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(54) **RESIDUE SLURRY BED HYDROCRACKING METHOD AND DEVICE**

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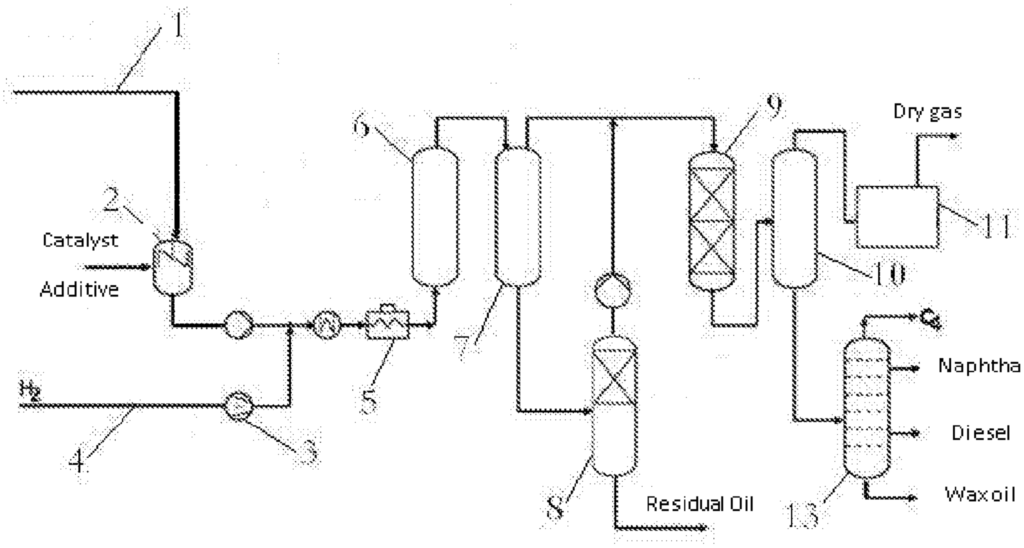
(57) **ABSTRACT**

A residue slurry bed hydrocracking method and device is used in the deep processing of crude oil. The processes of "slurry bed+fixed bed" reactor are applied. Raw materials, additives, catalysts and hydrogen are mixed, heated and pressurized before they are introduced into the slurry reactor, where thermal cracking and catalytic reactions occur under high hydrogen partial pressure. The coke, catalysts and additives in the reaction process are separated at the bottom of the heated high pressure separator (HHPS). Then they are transferred in a conventional fixed bed reactor to do further hydrocracking and hydrorefining, to product light oil products. The new Mo-Fe based catalyst developed in the invention can improve the activity of the main reactions, inhibit the reaction of coke production, and reduce system pressure from 20 Mpa to 17 Mpa, which can reduce device costs. Conversion rates can reach 90-95%, with the yield of light oil reaching 80-83%.



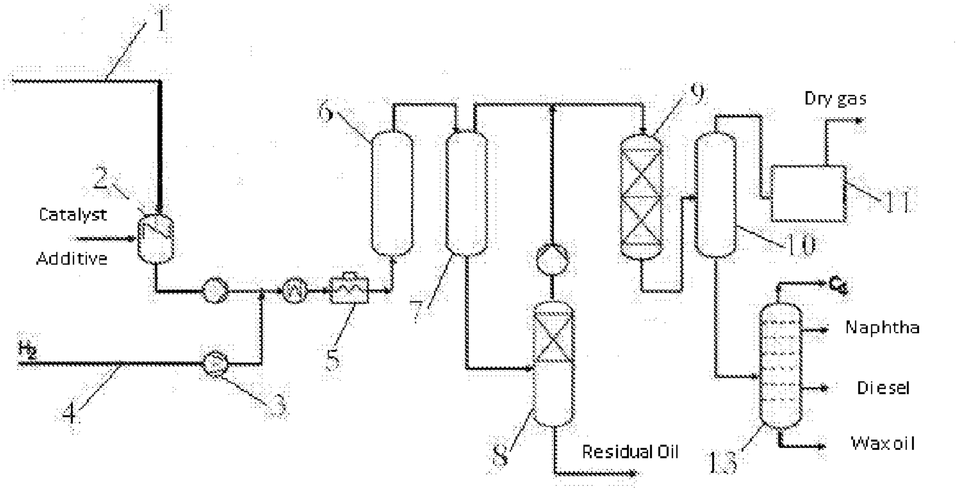


Figure 1

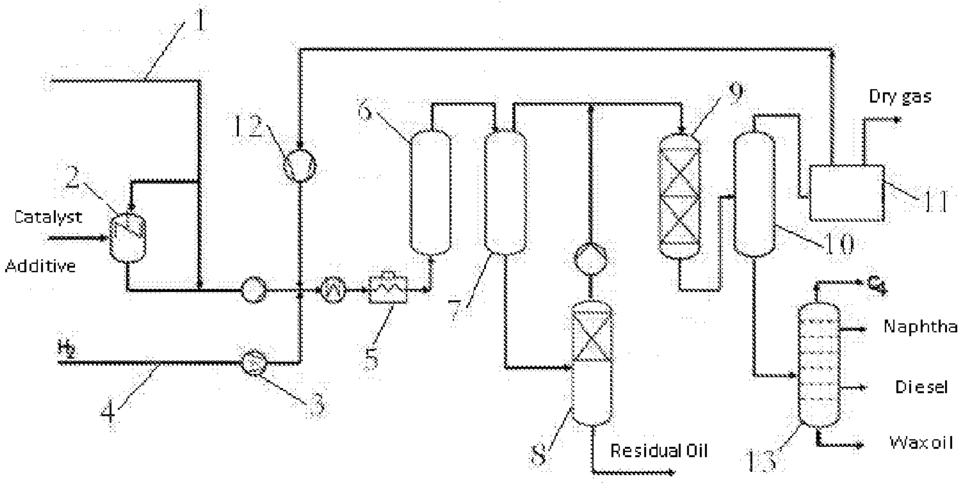


Figure 2

RESIDUE SLURRY BED HYDROCRACKING METHOD AND DEVICE

BACKGROUND OF THE INVENTION

[0001] Field of the invention

[0002] This invention relates to a residue slurry bed hydrocracking method and device, which is used in the field of deep processing of crude oil.

[0003] Description of the related art

[0004] There are 5 tons crude oil refined in China per year, and about 1.5 tons residual oil (heavy oil) are produced. Currently, the refinery mainly applies coking and hydrocracking, and the yield of light oil is around 55%, and the rest is coke with the lower production value, so the efficient use of resources does not achieve. China is a country with a shortage of resources, and the annual import of crude oil account for more than half of the total amount of refining. Because the fine processing of crude oil is not optimal, the refinery is often in a state of loss. The refining industry is in urgent need of a deep processing technology to improve the yield of light oil, to minimize the coke production, to improve the efficiency, and to ensure a profit.

[0005] Analyzing of crude oil processing process, the main problem is the low light oil yield and coke residue processing production, resulting in that crude oil has not been fully used, with poor efficiency. Especially most of the crude oil imported by China is heavy oil with higher sulfur content, residue produced in the oil refining is 30% on average, and many local refineries directly import heavy oil from abroad for processing; because the utilization rate is not high, residual oil (heavy oil) has a large room for improvement. The energy problem has been raised to the height of the national strategy We need to find new resources at home and abroad on the one hand, and on the other hand, should promote the existing crude oil processing capability, improve oil recovery rate, so as to indirectly increase the supply of energy.

[0006] Existing residue processing mainly uses suspension bed hydrogenation cracking (VCC) technology, including two processes which are liquid phase hydrogenation treatment (LPH) and gas liquid phase hydrogenation (GPH). Its principle is that:

> **[0007]** (1) The residue is mixed with the additive and hydrogen and then enters into the suspension bed reactor, in which undergoes a thermal cracking reaction, and is saturated with hydrogen under high pressure. The process of thermal cracking and hydrogenation saturation occurred under the action of a special additive in the residual carbon, resin and asphaltene.
>
> **[0008]** (2) The product of the suspension bed thermal cracking enters into the hot high pressure separator separation, gas cleaning products enters to fixed bed reactor for further hydrocracking and hydrotreating, and the productions are high quality naphtha and light diesel oil and gas oil. The solid substance, which is separated from the solid material, is mainly coke, which can be used for boiler fuel.

[0009] According to the existing development in foreign countries VCC technology has been able to improve the yield of light oil residue processing, which can reach close to 90%, but after the introduction into China, VCC technology still exist the problems of high processing pressure and the high cost of the imported catalyst, wherein the suspension bed working pressure is above 20 MPa. Therefore, it is urgent to develop new residue treatment methods.

SUMMARY OF THE INVENTION

[0010] In order to resolve the problems of high processing pressure and high cost of catalyst for the existing VCC technology, this invention provides a residue slurry bed hydrocracking method and device.

[0011] A residue slurry bed hydrocracking method, comprises the following steps:

[0012] Firstly, residual oil raw materials, additives, catalysts and hydrogen mix, and then they are heated and pressurized before introduced into a slurry bed reactor, where thermal cracking and catalytic reactions occur under high hydrogen partial pressure. The coke, asphaltene and heavy metals are adsorbed on the additive and catalyst during the reaction process, and then all the products are introduced into a heated high pressure separator (HHPS). The solid products are separated from the bottom of the HHPS, but the gases are separated from the top and are transferred in a fixed bed reactor to do further hydrocracking or hydrorefining. The said catalyst is a mixture of molybdate and iron, and the additive is vulcanizing agent, and the reaction pressure in the slurry bed reactor is 17-20 MPa.

[0013] Preferably, the additive is one or the mixture of two carbon disulfide, dimethyl sulfide, two methyl sulfide, two butyl mercaptan and sodium sulfide.

[0014] Preferably, the catalyst is made of iron powder and ammonium molybdate solution by spray granulation.

[0015] Preferably, the particle size of the catalyst is less than 10 μm and more preferably less than 5 μm.

[0016] Preferably, the mass percentage concentration of ammonium molybdate solution is 10%-50%.

[0017] Preferably, the ratio of the amount of iron and molybdenum in the catalyst is 1:150 to 1:200.

[0018] Preferably, the addition ratio of catalyst, additive and residual oil raw material was 0.8-1.2:2-4:100.

[0019] A residue slurry bed hydrocracking device is also provided, wherein a residue transportation pipeline connects an adding device for catalyst and additive firstly, and then connects a heating furnace after merging with a hydrogen conveying pipeline, and then connects a slurry bed reactor that connects HHPS. A fixed bed reactor connects the upper part of HHPS, and a vacuum flash tower connects the lower part; The said fixed bed reactor connects a chill high pressure separator (CHPS), a gas purification device connects the upper of CHPS, and a fractionating tower connects the lower part; The catalyst in the adding device is a mixture of molybdate and iron, and the reaction pressure in the slurry bed reactor is 17-20 MPa.

[0020] Preferably, the adding device is located on a branch pipe of the residue oil transmission pipeline. A part of residual oil is mixed with the catalyst and the additive in the adding device of the branch pipe, and then is combined with the main residue oil transmission pipeline.

[0021] Preferably, the gas purification device is connected with the heating furnace to recover the hydrogen gas through the circulating air compressor.

[0022] This residue slurry bed hydrocracking method applies the processes of "slurry bed+fixed bed" reactor. Raw materials, additives, catalysts and hydrogen mix, and then they are heated and pressurized before introduced into the slurry reactor, where thermal cracking and catalytic reactions occur under high hydrogen partial pressure. The coke, catalysts and additives in the reaction process are separated at the bottom of the heated high pressure separator (HHPS). Then they are transferred in a conventional fixed bed reactor to do further hydrocracking and hydrorefining, to produce naphtha, light diesel oil and wax etc.

[0023] The new Mo-Fe based catalyst developed in the invention can improve the activity of the main reactions and inhibit the reaction of coke production, and also can be the gathering core and carrier of the coke to make the coke form the reaction gathers on the surface of the catalyst instead of on the surface of the walls of the reactor and pipeline. The most essential effect is to reduce the system pressure from 20 Mpa to 17 Mpa, which can reduce the cost of the device greatly. The catalyst also has other advantages. Its mechanism is thermal cracking free radical mechanism, therefore it is cheap and can be disposable after use. It enters the reactor together with the raw material and doesn't need to be updated online. It doesn't need complicated catalyst handling system, so it covers a smaller area and needs less investment.

[0024] The conversion rate of this invention can reach 90-95%, and the yield of light oil can reach 80-83%.

BRIEF DESCRIPTION OF THE DRAWINGS

[0025] FIG. **1** is a diagram of the device and flow chart of the embodiment 1 of the invention;

[0026] FIG. **2** is a diagram of the device and flow chart of the embodiment 2 of the invention.

[0027] The labels in the figures are shown below:

[0028] **1**—residual oil pipeline, **2**—adding device, **3**—hydrogen compressor, **4**—hydrogen pipeline, **5**—furnace, **6**—slurry bed reactor, **7**—hot high pressure separator, **8**—vacuum flash tower, **9**—fixed bed reactor, **10**—cold high pressure separator, **11**—gas purification device, **12**—cyclic hydrogen compressor, **13**—fractionator.

DESCRIPTION OF THE EMBODIMENT

[0029] The invention is better explained by the embodiments in combination with the figures.

[0030] Embodiment 1

[0031] The embodiment is a pilot test of a single oil product in a continuous test cycle for 15 days, with a device and a process shown in FIG. **1**. The residue (raw material parameters are shown in Table 1) is transported by residual oil pipeline **1**, hydrogen is conveyed through the hydrogen compressor **3**, the mixture of residual oil and catalyst and additive are mixed in adding device **2** and then conveyed into the heating furnace **5** by hydrogen, and after heating-up and pressure boost-up into the slurry bed reactor **6**. The additive of the embodimentis carbon disulfide; the catalyst is made by mixing iron powder and ammonium molybdate solution and then spraying and granulation process, to ensure the smooth degree of the catalyst, wherein the mole ratio of iron and the effective component of molybdenum is 1:150. The catalyst is a small solid particle with a size of 5 μm or less, and is not soluble in oil and water. The ratio of each material can be seen in the following basic process parameters, and the reaction system is heterogeneous phase reaction.

[0032] Thermal cracking and catalytic reactions of the residue occur in the slurry bed reactor **6** based on the catalyst under high hydrogen partial pressure in the reaction process the coke, asphaltene, and heavy metals are adsorbed on the carbon disulfide, which ensures the long period operation of the slurry bed reactor. The exclusive newly developed catalyst can make the reaction faster, so as to overcome the problem that the reaction time is not enough in the reactor residue because of the backmixing of the residue, and can make the reaction pressure drop (see the following basic parameters) and inhibit the reaction of coke. The reaction products then enter the hot high pressure separator **7**, relatively clean gas products are isolated from the top of the hot high pressure separator **7**, and catalyst and additive with asphalt, residual carbon, sediment, metal and other solid enter into the vacuum distillation tower **8** from the bottom. The gas products enter into the conventional fixed bed reactor **9** and do further hydrogenation or cracking, since most of the asphaltene, carbon residue, sediment, metal etc. of the raw materials have been removed in the slurry bed reaction stage and from the bottom of the hot high pressure separator **7**, there is no serious influence on the fixed bed catalyst bedcaused by the them, which can guarantee a long period operation of the fixed bed reactor **9**. The gas product is further processed into the cold high pressure separator **10**, and the separated products are fractionated into naphtha, diesel oil, wax oil and so on in the fractionating tower **13**, while gas is desulfurization through the gas purification device **11**, and dry gas is discharged.

[0033] The basic process data of this embodiment are as follows:

TABLE 1

Properties of the raw crude oil

Properties	Mixed feeds
Specific gravity (20° C.) g/cm^3	1.044
Kinematic viscosity (100° C.) mm^2/s	2658.7
Condensation point	45
Carbon residue wt %	24.89
Ash content wt %	0.13
Acid value mg KOH/g	1.81
Component analysis wt %	
C	86.79
H	10.34
C/H mole ratio	1.39
S wt %	2.39
N wt %	0.83
Separation of four fractions wt %	
Saturates	23.24
Aromatics	39.5
Rs	24.61
Asphaltenes	12.59
Heavy metals μg/g	
Ni	108.2
V	402
Na	33.1
Fe	14.2
Cu	0.25

[0034] Basic process parameters of the slurry bed in this embodiment:

[0035] Temperature: 440-450° C.;

[0036] Experimental pressure: 17-18 Mpa;

[0037] Hydrogen to oil ratio: 900:1~1000:1;

[0038] Speed: 1.0 h-1;

[0039] Catalyst/feed residue: 1.2/100 (WT);

[0040] Curing agent/feed residue: 2.5/100 (WT);

[0041] Chemical hydrogen consumption of Slurry bed 2.3-2.5/1 (WT).

[0042] The following table is a comparison between the yield results of slurry bed of embodiment 1 and the present technology:

	Technology comparison		
Yield (wt %)	DC + FCC + Gasoline and Diesel Hydrotreating	VRDS + FCC + Gasoline and Diesel Hydrotreating	Embodoment 1
Acidic gas	3	4.31	4.2
C1-C2	7.7	9.03	6.0
C3-C4	6	16.06	3.0
Naphtha/gasoline	21.3	33.81	28.8
Diesel	29.2	25.24	55
Vacuum gas oil	0	0	0
Reaction residue	4.8	3.9	8
Petroleum coke/ coke	28	7.65	0
Yield of gasoline and diesel	50.5	59.05	83.8

[0043] As can be seen from the above table, the yield has been greatly improved, and the effect of the present invention is achieved.

[0044] Embodiment 2

[0045] The operation process of embodiment 2 is roughly the same with embodiment 1, as shown in FIG. **2**, wherein the adding device **2** is located on the branch pipe of the residue pipeline branch pipe **1**, a part of the residue, the catalyst and the additive premix in the adding device **2** on the branch pipe, and then it merges with the main residue pipeline, which can prevent unevenness caused by the direct mixture of the solid catalyst and the residue. In addition the gas purification device **11** is connected with the heating furnace to recover the remaining hydrogen gas through the cyclic hydrogen compressor **12**.

[0046] The raw oil is the same with embodiment 1. The mole ratio of iron and the effective active component Mo in the catalyst is 1:200. Similarly, it is made though spray granulation, and the size is less than 5 μm.

[0047] Basic process parameters of the slurry bed of embodiment 2:

[0048] Temperature: 450-460° C.;

[0049] Experimental pressure: 18-19 Mpa;

[0050] Hydrogen to oil ratio: 750:1~850:1;

[0051] Speed: 0.9h-1;

[0052] Catalyst/feed residue: 1/100 (WT);

[0053] Curing agent/feed residue: 3.5/100 (WT);

[0054] Chemical hydrogen consumption of Slurry bed (H2/feed): 2.0-2.3/1 (WT).

[0055] The following table is a comparison between the yield results of the slurry bed of embodiment 2 and the present technology:

	Technology comparison		
Yield (wt %)	DC + FCC + Gasoline and Diesel Hydrotreating	VRDS + FCC + Gasoline and Diesel Hydrotreating	embodiment 2
Acidic gas	3	4.31	4.0
C1-C2	7.7	9.03	6.2
C3-C4	6	16.06	2.8
Naphtha/ gasoline	21.3	33.81	26.3
Diesel	29.2	25.24	54
Vacuum gas oil	0	0	0
Reaction residue	4.8	3.9	6
Petroleum coke/ coke	28	7.65	0
Yield of gasoline and diesel	50.5	59.05	80.3

[0056] Seen from the embodiments, the invention realized an high light oil yield in a low pressure environment by improving the catalyst and process, which can significantly save costs and improve efficiency, and can make great contributions for relieving the tension of the raw oil and saving energy.

[0057] While the invention has been particularly shown and described with reference to preferred embodiments thereof, it will be understood by those skilled in the art that the foregoing and other changes in form and details can be made therein without departing from the spirit and scope of the invention.

We claim:

1. A residue slurry bed hydrocracking method, comprising the following steps:

firstly, residual oil raw materials, additives, catalysts and hydrogen mix, and then they are heated and pressurized before introduced into a slurry bed reactor, where thermal cracking and catalytic reactions occur under high hydrogen partial pressure; the coke, asphaltene and heavy metals are adsorbed on the additive and catalyst during the reaction process, and then all the products are introduced into a heated high pressure separator (HHPS); the solid products are separated from the bottom of the HHPS, but the gases are separated from the top and are transferred in a fixed bed reactor to do further hydrocracking or hydrorefining; the said catalyst is a mixture of molybdate and iron, and the additive is vulcanizing agent, and the reaction pressure in the slurry bed reactor is 17-20 MPa.

2. The method according to claim **1**, wherein the additive is one or the mixture of two carbon disulfide, dimethyl sulfide, two methyl sulfide, two butyl mercaptan and sodium sulfide.

3. The method according to claim **1**, wherein the catalyst is made of iron powder and ammonium molybdate solution by spray granulation.

4. The method according to claim **3**, wherein the particle size of the catalyst is less than 10 μm.

5. The method according to claim **3**, wherein the mass percentage concentration of ammonium molybdate solution is 10%-50%.

6. The method according to claim **3**, wherein the ratio of the amount of iron and molybdenum in the catalyst is 1:150 to 1:200.

7. The method according to claim **3**, wherein the addition ratio of the catalyst, additive and residual oil raw material is 0.8-1.2:2-4:100.

8. A residue slurry bed hydrocracking device, comprising: a residue transportation pipeline which connects an adding device for catalyst and additive firstly, and then connects a heating furnace after merging with a hydrogen conveying pipeline, and then connects a slurry bed reactor that connects HHPS; a fixed bed reactor which connects the upper part of HHPS, and a vacuum flash tower which connects the lower part; the said fixed bed reactor connecting a chill high pressure separator (CHPS), a gas purification device connecting the upper of CHPS, and a fractionating tower connecting the lower part; whereby the catalyst in the adding device is a mixture of molybdate and iron, and the reaction pressure in the slurry bed reactor is 17-20 MPa.

9. The device according to claim **8**, wherein the adding device is located on a branch pipe of the residue oil transmission pipeline; a part of residual oil is mixed with the catalyst and the additive in the adding device of the branch pipe, and then is combined with the main residue oil transmission pipeline.

10. The device according to claim **8**, wherein the gas purification device is connected with the heating furnace to recover the hydrogen gas through the circulating air compressor.

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