.

[0021] The original mixture, tar from West Siberia oil (its quality is shown in Table 1) was heated at 260 °C in heat exchangers, then at 385 °C in a furnace, and then fed into the lower section of the evaporator. At the same time, recirculate bottoms are fed from the lower part of the rectification column onto the first plate of the evaporator, in quantity 10% with respect to the original mixture. The secondary mixture, formed in the evaporator (a mixture of tar and bottoms) is heated in the furnace at 495 °C, and then directed to one of the alternately working coking chambers to produce coke.

[0022] Coking distillate products are transferred from the coking chambers to the rectification column for fractionating to produce a gas, benzene and light and heavy gasoils. The material balance of coking is shown in Table 1. Coking produced 141,600 tonne/year of benzene and 272,400 tonne/year of light gasoil, which are used as components in production of engine fuels. The period between overhauls was 180 days.

EXAMPLE 2 (using the proposed method)

[0023] Like in EXAMPLE 1, tar from West Siberia oil was coked. However, unlike in that example, heavy coking gasoil was used as the recirculate, obtained as a side withdraw from the rectification column and fed onto the first plate of the evaporator to the tune of 10% on the original mixture. Bottoms, 5% in quantity and at 380 °C, was received from the bottom of the rectification column and mixed with the secondary mixture heated in the furnace at 500 °C, and directed to the coking chamber. To ensure that the quantity of bottoms removed from the lower part of the rectification column was 5%, the temperature on the first plate in the lower part of the rectification column was maintained at 380 °C by feeding cooled heavy gasoil onto it.

[0024] The coking process produced 157,299 tonne/year of benzene and 288,000 of light gasoil. Quantities of light gasoil and bottoms are presented in Table 3. The time between two overhauls was 340 days.

EXAMPLE 3 (Using the proposed method)

[0025] Like in Example 1, tar from West Siberia oil was coked. In this example, 20% (on the original mixture) of heavy gasoil was fed into the evaporator for recirculation. Feeding cooled heavy gasoil onto the first plate in the lower section of the rectification column for circulation reflux reduced the temperature on the plate to 365 °C. The output of bottoms

increased to 10% on the original mixture. Bottoms, at 365 °C, were mixed with the secondary mixture and sent into the coking chambers for coking.

[0026] This coking process produced 168,000 tonne/year of benzene and 298,800 tonnes/year of gasoil. Qualitative characteristics of heavy coking gasoil and bottoms are shown in Fig. 3. The period between overhauls was 340 days.

[0027] One can see that using this technology of producing petroleum coke in delayed coking ensures that, feeding bottoms directly into the coking chambers, eliminates the possibility of coke particles carried by the distillate from the coking chambers coming into the reaction/heating furnaces and, consequently, prevents erosion of furnace pipes and their premature coking up, which lengthens the periods between overhauls.

[0028] Feeding bottoms into the coking together with the secondary mixture, will increase the output of coking distillates by approximately 50,000 tonne/year.

[0029] Controlling the quantity of heavy gasoil sent from the accumulator of the rectification column onto the first plate of the rectification column as reflux by the means of varying temperature on the plate, allows controlling both quality and quantity of both heavy coking gasoil and bottoms.

[0030] The opportunity to control the quantity and quality of bottoms, provided its qualitative and quantitative characteristics fit the standards, will produce additional distillate fractions to be used as raw materials for catalytic cracking or hydrocracking plants.

TABLE 1

Quality of the primary coking mixture (tar from West Siberia Oil)			
Characteristics		Quantitative values	
1. Density, ρ_4^{20}		0.9880	
2. Cokeability, mass%		15.9	
3. Kinematic viscosity, cSt at 80 °C 100 °C		2,164 633	
4. Chemical composition S _{tot} , mass% V, ppm Ni, ppm		2.33 140 23	
Fractional distillation according to TBP			
Order number	Fraction, °C	Density of narrow fractions, ρ_4^{20}	Fraction content, mass %
1	360-380	0.9200	0.27
2	380-400	0.9243	0.27
3	400-420	0.9343	0.24
4	420-440	0.9432	0.24
5	440-460	0.9514	0.54
6	460-480	0.9601	1.39
7	480-500	0.9721	4.18
8	>500	1.0027	92.88
	Total		100.00

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Table 2

Material Balance of Coking						
Name	Product output					
	Prototype Example 1		Proposed method			
			Example 2		Example 3	
	mass %	tonne/year	Mass %	tonne/year	mass %	tonne/year
Raw mixture	100.0	1200	10.0	1200	100.0	1200
Products						
1. CO ₂	8.2	98.4	8.5	102	8.9	106.8
2. Benzene (fr. nk-180°C)	11.8	141.6	13.1	157.2	14.0	168
3. Light gasoil (180-350 °C)	22.7	272.4	24.0	288	24.9	298
4. Heavy gasoil (fr.>350 °C)	29.5	354	26.4	316.8	23.9	286.8
5. Coke	27.8	333.6	28.0	336	28.3	339.6
Total	100.0	1200	100.0	1200	100.0	1200
Time between overhauls, days	180		340		340	
Recirculate	Bottoms		Heavy gasoil		Heavy gasoil	
Quantity of recirculate, on raw mixture, %		10		10		20
Quantity of bottoms into coking, % on raw mixture		10		5		10
Temperature on first plate, lower section of rectification column, °C		380		380		365

Table 3

Quality of The Rectification Column Heavy Products						
Characteristic	Prototype		Proposed method			
	Example 1		Example 2		Example 3	
	Heavy gasoil	Bottoms	Heavy gasoil	Bottoms	Heavy gasoil	Bottoms
Density, $\rho_{4^{20}}$	0.9528	0.9832	0.9438	0.9973	0.9382	0.9789
Cokeability, Mass %	0.85	5.0	0.57	6.3	0.32	4.1
Contents of carbides, mass %	-	1.4	-	1.9	-	0.4
Fractal composition: fraction output, mass %						
NC- 300 °C	4.1	1.6	5.5	2.0	7.3	4.6
300-400 °C	40.7	15.1	44.7	19.0	50.4	35.1
400-500 °C	53.6	64.3	49.2	55.0	42.3	50.3
Above 500 °C	1.6	19.0	0.6	24	-	1.0

Claims

1. A delayed coking method, which includes heating of an original mixture at 250-430 °C, feeding the heated mixture into the evaporator to be mixed with a recirculate, forming a secondary mixture, heating the secondary mixture at 460-510 °C, coking it in the coking chamber, fractionating the light fractions in the rectification column, producing a

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gas, benzene, light gasoil, heavy gasoil, and bottoms, different in that the preheated secondary mixture is mixed with bottoms prior to sending it into the coking chamber, and that the quality and quantity of both bottoms and heavy coking gasoil are controlled by varying the temperature on the first plate in the lower part of the rectification column by the means of feeding heavy coking gasoil onto that plate as reflux, and in that heavy coking gasoil is used as the recirculate.

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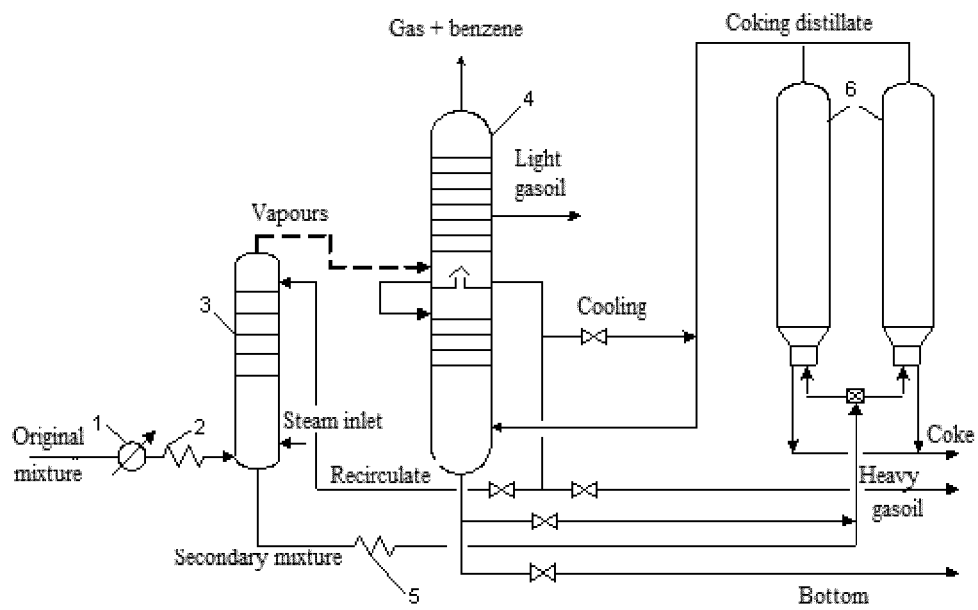


Fig. 1

INTERNATIONAL SEARCH REPORT

International application No.
PCT/RU 2010/000796

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, C10G 9/00, 9/06, 7/00, 7/04, 7/08, B01D 1/00, 3/00, 3/14 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) PAJ, Esp@cenet, PCT Online, CNIPR, SCOPUS, DWPI		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	RU 2209826 C1 (GUP "BASHGIPRONEFTEKHIM" et al.) 10.08.2003 [on-line] Found from BD esp@cenet, the abstract, page 3, right column, lines 12-44, drawing	1
A	RU 2075495 C1 (INSTITUT PROBLEM NEFTEKHIMPERERABOTKI AKADEMII NAUK RESPUBLIKI BASHKORTOSTAN) 20.03.1997, [on-line] Found from BD esp@cenet, the abstract, page 3, right column, lines 1-30, drawing	1
A	WO 1997/027273 A1 (YU HESHUI) 31.07.1997, the abstract, page 15, lines 15-35, page 16, lines 1-23, figure 5	1
☐ 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 28 July 2011 (28.07.2011)		Date of mailing of the international search report 18 August 2011 (18.08.2011)
Name and mailing address of the ISA/ Facsimile No.		Authorized officer Telephone No.

Form PCT/ISA/210 (second sheet) (July 1998)

REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- RU 2209826 [0005]

Non-patent literature cited in the description

- **G. G. VALYAVIN ; B. M. EZHOV ; O. M. SALYAKHOV.** Exploitation of Technological Equipment and How to Extend Working Periods of Delayed Coking Plants Between Overhauls. *Topical Review, Moscow: TsNIITE Neftekhim*, 1979, 30-33 [0002]