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(54) Petroleum residue recycling process and unit.

(57) Process for treating petroleum residues such as slop oils and sludges and recovering valuable products called P2R comprising the steps of pre-heating the petroleum residues in one or several heat exchanger(s) at a temperature from 90-150° C, dehydrating the petroleum residues in a flash drum, vaporizing the petroleum residues at 300-410° C in a heater, heated mainly with light fuels from the process, and feeding a distillation column with the vaporized petroleum residues, said column operating under a vacuum of at least 250 mbars absolute and being fed by a liquid reflux at the top and steam at the bottom, allowing to split the feedstock into three cuts : a top cut which comprises light fuels, a medium cut which comprises heavy gas oil and a bottom cut which comprises heavy fuel oil.

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Description

[0001] The present invention relates to a process for treating petroleum residues and more particularly marine petroleum residues such as slop oils and sludges and recovering valuable products such as light fuels, heavy gas oil and heavy fuel oil. Said process is called "P2R".

[0002] The present invention also relates to a modular unit for recycling said petroleum residues.

[0003] The petroleum exploitation, and particularly maritime transportation, produces important amounts of petroleum residues.

[0004] According to WWF report of January 2003 entitled "Rapport sur la pollution marine par les hydrocarbures et les dégazages en Méditerranée", a tanker of average size produces from 2 to 5 tons of petroleum residues per day. Accidental pollution represents more than 5 millions tons per year of hydrocarbons discharged into the sea.

[0005] Said pollution is mainly due to accidental or illegal "degassing", corresponding to the rejection of motor oil and motor fuel residues into the sea.

[0006] As a consequence of the 1978 Marpol International Convention for the prevention of pollution from ships, the presentation to the port authorities of certificate reporting waste unloading in the last port through an authorized Marpol collector is now compulsory.

[0007] Those certificates indicate all the collecting and cleaning operations performed on the ship by the qualified collector.

[0008] Thus, volumes of collected residues are and will be more and more important.

[0009] Slop oils and sludges are emulsions of water and oil containing solid sediments. The proportion of each of said three phases (water, oil and solids) is very variable from one emulsion to another; however, the aqueous phase is often the major phase, representing 40 to 80% of the mixture.

[0010] At the present time, petroleum residues constitute a waste with little valorization. Most of the treatment processes used today, i.e. static decantation or centrifugation as disclosed in EP-A-0 693 544, and burning allow only low valorization of hydrocarbon products.

[0011] WO-A-2004/067137 discloses a mobile device for reprocessing hydrocarbon wastes such as slops into valuable products, particularly heavy fuel oil and naphtha by atmospheric distillation. Said device for reprocessing slops has the drawback of not valorizing a heavy gas oil side cut useful as marine diesel fuel or bunker.

[0012] Thus there is a need to develop an alternative solution to the main processing methods used today which allows to carry out a complete separation of the different phases of petroleum residues while being optimal from an economic, ecological and also energetic point of view.

[0013] The applicant has worked out a process for treating decanted petroleum residues and recovering valuable products based on vacuum distillation which allows to obtain about 20 to 70% heavy gas oil useful as marine diesel fuel and about 20 to 70% heavy fuel oil useful as feedstock for cement works, boiler plants, power plants or flux oil for bitumen, the remaining being light fuels used as internal fuel for the process.

[0014] Said process has the capacity of treating up to 1000 tons/day of petroleum residues.

[0015] The present invention also relates to a modular unit for carrying out the above process.

[0016] An object of the present invention is to provide a process for treating petroleum residues and recovering valuable products comprising the steps of:

- pre-heating said petroleum residues in one or several heat exchanger(s) at a temperature from 90-150°C,
- dehydrating the petroleum residues and recovering light fuels in a flash drum,
- vaporizing the petroleum residues at 300-410° C in a heater, heated mainly with light fuels from the process,
- feeding a distillation column with the vaporized petroleum residues, said column operating under a vacuum of at least 250 mbars absolute and being fed by a liquid reflux at the top and steam at the bottom, allowing to split the feedstock into three cuts : a top cut which comprises light fuels, a medium cut which comprises heavy gas oil and a bottom cut which comprises heavy fuel oil,
- condensing the top cut of the column in a condenser or using a circulating reflux with a pump and a cooler, and separating the top condensates or the cooled liquid in the case of circulating reflux, in a reflux drum into two phases, a phase of light fuels partially driven to the top of the column as a liquid reflux and partially driven to the heater as feedstock and an aqueous phase comprising water contained in residues which is driven to a water treatment, the incondensable fraction being burnt in the heater,
- directing the medium cut to a stripping column which regulates the flash point of heavy gas oil by a superheated steam flow and,
- recovering the heavy fuel oil at the bottom of the column.

[0017] According to the present invention, the treated petroleum residues are more particularly marine slop oils and sludges.

[0018] Further characteristics and advantages of the present invention shall appear more clearly from the following description made by reference to the practical embodiment and the drawing given by way of mere non limitative example of the invention, wherein figure 1 is a schematic diagram of one embodiment of the process and unit according to the present invention.

[0019] The petroleum residues can contain solid particles, chemical waste, or any other pollutants, in a quantity compatible with valorization of heavy fuel oil and

heavy gas oil.

[0020] The petroleum residues feed the unit through pump (P001) and are preheated in a heat exchanger (E001) at a temperature from 90°C to 150°C.

[0021] They are then directed to a flash drum (V001) which allows to dehydrate the inlet petroleum residues and to separate vapor and light fuels which are condensed in the condenser (E005) and driven to the drum (D003) from which decanted water is separated and driven to tank (T001) through line 6 by means of pump (P005). Liquid light fuels are driven through pump (P006) and line 4 to tank (T002). Incondensable gases (5) are burnt in the burners of the heater (H001).

[0022] Dehydrated petroleum residues are driven through pump (P002) to the heater (H001) wherein they are vaporized at 300°-410° C. The heater produces steam in connection with a steam drum (D001).

[0023] Cold soft water is conveyed through line 8 to the heater through the steam drum to produce superheated steam which is used for feeding the bottom of the distillation column (C001) and the stripping column (C002).

[0024] Excess low pressure steam is evacuated through line 9.

[0025] The vaporized petroleum residues are driven to a distillation column (C001) which operates under a vacuum of at least of 250 mbars absolute. Distillation allows splitting the feedstock into three cuts:

- a top cut which comprises light fuels,
- a medium cut which comprises heavy gas oil,
- a bottom cut which comprises heavy fuel oil.

[0026] The top cut is condensed in a condenser (E002). In case of a circulating reflux, the condenser (E002) will be replaced by a pump and a cooler.

[0027] The top condensates or the cooled liquid in the case of circulation reflux feed the reflux drum D004. The liquid in the reflux drum (D004) is separated into two phases:

- a phase of light fuels partially driven to the top of the column as a liquid reflux and partially driven through pump (P009) through line 4 to a tank (T002) and then to the heater (H001) as feedstock through pump (P010);
- an aqueous phase comprising water contained in the petroleum residues which is driven through pump (P008) and line 6 to tank (T001) of decanted water from which it is then driven to a water treatment.

[0028] Non-condensable gases from the reflux drum (D004) are driven to drum (D003) through a vacuum system (S001). They are then driven through line 5 to the burners of the heater (H001).

[0029] In case of surpressure, non-condensable gases are evacuated through line 7 to blow down drum.

[0030] Water separated in drum (D003) is conducted through pump (P005) and line 6 to tank (T001) of decanted water and is then driven to a water treatment.

[0031] The medium cut comprising heavy gas oil is directed to a stripping column (C002) which regulates the flash point of heavy gas oil by a superheated steam flow produced in the heater (H001). A reflux of heavy gas oil from the stripping column (C002) returns to the upper part of the distillation column (C001).

[0032] Heavy gas oil is driven through pump (P004), heat exchanger (E004) and line 3 to tank (T003).

[0033] Heavy fuel oil is driven from the bottom of the distillation column (C001) through pump (P003), heat exchanger (E003) and line 2 to tank (T004).

[0034] Regulating means are provided for controlling:

- the vacuum in the distillation column : at least 250 mbars absolute (maximum pressure),
- the heater temperature between 300 and 410° C,
- the reflux of light fuels from the reflux drum (D004) to the top of the distillation column (C001) and,
- the reflux of the heavy gas oil from the stripping column (C002) into the distillation column (C001).

[0035] The heater (H001) is heated by burning incondensable gases extracted from drums D004 and D003 through line 5 as well as light fuels produced as the top cut of the distillation column (C001).

[0036] A vacuum system (S001) produces a vacuum of at least 250 mbars absolute (maximum absolute pressure) in the distillation column (C001).

[0037] The inlet petroleum residues have the following characteristics:

- a water content less than 10% by weight,
- a flash point from 20°C to 100°C,
- a viscosity at 40°C from - 80 to 200 mm^2/s and,
- a viscosity at 100°C from 10 to 20 mm^2/s.

[0038] The typical characteristics of recovered heavy gas oil are as follows:

- a water content less than or equal to 0.10% by weight,
- a flash point equal to or higher than 60°C,
- a viscosity at 40°C from 1.50 to 6.00 mm^2/s, and
- a density at 15°C not higher than 890 kg/ mm^3.

[0039] Recovered heavy fuel oil has the following typical characteristics:

- a water content less than or equal to 1.5% by weight,
- a flash point equal to or higher than 70°C,
- a viscosity higher than 9,5 mm^2/s at 20°C and lower than 40 mm^2/s at 100°C.

[0040] The flash point is measured according to NF EN ISO 2719.

[0041] The viscosity is measured according to NF EN

ISO 3104.

[0042] The density is measured according to NF EN ISO 12185.

[0043] One of the advantages of the process of the present invention is its flexibility with regard to the specified characteristics of the outlet products.

[0044] The operating conditions (temperature, reflux flows, vacuum conditions) can be adapted to reach specified characteristics of the outlet products. Of course, the percentage of each outlet product is strongly dependent on characteristics of inlet petroleum residues.

[0045] A further object of the present invention is to provide a modular unit for recycling petroleum residues and recovering valuable products which comprises:

- a heater (H001) providing heating and vaporization of the slop feedstock (1), production of steam in conjunction with a steam drum (D001) and burning of incondensable gases (5),
- a distillation column (C001) operating under vacuum, which is fed by a liquid reflux from a reflux drum (D004) at the top and steam from the heater (H001) at the bottom, allowing to split the feedstock into three cuts : a top cut which comprises light fuels (4), a medium cut which comprises heavy gas oil (3) and a bottom cut which comprises heavy fuel oil (2),
- a vacuum system (S001) producing a vacuum of at least of 250 mbars absolute (maximum pressure at the top of the column C001),
- heat exchangers (E001 to E005) having a heating or cooling function,
- drums (D003, D004 and V001) allowing separation of hydrocarbons, aqueous phases, vapor phases and non-condensable gases,
- pumps (P001 to P010) providing fluid transfer,
- a stripping column (C002) regulating the flash point of the gas oil medium cut (3) by a superheated steam flow and,
- regulating means controlling the vacuum in the distillation column (C001) to at least 250 mbars absolute, the heater (H001) temperature between 300 and 410°C and the refluxes of light fuels from the reflux drum (D004) and of heavy gas oil from the stripper (C002) into the distillation column (C001).

[0046] The unit of the present invention further comprises storage tanks for decanted water (T001), light fuels (T002), heavy gas oil (T003) and heavy fuel oil (T004).

Claims

1. A process for treating petroleum residues such as slop oils and sludges and recovering valuable products, **characterized in that** it comprises the steps of :

- pre-heating petroleum residues in one or several heat exchanger(s) at a temperature from 90-150°C,
- dehydrating the petroleum residues and recovering light fuels in a flash drum,
- vaporizing the petroleum residues at 300-410°C in a heater, heated mainly with light fuels from the process,
- feeding a distillation column with the vaporized petroleum residues, said column operating under a vacuum of at least of 250 mbars absolute (maximum pressure at the top of the column) and being fed by a liquid reflux at the top and steam at the bottom, allowing to split the feedstock into three cuts: a top cut which comprises light fuels, a medium cut which comprises heavy gas oil and a bottom cut which comprises heavy fuel oil,
- condensing the top cut of the column in a condenser or using a circulating reflux with a pump and a cooler and separating the top condensates, or the cooled liquid in the case of circulating reflux, in a reflux drum into two phases, a phase of light fuels partially driven to the top of the column as a liquid reflux and partially driven to the heater as feedstock and an aqueous phase comprising water contained in the residues which is driven to a water treatment, the incondensable fraction being burnt in the heater,
- directing the medium cut to a stripping column which regulates the flash point of heavy gas oil by a superheated steam flow and
- recovering the heavy fuel oil at the bottom of the column.

2. A process according to claim 1, **characterized in that** the petroleum residues have a water content less than 10% by weight, a flash point from 20°C to 100°C, a viscosity at 40°C from - 80 to 200 mm^2/s and a viscosity at 100°C from 10 to 20 mm^2/s.

3. A process according to claim 1 or 2, **characterized in that** the recovered valuable products comprise about 20 to 70% of heavy gas oil and about 20 to 70% of heavy fuel oil, the remaining being light fuels used as internal fuel for the process.

4. A process according to anyone of claims 1 to 3, **characterized in that** recovered heavy gas oil has a water content less than or equal to 0.10% by weight, a flash point equal to or higher than 60°C, a viscosity at 40°C from 1.50 to 6.00 mm^2/s and a density at 15°C not higher than 890 kg/ mm^3.

5. A process according to anyone of claims 1 to 4, **characterized in that** recovered heavy fuel oil has a water content less than or equal to 1.5% by weight, a flash point equal to or higher than 70°C, a viscosity higher than 9.5 mm^2/s at 20°C and lower than 40

mm^2/s at 100°C.

6. A modular unit for recycling petroleum residues and recovering valuable products, **characterized in that** it comprises:

- a heater (H001) providing heating and vaporization of the slop feedstock (1), production of steam in conjunction with a steam drum (D001) and burning of incondensable gases (5),
- a distillation column (C001) operating under vacuum, which is fed by a liquid reflux from a reflux drum (D004) at the top and steam from the heater (H001) at the bottom, allowing to split the feedstock into three cuts : a top cut which comprises light (4), a medium cut which comprises heavy gas oil (3) and a bottom cut which comprises heavy fuel oil (2),
- a vacuum system (S001) producing a vacuum at least of 250 mbars absolute (maximum pressure at the top of the column C001),
- heat exchangers (E001 to E005) having a heating or cooling function,
- drums (D003, D004 and V001) allowing separation of hydrocarbons, aqueous phases, vapor phases and incondensable gases,
- pumps (P001 to P010) providing fluid transfer,
- a stripping column (C002) regulating the flash point of the gas oil medium cut (3) by a superheated steam flow and,
- regulating means controlling the vacuum in the distillation column (C001) to at least 250 mbars absolute, the heater (H001) temperature between 300 and 410° C and the refluxes of light fuels from the reflux drum (D004) and of heavy gas oil from the stripping column (C002) into the distillation column (C001).

7. **A** unit according to claim 6, **characterized in that** it further comprises storage tanks for decanted water (T001), light fuels (T002), heavy gas oil (T003) and heavy fuel oil (T004).

8. A unit according to claim 6 or 7, **characterized in that** it comprises one or several heat exchanger(s) (E001) intended to preheat the petroleum residues at a temperature from 90 to 150° C.

9. A unit according to anyone of claims 6 to 8, **characterized in that** the heater (H001) is heated by burning incondensable gases and light fuels produced as a top cut of the distillation column (C001).

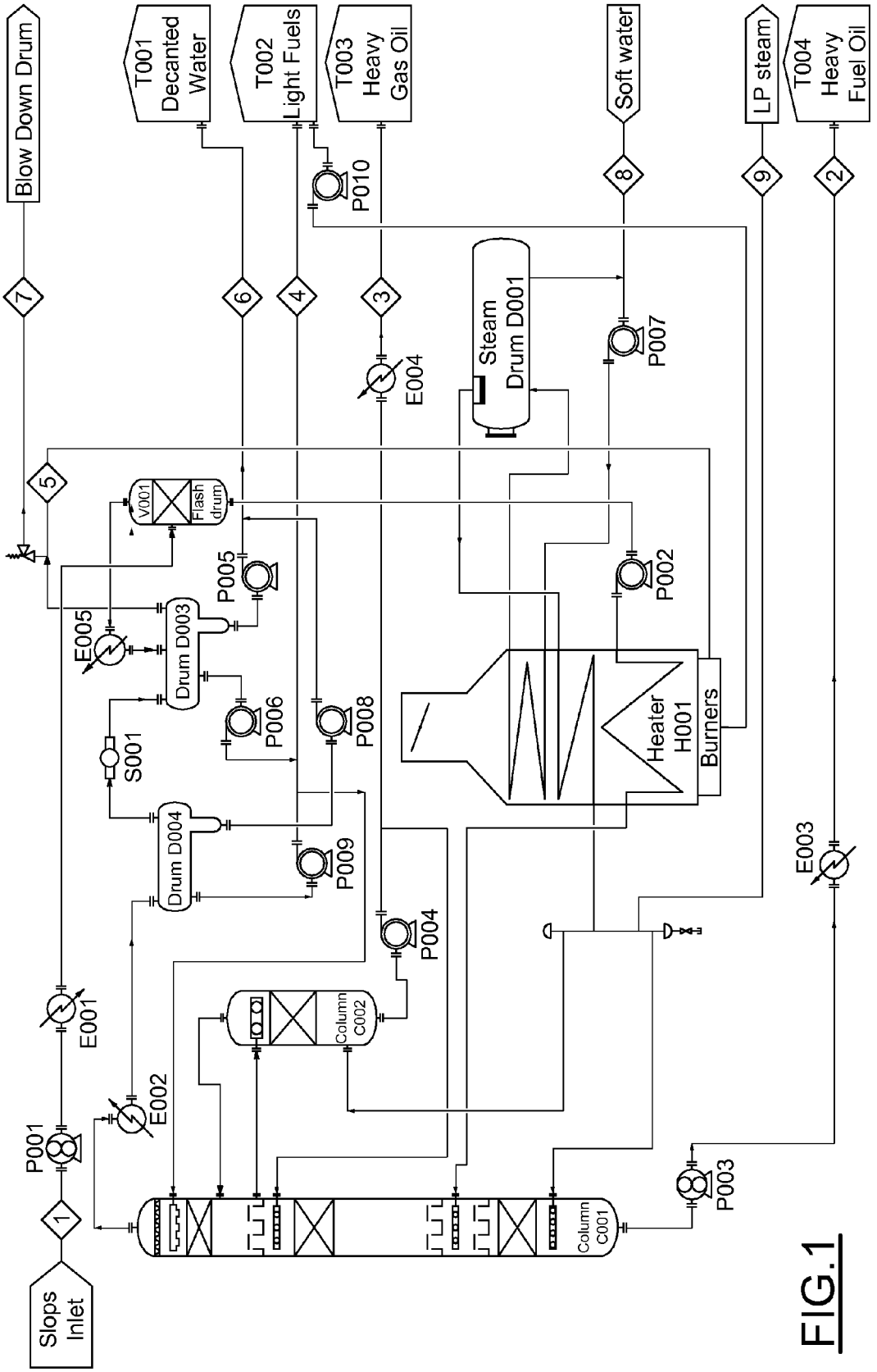
Slops Inlet
Blow Down Drum
T001 Decanted Water
T002 Light Fuels
T003 Heavy Gas Oil
Soft water
LP steam
T004 Heavy Fuel Oil
1
2
3
4
5
6
7
8
9
P001
P002
P003
P004
P005
P006
P007
P008
P009
P010
E001
E002
E003
E004
E005
S001
V001 Flash drum
Drum D003
Drum D004
Steam Drum D001
Heater H001
Burners
Column C002
Column C001

FIG.1

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EUROPEAN SEARCH REPORT

Application Number
EP 08 16 6393

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
Y	US 3 953 298 A (HOGAN JIM SMITH) 27 April 1976 (1976-04-27) * claims 1,8; figure 2 * * column 4, lines 56-61 * * column 5, lines 5-32 * * column 5, line 50 - column 6, line 29 * * column 6, line 64 - column 7, line 12 * * column 7, lines 32-38 * * column 8, lines 57-62 *	1-5	INV. B01D3/14 C10G7/06 C10G7/00 B01D3/32
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A	FR 2 875 145 A (MANUF DE PROD CHIM DE TOURNAN [FR]) 17 March 2006 (2006-03-17) * claims 8-10; figure 1 *	1-9	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
Munich	22 April 2009	Harf, Julien

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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EPO FORM 1503 03.82 (P04C01)

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This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
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22-04-2009

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For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

REFERENCES CITED IN THE DESCRIPTION

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- WO 2004067137 A **[0011]**