(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) **EP 1 798 275 A1**

(12) EUROPEAN PATENT APPLICATION

published in accordance with Art. 158(3) EPC

(43) Date of publication:
20.06.2007 Bulletin 2007/25

(21) Application number: **05778519.8**

(22) Date of filing: **02.09.2005**

(51) Int Cl.:
C10G 67/02 $^{(2006.01)}$ ***C10G 69/02*** $^{(2006.01)}$

(86) International application number:
PCT/JP2005/016572

(87) International publication number:
WO 2006/028196 (16.03.2006 Gazette 2006/11)

(84) Designated Contracting States:
AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HU IE IS IT LI LT LU LV MC NL PL PT RO SE SI SK TR

(30) Priority: **06.09.2004 JP 2004258719**

(71) Applicant: **Nippon Oil Corporation**
Tokyo 105-8412 (JP)

(72) Inventors:
- **AOKI, Nobuo, NIPPON OIL CORPORATION**
  Yokohama-shi, Kanagawa 2310815 (JP)
- **WAKU, Toshio, NIPPON OIL CORPORATION**
  Yokohama-shi, Kanagawa 2310815 (JP)
- **SAHARA, Wataru, NIPPON OIL CORPORATION**
  Yokohama-shi, Kanagawa 2310815 (JP)
- **TANAKA, Yuichi, NIPPON OIL CORPORATION**
  Yokohama-shi, Kanagawa 2310815 (JP)
- **HAYASAKA, Kazuaki, NIPPON OIL CORPORATION**
  Yokohama-shi, Kanagawa 2310815 (JP)
- **KONNO, Hirofumi, NIPPON OIL CORPORATION**
  Yokohama-shi, Kanagawa 2310815 (JP)

(74) Representative: **Bradley, Josephine Mary et al**
D Young & Co
120 Holborn
London EC1N 2DY (GB)

(54) METHOD FOR DESULFURIZATION OF HEAVY OIL

(57) The present invention provides a process of desulfurizing a heavy oil, which comprises diluting the heavy oil with a dilution medium to 90 percent by mass or less and cracking the diluted heavy oil at a cracking rate of 10 percent or less thereby prolonging the lifetime of a catalyst for desulfurizing a heavy oil.

Printed by Jouve, 75001 PARIS (FR)

Description

[Field of the Invention]

[0001] The present invention relates to processes of desulfurizing heavy oils continuously for a long period of time. More specifically, the present invention relates to a process of desulfurizing a heavy oil such as an atmospheric residual oil continuously for a long period of time, without exchanging a catalyst.

[Background of the Invention]

[0002] Heavy oils such as atmospheric and vacuum residual oils produced in a petroleum refining process usually contain a few percent by mass of sulfur components and thus can not be put in markets as they are. Therefore, such heavy oils are desulfurized in the presence of high pressured hydrogen using a catalyst so as to lower the sulfur concentration. A substantial part of the reaction product resulting from desulfurization of the heavy oils is further subjected to a secondary treatment to be converted to various useful products such as gasoline, kerosene, and gas oil. The process of desulfurization of heavy oils thus takes an important role in the current petroleum refining (see, for example, Non-Patent Document 1). If the desulfurization operation is ceased, other processes are adversely affected, and in this connection, the whole refinery is adversely affected in terms of economical efficiency. Therefore, how the lifetime of a catalyst is prolonged, i.e., how the operation with a catalyst once charged can be prolonged has been a serious issue in the petroleum refining industry. It is thus necessary to operate a desulfurization unit for heavy oil stably over an extended period of time in order to improve the economical efficiency of petroleum refining.

[0003] However, under the current circumstances, the lifetime of a catalyst can not be prolonged sufficiently due to deactivation factors mainly caused by coking on the catalyst and there is thus no other choice than to cease the operation in a relatively short period of time for exchanging the catalyst. The petroleum industry has been vigorously engaged in studies to prolong the lifetime of a desulfurization catalyst so as to enable the desulfurization process of heavy oils to be operated for a long period of time and has vigorously undertaken research and development to improve the catalyst, i.e., to prolong the lifetime thereof by selecting optimum supported metals and catalyst supports (see, for example, Patent Documents 1 and 2 below). However, no satisfactory result has been attained, and a view that it is impossible to prolong the lifetime of the desulfurization catalyst for heavy oil has been dominating in the industry.

(1) Patent Document 1: Japanese Patent Laid-Open Publication No. 10-180109
(2) Patent Document 1: Japanese Patent Laid-Open Publication No. 11-151441
(3) Non-Patent Document 1: "Sekiyu Seisei Purosesu (Petroleum Refining Process)" by the Japan Petroleum Institute, 1998, page 88

[Disclosure of the Invention]

[0004] The present invention has an object to improve the economic efficiency of petroleum refining by prolonging the lifetime of a catalyst for desulfurization of heavy oils.

[0005] As a result of extensive researches and studies, the present invention was achieved by the finding that the lifetime of a desulfurization catalyst was able to be prolonged by a process of desulfurization of a heavy oil, comprising diluting the heavy oil with a dilution medium and then cracking the diluted heavy oil at a low cracking rate.

[0006] That is, the present invention relates to a process of desulfurizing a heavy oil, comprising diluting the heavy oil with a dilution medium to 90 percent by mass or less and cracking the diluted heavy oil at a cracking rate of 10 percent or less.

[0007] The present invention also relates to a process of desulfurizing a heavy oil, comprising diluting the heavy oil with a dilution medium to 90 percent by mass or less, cracking the diluted heavy oil at a cracking rate of 10 percent or less, and desulfurizing the cracked heavy oil after removal of the dilution medium therefrom.

[0008] The present invention will be described in more detail below.

[0009] The heavy oil used in the present invention denotes a heavy oil mainly composed of carbon and hydrogen and containing 90 percent by mass or more of a fraction with an initial boiling point of 300°C or higher and a boiling point of 360°C or higher.

[0010] There is no particular restriction on the type of heavy oil used in the present invention. Typical examples include atmospheric residual oils and vacuum residual oils, produced during a petroleum refining process.

[0011] There is no particular restriction on the dilution medium used in the present invention except that it is inactive to the heavy oil to be treated. The dilution medium is preferably compatible with the heavy oil to be treated at a cracking temperature and particularly preferably a dilution medium with a boiling point of 120°C or higher.

[0012] Preferred examples of the dilution medium include aromatic hydrocarbons such as benzene and toluene. The use of the dilution medium can evenly dilute the heavy oil.

[0013] In the present invention, the heavy oil is diluted with the diluting medium to 90 percent by mass or less, preferably 85 percent by mass or less, and particular preferably 80 percent by mass of less. If the concentration of the heavy oil is in excess of 90 percent by mass, the effect of prolonging the lifetime of a catalyst can not be obtained sufficiently. There is no particular restriction on the lower limit concentration. However, the concentration is preferably 20 percent by mass or more and more preferably 30 percent by mass or more in view of the process efficiency.

[0014] There is no particular restriction on the method of diluting the heavy oil. However, the heavy oil is usually diluted in a mixing bath or through line-mixing. Thereupon; the mixing temperature is preferably 60°C or higher in order to mix the dilution medium with the heavy oil with a sufficiently lowered viscosity.

[0015] Next, the heavy oil diluted to 90 percent by mass or less with the dilution medium is cracked. The cracking is necessarily carried out at a low cracking rate such as 10 percent or lower. The cracking rate used herein denotes the rate (on the basis of mass) of a fraction resulting from the cracking, which is lighter than the feedstock heavy oil (i.e. a fraction with a boiling point lower than the initial boiling point of the feedstock heavy oil but not including the diluting medium), in the produced oil.

[0016] In the present invention, the cracking rate is adjusted to 10 percent or lower and more preferably 8 percent or lower. If the cracking rate is higher than 10 percent, the effect of prolonging the lifetime of a catalyst would be insufficient. There is no particular restriction on the lower limit cracking rate. However, the lower limit cracking rate is preferably 1 percent or higher and more preferably 2 percent or higher.

[0017] In the present invention, the cracking of the heavy oil is carried out by thermal cracking. The temperature range at which the thermal cracking is carried out is preferably from 400 to 600°C and more preferably from 420 to 540°C. The LHSV range is from 6 to 20 h^{-1} and more preferably from 8 to 15 h^{-1}. There is no particular restriction on the pressure. The cracking may be carried out at a pressure ranging from atmospheric pressure to slight pressure but is usually carried out at atmospheric pressure.

[0018] As mentioned above, after the diluted heavy oil is cracked at a low cracking rate, the diluted medium is removed from the resulting oil, followed by desulfurization thereof.

[0019] There is no particular restriction on the method of removing the dilution medium. However, the dilution medium is removed using atmospheric distillation.

[0020] There is no particular restriction on the catalyst or conditions for the desulfurization. There may be used any known catalyst and conditions which are used for a conventional desulfurization reaction of heavy oils. Examples of such a catalyst include those supporting molybdenum or tungsten on alumina. Typical examples of the reaction conditions include a reaction temperature of 380 to 480°C, a reaction pressure of 5 to 20 MPa, and an LHSV of 0.1 to 2.0 h^{-1}.

[0021] The desulfurized oil is then subjected to a secondary treatment like as usual. The resulting oil can be used as a base oil for various products such as gasoline, kerosene, gas oil, and heavy fuel oil.

[Applicability in the Industry]

[0022] As described above, the deactivation rate of the catalyst can be retarded by cracking a heavy oil diluted with a dilution medium at a low cracking rate and then desulfurizing the cracked oil, thereby making it possible to prolong the lifetime of the catalyst.

[Best Mode for Carrying out the Invention]

[0023] The present invention will be described in more details with reference to the following examples but is not limited thereto.

(Example 1)

[0024] Into a tower for cracking with its inlet temperature kept at 480°C was fed a vacuum residual oil (initial boiling point: 580°C, sulfur content: 4.3 percent by mass) diluted to 78 percent by mass with benzene at an LHSV of 10 h^{-1}. After the benzene is distilled out, the resulting oil contained 7.7 percent by mass (cracking rate: 7.7 percent) of a cracked product with a boiling point of lower than 580°C. The resulting oil is fed together with hydrogen to a reaction tower charged with a commercially available catalyst for desulfurizing heavy oil. The reaction tower was operated for 30 days under conditions of an LHSV of 0.2 h^{-1} and a reaction pressure of 15 MPa, controlling the reaction temperature so that the resulting oil after the reaction was reduced in sulfur content to 0.4 percent by mass. The reaction temperature was gradually increased substantially at a constant rate, from 452.0°C at the time of the initiation of the reaction and was higher by 1. 6°C than the initial reaction temperature when the reaction was completed. The average deactivation rate of the catalyst during the reaction was 0.053°C/day.

(Comparative Example 1)

[0025] The operation same as that of Example 1 was carried out except for omitting the dilution and cracking steps. The reaction temperature was increased by 4.8°C. The average deactivation rate of the catalyst was 0.160°C/day.

(Comparative Example 2)

[0026] The vacuum oil same as that used in Example 1 was cracked at a low cracking rate without using benzene, i.e., without dilution. The resulting oil contained 9.7 percent by mass of a cracked product. The resulting oil was desulfurized similarly to Example 1. The reaction temperature was increased by 3.5°C for 30 days. The average deactivation rate of the catalyst was 0.117°C/day.

(Comparative Example 3)

[0027] The cracking of Example 1 was carried out except that the LHSV was changed to 5 h^{-1}. The resulting oil contained 14.7 percent by mass of a cracked product. The resulting oil was desulfurized similarly to Example 1. The reaction temperature was increased by 4.6°C for 30 days. The average deactivation rate of the catalyst was 0.153°C/day.

(Example 2)

[0028] The cracking operation same as that of Example 1 was carried out except that toluene was used instead of benzene. The resulting oil contained 8.7 percent by mass of a cracked product. The resulting oil was desulfurized similarly to Example 1. The reaction temperature was increased by 1.9°C for 30 days. The average deactivation rate of the catalyst was 0.063°C/day.

Claims

1. A process of desulfurizing a heavy oil, comprising diluting the heavy oil with a dilution medium to 90 percent by mass or less and cracking the diluted heavy oil at a cracking rate of 10 percent or less.

2. A process of desulfurizing a heavy oil, comprising diluting the heavy oil with a dilution medium to 90 percent by mass or less, cracking the diluted heavy oil at a cracking rate of 10 percent or less, and desulfurizing the cracked heavy oil after removal of the dilution medium therefrom.

3. The process according claim 1 or 2, wherein said dilution medium is selected from the group consisting of benzene and toluene.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2005/016572

A. CLASSIFICATION OF SUBJECT MATTER
C10G67/02(2006.01), *C10G69/02*(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)
C10G67/02(2006.01), *C10G69/02*(2006.01)

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

Jitsuyo Shinan Koho	1922-1996	Jitsuyo Shinan Toroku Koho	1996-2005
Kokai Jitsuyo Shinan Koho	1971-2005	Toroku Jitsuyo Shinan Koho	1994-2005

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 1-103697 A (Chiyoda Corp.), 20 April, 1989 (20.04.89), Claims (Family: none)	1-3
A	JP 58-201889 A (Shell International Research Maatschappy B.V.), 24 November, 1983 (24.11.83), & US 4400264 A & EP 90437 A1	1-3
A	JP 51-53505 A (Showa Oil Co.), 12 May, 1976 (12.05.76), & US 4017379 A	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 25 November, 2005 (25.11.05)	Date of mailing of the international search report 06 December, 2005 (06.12.05)
Name and mailing address of the ISA/ Japanese Patent Office Facsimile No.	Authorized officer Telephone No.

Form PCT/ISA/210 (second sheet) (April 2005)

REFERENCES CITED IN THE DESCRIPTION

Patent documents cited in the description

- JP 10180109 A **[0003]**
- JP 11151441 A **[0003]**

Non-patent literature cited in the description

- Sekiyu Seisei Purosesu. Japan Petroleum Institute, 1998, 88 **[0003]**