

Distillate Oil Combined Hydrogenation Method and Distillate Oil Combined Hydrogenation Apparatus



159159

Cross Reference

This application claims priority to Chinese Application No. 201210432679.2, filed on November 3, 2012, entitled "Distillate Oil Combined Hydrogenation Method", which are specifically and entirely incorporated by reference.

G00002



Field of the Invention

The present invention relates to a distillate oil combined hydrogenation method, in particular to a combined hydrogenation method of distillate oil feedstocks in different qualities and a distillate oil combined hydrogenation apparatus that implements the distillate oil combined hydrogenation method.

Background of the Invention

As people's environmental awareness becomes stronger increasingly and environmental protection laws and regulations put forth increasingly stringent requirements for engine exhaust emission, fuel oil standards stipulate increasingly rigorous requirements for S and N contents. In addition, as crude oil yield increases and conventional crude oil reserves decreases, the quality of crude oil becomes poorer and poorer, and the S and N contents in intermediate distillate oil obtained from straight-run distillation of crude oil and intermediate distillate oil obtained from secondary processing (e.g., coking and catalytic cracking, etc.) increase accordingly. How to process intermediate distillate oil that have high impurity contents (e.g., S and N) into products that meet environmental requirements is a common challenge for the oil refineries.

Hydrogenation process is the most cost-effective solution for removing impurities

from intermediate distillates. Most existing hydrogenation apparatuses employ high hydrogen-to-oil ratio and high hydrogen partial pressure, to ensure the service life of the catalyst and facilitate reactions such as hydrodesulfurization, hydrodenitrification, aromatic saturation, and cracking, etc. However, a high-pressure hydrogen circulation system requires high investment and operation cost, and causes increased oil production cost indirectly. With such conventional hydrogenation techniques, the reactions are three-phase actions, involving gas phase (mainly hydrogen gas), liquid phase (feedstock), and solid phase (catalyst), and the reactors mainly include trickle bed reactor, ebullated bed reactor, expanded bed reactor, and counter-flow bed reactor, etc.; a major characteristic of the reaction process is: the hydrogen gas volume is much more than the volume required by the reactions, and a high volume of unreacted hydrogen gas is cycled and reused. In the present invention, the above-mentioned techniques are referred to as gas-phase circulating hydrogenation techniques generally.

As technicians acquired deeper understanding on hydrogenation techniques, a two-phase hydrogenation technique was developed. Supersaturated hydrogen gas is dissolved in the feedstock and diluent oil, and the materials are fed directly into the reactor to undergo hydrogenation reaction; thus, the circulating hydrogen system is canceled, and the cost is reduced. Since the circulating hydrogen system is canceled, the adaptability of the process to feedstocks is limited. That technique mainly involves two phases in the reaction process, i.e., liquid phase (feedstock and diluent oil) and solid phase (catalyst). In the present invention, that process is referred to as a two-phase hydrogenation process.

Patent document US6881326 introduces a two-phase hydro-pretreating technique. The technical process is: fresh feedstock, circulating oil, and hydrogen gas are driven to pass through a hydrogen mixer to dissolve hydrogen gas in the oil, the oil with dissolved hydrogen flows into a small reactor and contacts with a catalyst to undergo hydrogenation reaction, to remove impurities from the oil. A part of the reactor effluent is cycled back to the hydrogen mixer, and the other part of the reactor

effluent is discharged as product from the apparatus. With that method, required hydrogen gas is dissolved in the oil before the feedstock and circulating oil enter into the reactor; therefore, a circulating hydrogen system can be canceled. However, the impurity removal rate often doesn't meet the criterion when that method is used to treat secondarily processed intermediate distillate oil. In all the existing two-phase hydrogenation techniques, a part of the reaction product is cycled as circulating oil. The major shortcomings of those techniques include: a high-temperature and high-pressure circulating oil system is required, the equipment investment and operation cost are high, and the hydrogen sulfide dissolved in the oil phase is difficult to remove effectively and is accumulated in the reaction system as the oil is cycled partially; therefore, the hydrogen sulfide causes severe inhibiting effect to the hydrogenation reaction. Though the hydrogen sulfide can be removed with some methods (e.g., steam stripping method), the equipment investment and operation cost will be increased, since the hydrogen sulfide is in a high-temperature and high-pressure system.

Summary of the Invention

To overcome the shortcomings in the prior art, the present invention provides a distillate oil combined hydrogenation method and a distillate oil combined hydrogenation apparatus. Distillate oil from which impurities are difficult to remove is processed with the conventional gas-phase circulating hydrogenation technique, the generated oil flows out of the high-pressure separator and then is directly mixed with the feedstocks that have dissolved hydrogen and is to be treated by two-phase hydrogenation; then, the mixed materials enter into a two-phase hydrogenation reactor and undergo hydrogenation reaction. The present invention combines seamlessly the conventional gas-phase circulating hydrogenation technique with a two-phase hydrogenation technique. The method provided in the present invention can be used to process different feedstocks according to the advantages of the

conventional gas-phase circulating hydrogenation technique and the two-phase hydrogenation technique respectively.

The distillate oil combined hydrogenation method provided in the present invention comprises the following steps:

- a) Dividing the distillate oil feedstocks by sulfur content into high-sulfur distillate oil feedstocks and low-sulfur distillate oil feedstocks, processing the high-sulfur distillate oil feedstocks with gas-phase circulating hydrogenation technique, driving the material processed with gas-phase circulating hydrogenation technique into a high-pressure separator and separating the material to obtain gas phase material and liquid phase material, wherein, the sulfur content according to which the distillate oil feedstocks are divided into high-sulfur distillate oil feedstocks and low-sulfur distillate oil feedstocks is at any value within 1,000~12,000 $\mu\text{g/g}$, and the sulfur content in the material processed with gas-phase circulating hydrogenation technique is lower than 100 $\mu\text{g/g}$;
- b) Feeding the liquid phase material obtained by separation in the high-pressure separator in step a) and the low-sulfur distillate oil feedstocks with dissolved hydrogen into a two-phase hydrogenation reactor in a two-phase hydrogenation unit for two-phase hydrotreating to obtain a hydrogenated distillate oil product, wherein, the two-phase hydro-processing doesn't use circulating oil.

The two-phase hydrogenation unit refers to a series of apparatuses that implement two-phase hydro-processing. Generally, two-phase hydrogenation units in the art include hydrogen dissolving apparatuses for feedstocks, two-phase hydrogenation reactors, circulating oil systems, and heating furnaces, etc. In the present invention, the circulating oil system is canceled in the two-phase hydrogenation unit.

Preferably, to meet the standards for different grades of clean fuels, the sulfur content in the material processed with gas-phase circulating hydrogenation technique is lower than 60 $\mu\text{g/g}$, preferably is lower than 50 $\mu\text{g/g}$, more preferably is lower than 15 $\mu\text{g/g}$, optimally is lower than 10 $\mu\text{g/g}$.

Since the purpose of dividing the distillate oil feedstocks into high-sulfur distillate oil feedstocks and low-sulfur distillate oil feedstocks is to process them differently, those skilled in the art can determine an appropriate value for dividing, according to the requirements and processing effects of gas-phase circulating hydrogenation technique and two-phase hydrogenation technique. Preferably, in step (a), the sulfur content according to which the distillate oil feedstocks are divided into high-sulfur distillate oil feedstocks and low-sulfur distillate oil feedstocks is at any value within 2,000~8,500 $\mu\text{g/g}$, i.e., a distillate oil feedstock with sulfur content equal to or higher than the value for dividing is high-sulfur distillate oil feedstock, and a distillate oil feedstock with sulfur content lower than the value for dividing is low-sulfur distillate oil feedstock.

In the present invention, the high-sulfur distillate oil feedstocks usually come from secondarily processed distillate oil, such as at least one selected from the group consisting of coked distillate oil, catalytic cracked distillate oil, and coal liquefied distillate oil; the low-sulfur distillate oil feedstocks usually comprise straight-run distillate oil obtained from crude oil distillation, and may contain some secondarily processed distillate oil. The high-sulfur distillate oil feedstocks and low-sulfur distillate oil feedstocks usually are at least one selected from the group consisting of kerosene distillates, diesel distillates, and VGO distillates, and the distillation range is preferably 130~450 $^{\circ}\text{C}$, more preferably 150~380 $^{\circ}\text{C}$, optimally 200~380 $^{\circ}\text{C}$.

The operating conditions of the gas-phase circulating hydrogenation technique described in step a) can include: reaction temperature: 100~400 $^{\circ}\text{C}$, preferably 260~380 $^{\circ}\text{C}$; reaction pressure: 2.5~10.0MPa, preferably 4.0~8.0MPa; volume ratio of hydrogen/oil: 50:1~1,000:1, preferably 300:1~800:1; liquid hourly space velocity: 0.6~5.0 h^{-1} , preferably 1.0~2.5 h^{-1} . Wherein, the hydrogen gas in the gas phase material separated in the high-pressure separator is returned to the gas phase hydrogenation reactor and reused. The gas-phase circulating hydrogenation technique can employ any reactor in an appropriate form, such as trickle bed reactor, ebullated bed reactor,

expanded bed reactor, counter-flow bed reactor, etc.

The two-phase hydrogenation reactor described in step b) can employ a top-charge and bottom-discharge operation mode or a bottom-charge and top-discharge operation mode. The operating conditions of the two-phase hydrogenation reactor described in step b) can include: reaction temperature: 100~400 °C, preferably 260~380 °C; reaction pressure: 1.5~8.0MPa, preferably 2.0~6.0MPa; liquid hourly space velocity: 0.6~5.0h⁻¹, preferably 1.0~2.5h⁻¹; the volume mixing ratio of liquid phase material separated in the high-pressure separator / low-sulfur distillate oil feedstocks can be 0.5:1~4.0:1, preferably 1.0:1~3.0:1.

The catalyst used in above steps can be any ordinary hydrotreating catalyst in the art, wherein, the active metal component of the catalyst can be at least one selected from the group consisting of nickel, cobalt, molybdenum, and tungsten, and the catalyst is preferably sulfurized before it is used, to convert the active metal component into sulfurized state. Based on the weight of the catalyst, the catalyst can comprise: nickel or cobalt: 0.5%~10% (calculated by oxide), molybdenum or tungsten: 1%~25% (calculated by oxide), and carrier, which can be at least one selected from the group consisting of aluminum oxide, silicon oxide, aluminum oxide-silicon oxide and titanium oxide. The catalyst is in extruded form or spherical form. The bulk density of the catalyst can be 0.5~1.1g/cm³, the particle diameter (diameter of sphere or diameter of bar) of the catalyst can be 0.04~4.0mm, and the specific surface area can be 80~350m²/g.

According to the present invention, preferably, the material processed with gas-phase circulating hydrogenation technique undergoes a heat exchange procedure before it enters into the high-pressure separator. For example, the heat exchange can be: at least a part of the material processed with gas-phase circulating hydrogenation technique undergo heat exchange with the high-sulfur distillate oil feedstocks. More preferably, the material processed with gas-phase circulating hydrogenation technique is heated up before heat exchange, and the high-sulfur distillate oil feedstocks after

heat exchange reaches to the temperature required by the gas-phase circulating hydrogenation technique. More preferably, the two-phase hydrogenation unit is not equipped with a heating furnace, the low-sulfur distillate oil feedstocks undergo heat exchange with the hydrogenated distillate oil product first, and then is directly mixed with the liquid phase material that flows out of the high-pressure separator, and the temperature of the mixture reaches to the required inlet temperature of the two-phase hydrogenation reactor. To attain that purpose, the operating temperature of the high-pressure separator must be higher than the inlet temperature of the two-phase hydrogenation reactor; preferably, the operating temperature of the high-pressure separator is higher than the inlet temperature of the two-phase hydrogenation reactor by $5^{\circ}\text{C}\sim 150^{\circ}\text{C}$, more preferably $10\sim 80^{\circ}\text{C}$, in order to ensure the hydrogenation effect of the two-phase hydrogenation process while avoiding energy waste resulted from excessively high temperature attained with the heating device. Those skilled in the art can choose an appropriate temperature rise value for the material processed with gas-phase circulating hydrogenation technique as required; preferably, the material processed with gas-phase circulating hydrogenation technique is heated up by $5\sim 120^{\circ}\text{C}$, more preferably $15\sim 80^{\circ}\text{C}$.

Since the circulating hydrogen system is canceled in the two-phase hydrogenation process and the feedstocks with dissolved hydrogen contact with the hydrogenation catalyst and undergo hydrogenation reaction, the dissolved amount of hydrogen gas in the feedstocks has direct influences on the depth of the hydrogenation reaction. The solubility of hydrogen gas in hydrocarbons will increase as the pressure increases. In the present invention, preferably the pressure in the circulating hydrogen system that utilizes the gas-phase circulating hydrogenation technique is higher than the reaction pressure in the two-phase hydrogenation apparatus; therefore, in relation to the reaction pressure in the two-phase hydrogenation apparatus, hydrogen gas in the liquid phase material in the high-pressure separator is in over-saturated state; thus, more reacting hydrogen gas can be provided for the two-phase hydrogenation reaction, and the impurities removal rate of the feedstocks can be improved.

Preferably, the pressure of the reaction with the gas-phase circulating hydrogenation technique is higher than the reaction pressure in the two-phase hydrogenation reactor by 1~4MPa.

According to the present invention, in step b), the liquid phase material separated in the high-pressure separator can selectively undergo a hydrogen dissolving procedure before the two-phase hydro-processing. As described above, the material processed by gas phase hydrogenation is essentially in hydrogen saturated state, and can be directly loaded into the two-phase hydrogenation reactor without hydrogen dissolving treatment, as shown in Figure 1. Alternatively, hydrogen dissolving treatment can be made for the liquid phase material separated in the high-pressure reactor; more preferably, this hydrogen dissolving procedure is executed with the hydrogen dissolving procedure for the low-sulfur distillate oil feedstocks in the same apparatus, as shown in Figure 2.

The present invention provides a distillate oil combined hydrogenation apparatus. As shown in Figure 1, the apparatus comprises a gas-phase circulating hydrogenation reactor 1, a high-pressure separator 2, and a two-phase hydrogenation unit that are connected sequentially, wherein, the two-phase hydrogenation unit comprises a hydrogen dissolving device 3 for the feedstocks to be processed by two-phase hydrogenation and a two-phase hydrogenation reactor 4, the hydrogen dissolving device 3 for the feedstocks to be processed by two-phase hydrogenation has a separate feed inlet, the gas-phase circulating hydrogenation reactor 1 and the two-phase hydrogenation reactor 4 communicate with a separate fresh feedstock feeding device respectively, the liquid phase outlet pipeline of the high-pressure separator 2 communicates with the two-phase hydrogenation unit, and a circulating oil system is canceled in the two-phase hydrogenation unit. To attain the purpose of gas-phase circulating hydrogenation, a return pipeline to the gas-phase circulating hydrogenation reactor 1 is arranged on the top end of the high-pressure separator, for circulating the hydrogen gas. Wherein, the gas-phase circulating hydrogenation reactor 1 communicates with a high-sulfur distillate oil feedstocks feeding device,

and the two-phase hydrogenation reactor 4 communicates with a low-sulfur distillate oil feedstocks feeding device. In the present invention, the "communication" (or "communicate") refers to direction communication or indirect communication.

Preferably, as shown in Figure 2, a first heat exchanger 11 is arranged between the gas-phase circulating hydrogenation reactor 1 and the high-pressure separator 2, to accomplish heat exchange between the feedstocks and effluents of the gas-phase circulating hydrogenation reactor 1.

Preferably, as shown in Figure 2, the gas-phase circulating hydrogenation reactor 1 further communicates with the high-pressure separator 2 directly through another pipeline. Thus, the material from the gas-phase circulating hydrogenation reactor 1 can flow into the heat exchanger 11 partially. In that way, the amount of materials subject to heat exchange can be adjusted, so that the degree of heat exchange with the feedstocks of the gas-phase circulating hydrogenation reactor 1 can be controlled flexibly.

Preferably, as shown in Figure 2, a heating device 10 is arranged between the gas-phase circulating hydrogenation reactor 1 and the first heat exchanger 11. With the heating device 10, the temperature of the effluents of the gas-phase circulating hydrogenation reactor 1 can be increased; thus, on one hand, the temperature of the feedstocks of the gas-phase circulating hydrogenation reactor 1 can meet the requirement of the gas-phase circulating hydrogenation process via the subsequent heat exchange process; on the other hand, after the effluents are mixed subsequently with the feedstocks to be processed by two-phase hydrogenation, the temperature of the mixture can meet the requirement of the two-phase hydrogenation process. In that way, the heat requirement of two-step hydro-processing can be met with only one heating device; therefore, the equipment cost is reduced.

According to the present invention, the purpose of the hydrogen dissolving device 3 for the feedstocks to be processed by two-phase hydrogenation is to dissolve hydrogen in the feedstocks of the two-phase hydrogenation reactor. The hydrogen

dissolving device 3 can be arranged separately, as shown in Figure 1; or, it can be arranged between the high-pressure separator 2 and the two-phase hydrogenation reactor 4, as shown in Figure 2. As described above, if hydrogen dissolving treatment is unnecessary for the liquid phase material separated in the high-pressure separator 2, the hydrogen dissolving device 3 for the feedstocks to be processed by two-phase hydrogenation is preferably arranged separately; if hydrogen dissolving treatment is required for the liquid phase material separated in the high-pressure separator 2, the hydrogen dissolving device 3 for the feedstocks to be processed by two-phase hydrogenation is preferably arranged between the high-pressure separator 2 and the two-phase hydrogenation reactor 4.

Preferably, as shown in Figure 2, the two-phase hydrogenation unit further comprises a second heat exchanger 12 designed to accomplish heat exchange between the feedstocks and the effluents of the two-phase hydrogenation unit, so as to further reduce energy consumption.

An advantage of the present invention is: a circulating oil procedure is canceled in the two-phase hydrogenation process, because the low-sulfur liquid phase material processed by gas-phase circulating hydrogenation can substitute circulating oil and is used in the follow-up two-phase hydrogenation step to attain the purpose of increasing the carrying amount of hydrogen; in addition, the method provided in the present invention overcomes the shortcoming of sulfur impurity accumulation related with the use of circulating oil, and improves the efficiency of the entire process and apparatus.

Moreover, the combined hydrogenation method and equipment provided in the present invention have the following advantages:

1. The present invention combines seamlessly the conventional gas circulating hydrogenation technique with a two-phase hydrogenation technique. The method provided in the present invention can be used to process different feedstocks according to the advantages of the conventional gas-phase circulating

hydrogenation technique and the two-phase hydrogenation technique respectively. A lower-pressure separator is canceled in the conventional gas-phase circulating hydrogenation apparatus, a high-temperature and high-pressure hot oil circulation system is canceled in the two-phase hydrogenation apparatus, the size of the hydrogen dissolving device is reduced, and the two apparatuses can share one distillation system; therefore, the equipment investment and operation cost are reduced.

2. The dissolved hydrogen in the liquid phase material separated in the high-pressure separator is utilized fully. After the two-phase hydrogenation reaction, the hydrogen gas dissolved in the liquid phase material is essentially depleted; therefore, the amount of waste hydrogen in the reaction product from the lower pressure separator is greatly reduced, the hydrogen gas consumption in the entire combined process is reduced, the size of the post-treatment device is decreased, and the operation cost is reduced.
3. The circulating hydrogen pressure drop in the gas-phase circulating hydrogenation process is higher than the reaction pressure of the two-phase hydrogenation process; therefore, the liquid phase material separated in the high-pressure separator is in hydrogen over-saturated state, and more reacting hydrogen gas can be provided for two-phase hydrogenation; thus, the impurities removal rate of the feedstock can be improved.
4. Since a large amount of hydrogen gas exists in the high-pressure separator, most hydrogen sulfide in the liquid phase can be carried away; therefore, the impact on the catalyst used in the two-phase hydrogenation reactor is decreased. In contrast, with a two-phase hydrogenation technique that employs a liquid phase circulating system, it is difficult to remove the hydrogen sulfide in the circulating oil effectively; as a result, the impact on deep hydrodesulfurization is apparent. Even though a hydrogen sulfide removing device can be arranged for the circulating oil, the equipment investment and operation cost will be very high, because there is

no cost-effective technique.

5. In a preferred embodiment of the present invention, only one heating device is arranged for the two hydrogenation reactors; therefore, the equipment investment is low; the heating device heats up the high-temperature material and is helpful for improving the energy utilization efficiency at high temperature; since the operating temperature of the high-pressure separator is high, the hydrogen sulfide, ammonia, and light hydrocarbons can be removed from the reaction product of gas-phase circulating hydrogenation as much as possible, so that they will not affect the two-phase hydrogenation reaction process (high-sulfur distillate oil usually contain more impurities and more light distillates); the low-sulfur distillate oil feedstocks are mixed directly with the high-temperature liquid phase material and reaches to the temperature required for the reaction; the equipment is the simplest and the heat utilization ratio is the highest when direct mixing is used.
6. By treating the feedstocks differently on the basis of sulfur content, shortcomings in the processes that all feedstocks are treated by gas phase hydrogenation or two-phase hydrogenation solely or treated by gas phase hydrogenation and two-phase hydrogenation sequentially in the prior art are eliminated; therefore, the processing method and apparatus provided in the present invention have higher adaptability to different feedstocks.

Brief Description of the Drawings

Figure 1 shows a flow diagram of the distillate oil combined hydrogenation method and a schematic diagram of the distillate oil combined hydrogenation apparatus in the present invention.

Figure 2 shows a flow diagram of another distillate oil combined hydrogenation method and a schematic diagram of the distillate oil combined hydrogenation apparatus in the present invention.

Brief Description of the Symbols in the Drawings

- 1 Gas-phase circulating hydrogenation reactor
- 2 High-pressure separator
- 3 Hydrogen dissolving device for the feedstocks to be processed by two-phase hydrogenation
- 4 Two-phase hydrogenation reactor
- 10 Heating device
- 11 First heat exchanger
- 12 Second heat exchanger

Detailed Description of the Embodiments

To further explain the technical features of the present invention, hereinafter, the present invention will be detailed with reference to the accompanying drawings.

As shown in Figure 1, the process of a distillate oil combined hydrogenation method in the present invention is:

A high-sulfur distillate oil feedstock 6 is mixed with make-up hydrogen gas 5 and circulating hydrogen, and the mixture enters into a gas phase circulating hydrogenation reactor 1; the material processed by hydrogenation is cooled and then enters into a high-pressure separator 2 and is separated into gas phase material and liquid phase material; the hydrogen gas in the gas phase material is cycled back to the inlet of the gas-phase circulating hydrogenation reactor 1. A low-sulfur distillate oil feedstock 7 undergoes hydrogen dissolving treatment in a hydrogen dissolving device 3 for the feedstock to be processed by two-phase hydrogenation, and is mixed with the liquid phase material from the high-pressure separator 2; the mixture is charged into a two-phase hydrogenation reactor 4 from the bottom of the reactor and contacts with a catalyst to undergo two-phase hydrogenation reaction; the hydrogenated

distillate oil product 8 is discharged from the top of the reactor.

As shown in Figure 2, in a preferred embodiment of the present invention, a high-sulfur distillate oil feedstock 6 is mixed with make-up hydrogen gas 5 and circulating hydrogen, and the mixture exchanges heat with the effluent of a gas-phase circulating hydrogenation reactor 1 in a heat exchanger 11, and then enters into a gas phase circulating hydrogenation reactor 1 and is hydrogenated; the treated material is heated up by a heating device 10, and then flows through the heat exchanger 11 partially or entirely, enters into a high-pressure separator 2 and is separated into liquid phase material and gas phase material; the hydrogen gas in the gas phase material is mixed with make-up hydrogen gas 5 and feedstock 6 and then cycled back to the inlet of the gas-phase circulating hydrogenation reactor 1. A low-sulfur distillate oil feedstock 7 exchanges heat with the hydrogenated distillate oil product 8, and then enters into a hydrogen dissolving device 3 for the feedstock to be processed by two-phase hydrogenation and undergoes hydrogen dissolving treatment and is mixed with the liquid phase material from the high-pressure separator 2 in the hydrogen dissolving device 3; then, the mixture is charged into a two-phase hydrogenation reactor 4 from the bottom of the reactor and contacts with a catalyst to undergo two-phase hydrogenation reaction; the hydrogenated distillate oil product 8 is discharged from the top of the reactor.

To further explain the technical scheme and beneficial effects of the present invention, hereunder some examples will be described:

Example 1

This example is a specific implementation scheme of the distillate oil combined hydrogenation method and apparatus. The process flow diagram is shown in Figure 1.

A high-sulfur distillate oil feedstock 6 is mixed with make-up hydrogen gas 5 and circulating hydrogen, and the mixture enters into a gas phase circulating hydrogenation reactor 1; the material processed by hydrogenation is cooled and then

enters into a high-pressure separator 2 and is separated into gas phase material and liquid phase material; the hydrogen gas in the gas phase material is cycled back to the inlet of the gas-phase circulating hydrogenation reactor 1. A low-sulfur distillate oil feedstock 7 undergoes hydrogen dissolving treatment in a hydrogen dissolving device 3 for the feedstock to be processed by two-phase hydrogenation, and is mixed with the liquid phase material from the high-pressure separator 2; the mixture is charged into a two-phase hydrogenation reactor 4 from the bottom of the reactor and contacts with a catalyst to undergo two-phase hydrogenation reaction; the hydrogenated distillate oil product 8 is discharged from the top of the reactor.

The properties of the feedstocks used in the test are shown in Table 1. The volume ratio of high-sulfur distillate oil feedstock 6 / low-sulfur distillate oil feedstock 7 is 2:1. The same catalyst is used in the gas-phase circulating hydrogenation reactor 1 and the two-phase hydrogenation reactor 4. The properties of the catalyst are shown in Table 2 (the catalyst is vulcanized before it is used); the volume ratio of catalyst used in the gas-phase circulating hydrogenation reactor 1 / catalyst used in the two-phase hydrogenation reactor 4 is 2:1. The reaction conditions in the gas-phase circulating hydrogenation reactor 1 and two-phase hydrogenation reactor 4 and the properties of hydrogenated distillate oil product 8 are shown in Table 3.

Comparative Example 1

The low-sulfur distillate oil feedstock 7 is treated by two-phase hydrogenation. The feedstock properties, two-phase hydrogenation conditions, and reactor are the same as those used in the two-phase hydrogenation process in example 1, with the following difference: a circulating oil system is added, and the reaction product is cycled and reused.

The properties of the hydrogenated distillate oil product 8 are shown in Table 3.

Comparative Example 2

Distillate oil combined hydrogenation is carried out in the apparatus used in example 1, with the following difference: the high-sulfur distillate oil feedstock 6 and low-sulfur distillate oil feedstock 7 are mixed at 2:1 volume mixing ratio, the total amount of the mixed feedstock is the same as the amount of the feedstock in example 1, the mixed feedstock is processed by gas-phase circulating hydrogenation first, and then the liquid phase product obtained from the gas-phase circulating hydrogenation process is processed by two-phase hydrogenation.

The conditions of hydrogenation process and the properties of the hydrogenated distillate oil product 8 are shown in Table 3.

Comparative Example 3

Distillate oil combined hydrogenation is carried out in the apparatus and under the processing conditions used in the comparative example 2, with the following difference: a circulating oil system is added, and the reaction product is cycled and reused.

The conditions of hydrogenation process and the properties of the hydrogenated distillate oil product 8 are shown in Table 3.

Comparative Example 4

Distillate oil combined hydrogenation is carried out in the apparatus and under the processing conditions used in the comparative example 3, with the following difference: a hydrogen sulfide removing device is added in the circulating oil system, to reduce the hydrogen sulfide concentration in the circulating oil to approx. 100 μ g/g.

The conditions of hydrogenation process and the properties of the hydrogenated distillate oil product 8 are shown in Table 4.

Comparative Example 5

Distillate oil combined hydrogenation is carried out in the apparatus and under the processing conditions used in example 1, with the following difference: the reaction severity is decreased, so that the sulfur content in the reaction product of gas-phase circulating hydrogenation is approx. 500 $\mu\text{g/g}$; then, the liquid phase material obtained from the reaction product of gas-phase circulating hydrogenation is mixed with the feedstock to be processed by two-phase hydrogenation, and then the mixture is processed by two-phase hydrogenation, through the process described in example 1.

The conditions of hydrogenation process and the properties of the hydrogenated distillate oil product 8 are shown in Table 4.

Table 1 Properties of Feedstock

Feedstock Properties	Feedstock to be treated by gas-phase circulating hydrogenation	Feedstock to be treated by two-phase hydrogenation
Density (20°C) / $\text{g}\cdot\text{cm}^{-3}$	0.8554	0.8378
Distillation range / °C	170~372	159~346
S content / $\mu\text{g}\cdot\text{g}^{-1}$	9746	5728
N content / $\mu\text{g}\cdot\text{g}^{-1}$	366	129

Table 2 Physical and Chemical Properties of Catalyst

Item	Data
Active components of catalyst	Mo、Ni、W
Content of active components (calculated by oxide), wt%	29
Carrier	Aluminum oxide
Shape	Trefoil
Diameter, mm	3.1
Pore volume / $\text{mL}\cdot\text{g}^{-1}$	0.41
Specific surface area / $\text{m}^2\cdot\text{g}^{-1}$	235

Table 3 Conditions of Hydrogenation Process

Process Condition	Example 1		Comparative Example 1	Comparative Example 2		Comparative Example 3	
	Gas phase	Two-phase	Two-phase	Gas phase	Two-phase	Gas phase	Two-phase
Reaction pressure / MPa	6.5	4.0	4.0	6.5	4.0	6.5	4.0
Reaction temperature / °C	360	360	360	360	360	360	360
Feed ratio of feedstock to be treated by two-phase hydrogenation	-	2:1*	2:1**	-	-	-	2:1**
Volume ratio of hydrogen/oil	550:1	-	-	550:1	-	550: 1	-
Liquid hourly space velocity / h ⁻¹ [note]	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Properties of generated oil:							
S content, µg/g	13.9	8.8	457.5	437.2	118.4	437.2	39.1
N content, µg/g	2.3	3.6	35.7	22.4	12.6	22.4	11.2
Distillation range, °C	167-365	151-366	150-342	154-370	152-368	153-370	150-368

* Volume ratio of liquid phase material from the high-pressure separator in the gas-phase circulating hydrogenation apparatus / fresh material fed to the two-phase hydrogenation apparatus, the same below. ** Volume ratio of cycled amount of liquid phase material from the two-phase hydrogenation reactor / fresh material fed to the two-phase hydrogenation apparatus, the same below. "Gas phase" represents the processing conditions of the gas-phase circulating hydrogenation apparatus, while "two-phase" represents the processing conditions of the two-phase circulating hydrogenation apparatus, the same below. The oil generated through the gas-phase circulating hydrogenation procedure refers to the liquid phase oil generated in the high pressure separator, the same below.

[Note] In the examples 1-4 and comparative examples 1-5 shown in Tables 3, 4, and 5, the liquid hourly space velocity in the gas-phase circulating hydrogenation reactor is calculated on the basis of the feedstock of gas-phase circulating hydrogenation, and the liquid hourly space velocity in the two-phase hydrogenation reactor is calculated on the basis of the feedstock of two-phase hydrogenation. The examples 1 and comparative examples 1-4 show comparison among results obtained with different technical schemes when the same amount of feedstock is processed under the same operating conditions with the same amount of catalyst.

Table 4 Conditions of Hydrogenation Process

Process Condition	Comparative Example 4		Comparative Example 5	
	Gas phase	Two-phase	Gas phase	Two-phase
Reaction pressure / MPa	6.5	4.0	4.5	4.0
Reaction temperature / °C	360	360	360	360
Feed ratio of feedstock to be treated by two-phase hydrogenation	-	2:1**	-	2:1*
Volume ratio of hydrogen/oil	550:1	-	550:1	-
Liquid hourly space velocity / h ⁻¹ [note]	1.5	1.5	1.5	1.5
Properties of generated oil:				
S content, µg/g	437.2	8.6	483.5	202.5
N content, µg/g	22.4	3.5	20.7	14.3
Distillation range, °C	153-370	150-365	168-367	153-369

Examples 2-4

The process flow of the examples 2-4 is illustrated in Figure 2.

A high-sulfur distillate oil feedstock 6 is mixed with make-up hydrogen gas 5 and circulating hydrogen, and the mixture exchanges heat with the effluent of a gas-phase circulating hydrogenation reactor 1 in a heat exchanger 11, and then enters into a gas phase circulating hydrogenation reactor 1 and is hydrogenated; the treated material is heated up by a heating device 10, and then flows through the heat exchanger 11 partially, enters into a high-pressure separator 2 and is separated into liquid phase material and gas phase material; the hydrogen gas in the gas phase material is mixed with make-up hydrogen gas 5 and feedstock 6 and then cycled back to the inlet of the gas-phase circulating hydrogenation reactor 1. A low-sulfur distillate oil feedstock 7 exchanges heat with the hydrogenated distillate oil product 8 generated from reaction, and then enters into a hydrogen dissolving device 3 for the feedstock to be processed

by two-phase hydrogenation and undergoes hydrogen dissolving treatment and is mixed with the liquid phase material from the high-pressure separator 2 in the hydrogen dissolving device 3; then, the mixture is charged into a two-phase hydrogenation reactor 4 from the bottom of the reactor and contacts with a catalyst to undergo two-phase hydrogenation reaction; the hydrogenated distillate oil product 8 is discharged from the top of the reactor.

The properties of the feedstock are shown in Table 1. The same catalyst is used in the gas-phase circulating hydrogenation reactor 1 and the two-phase hydrogenation reactor 4. The properties of the catalyst are shown in Table 2. The reaction conditions in the gas-phase circulating hydrogenation reactor 1 and two-phase hydrogenation reactor 4 and the properties of hydrogenated distillate oil product 8 are shown in Table 5.

Table 5 Conditions of Hydrogenation Process

Process Condition	Example 2		Example 3		Example 4	
	Gas phase	Two-phase	Gas phase	Two-phase	Gas phase	Two-phase
Reaction pressure / MPa	8.0	6.0	6.0	2.0	4.0	3.0
Reaction temperature / °C	260	260	320	320	380	380
Feed ratio of feedstock to be treated by two-phase hydrogenation	-	3:1	-	2:1	-	1.5:1
Volume ratio of hydrogen/oil	800	-	500	-	300	-
Liquid hourly space velocity / h ⁻¹	1	1	2	2	2.5	2.5
Heating temperature / °C	10	-	80	-	40	-
Properties of generated oil:						
S content, µg/g	86.4	32.6	14.5	7.6	13.1	8.7
N content, µg/g	17	11	7	6	6	5
Distillation range, °C	168-371	155-364	166-367	152-361	160-364	148-361

Wherein, the heating temperature refers to the temperature rise of the material after the material is heated up by the heating device 10.

It can be seen from the comparison of result between example 1 and comparative examples 1-2: with the combined method provided in the present invention, the sulfur content and nitrogen content in the generated oil product after hydrogenation can be reduced greatly.

It can be seen from the comparison of result between example 1 and comparative example 3: with the combined method provided in the present invention, a circulating oil system is canceled in the two-phase hydrogenation apparatus; therefore, the overall equipment investment of the process and the energy consumption during operation can be reduced.

It can be seen from the comparison of result between example 1 and comparative example 4: to attain a reaction effect similar to the reaction effect obtained in the present invention, a circulating oil system and a hydrogen sulfide removing device for circulating oil have to be used in the two-phase hydrogenation apparatus in the prior art. In contrast, with the method provided in the present invention, the quantity of devices is greatly decreased, and the operation cost is reduced significantly.

It is seen from the comparison of result between example 1 and comparative example 5: in the present invention, feedstocks that have different properties are treated separately in the hydrogenation process, and the reaction depth in each hydrogenation procedure is controlled, to ensure a clean fuel product that meets the most stringent standard is obtained; in addition, the equipment investment and operation cost are low, and the overall technical effect of the present invention is outstanding.

It can be seen from the comparison of result between example 1 and examples 2-4: with the process and apparatus shown in Figure 2, only one heating furnace is used to supply heat required for reaction in the two apparatuses; therefore, that is helpful for reducing the energy consumption and equipment investment of heating furnace.

Claims

1. A distillate oil combined hydrogenation method, comprising the following steps:
 - a) Dividing the distillate oil feedstocks by sulfur content into high-sulfur distillate oil feedstocks and low-sulfur distillate oil feedstocks, processing the high-sulfur distillate oil feedstocks with gas-phase circulating hydrogenation technique, driving the material processed with gas-phase circulating hydrogenation technique into a high-pressure separator and separating the material to obtain gas phase material and liquid phase material, wherein, the sulfur content according to which the distillate oil feedstocks are divided into high-sulfur distillate oil feedstocks and low-sulfur distillate oil feedstocks is at any value within 1,000~12,000 $\mu\text{g/g}$, and the sulfur content in the material processed with gas-phase circulating hydrogenation technique is lower than 100 $\mu\text{g/g}$;
 - b) Feeding the liquid phase material obtained by separation in the high-pressure separator in step a) and the low-sulfur distillate oil feedstocks with dissolved hydrogen into a two-phase hydrogenation reactor in a two-phase hydrogenation unit for two-phase hydrotreating to obtain a hydrogenated distillate oil product, wherein, the two-phase hydro-processing doesn't use circulating oil.
2. The method according to claim 1, wherein, the sulfur content in the material processed with gas-phase circulating hydrogenation technique is lower than 60 $\mu\text{g/g}$, preferably is lower than 50 $\mu\text{g/g}$, more preferably is lower than 15 $\mu\text{g/g}$, optimally is lower than 10 $\mu\text{g/g}$.
3. The method according to claim 1, wherein, the material processed with gas-phase circulating hydrogenation technique undergoes a heat exchange procedure before it enters into the high-pressure separator.
4. The method according to claim 3, wherein, the heat exchange method comprises: controlling at least a part of the material processed with gas-phase circulating

hydrogenation technique to undergo heat exchange with the high-sulfur distillate oil feedstocks.

5. The method according to claim 4, wherein, the material processed with gas-phase circulating hydrogenation technique is heated up before heat exchange, and the temperature of the high-sulfur distillate oil feedstocks after heat exchange reaches to the temperature required for the gas-phase circulating hydrogenation technique.
6. The method according to claim 5, wherein, the two-phase hydrogenation unit is not equipped with a heating furnace, the low-sulfur distillate oil feedstocks undergo heat exchange with the hydrogenated distillate oil product first, and then are directly mixed with the liquid phase material that flows out of the high-pressure separator, and the temperature of the mixture reaches to the required inlet temperature of the two-phase hydrogenation reactor.
7. The method according to claim 6, wherein, the operating temperature of the high-pressure separator is higher than the inlet temperature of the two-phase hydrogenation reactor by $5^{\circ}\text{C}\sim 150^{\circ}\text{C}$, preferably $10^{\circ}\text{C}\sim 80^{\circ}\text{C}$.
8. The method according to any of previous claims, wherein, the sulfur content according to which the distillate oil feedstocks are divided by sulfur content into high-sulfur distillate oil feedstocks and low-sulfur distillate oil feedstocks is at any value within $2,000\sim 8,500\mu\text{g/g}$.
9. The method according to any of previous claims, wherein, the high-sulfur distillate oil feedstocks come from secondarily processed distillate oils, including at least one selected from the group consisting of coked distillate oils, catalytic cracked distillate oils, and coal liquefied distillate oils; the low-sulfur distillate oil feedstocks comprise straight-run distillate oils obtained from crude oil distillation.
10. The method according to any of previous claims, wherein, the high-sulfur distillate oil feedstocks and low-sulfur distillate oil feedstocks are at least one selected from the group consisting of kerosene distillates, diesel distillates, and VGO distillates.

11. The method according to any of previous claims, wherein, the distillation range of the high-sulfur distillate oil feedstocks and low-sulfur distillate oil feedstocks are 130~450°C, preferably 200~380°C.
12. The method according to any of previous claims, wherein, in step a), the reaction temperature of the gas-phase circulating hydrogenation technique is 100~400°C, preferably 260~380 °C ; the reaction pressure is 2.5~10.0MPa, preferably 4.0~8.0MPa; the volume ratio of hydrogen/oil is 50:1~1,000:1, preferably 300:1~800:1; the liquid hourly space velocity is 0.6~5.0h⁻¹, preferably 1.0~2.5h⁻¹.
13. The method according to any of previous claims, wherein, in step a), the gas-phase circulating hydrogenation technique employs a trickle bed reactor, ebullated bed reactor, expanded bed reactor, or counter-flow bed reactor.
14. The method according to any of previous claims, wherein, in step b), the two-phase hydrogenation reactor employs a top-charge and bottom-discharge operation mode or a bottom-charge and top-discharge operation mode; the operating conditions of the two-phase hydrogenation reactor described in step b) include: reaction temperature: 100~400 °C , preferably 260~380 °C ; reaction pressure: 1.5~8.0MPa, preferably 2.0~6.0MPa; liquid hourly space velocity: 0.6~5.0h⁻¹, preferably 1.0~2.5h⁻¹; the volume mixing ratio of liquid phase material separated in the high-pressure separator / low-sulfur distillate oil feedstocks is 0.5:1~4.0:1, preferably 1.0:1~3.0:1.
15. The method according to any of previous claims, wherein, the reaction pressure of the gas-phase circulating hydrogenation technique is higher than the reaction pressure of the two-phase hydrogenation reactor by 1~4MPa.
16. The method according to any of previous claims, wherein, the catalyst used in step a) and step b) is a hydro-treating catalyst, the active metal component of the catalyst is at least one selected from the group consisting of nickel, cobalt, molybdenum, and tungsten, and the catalyst is sulfurized before it is used, to

convert the active metal component into sulfurized state.

17. A distillate oil combined hydrogenation apparatus, comprising a gas-phase circulating hydrogenation reactor (1), a high-pressure separator (2), and a two-phase hydrogenation unit that are connected sequentially, wherein, the two-phase hydrogenation unit comprises a hydrogen dissolving device (3) for the feedstocks to be processed by two-phase hydrogenation and a two-phase hydrogenation reactor (4), the hydrogen dissolving device (3) for the feedstocks to be processed by two-phase hydrogenation has a separate feed inlet, the gas-phase circulating hydrogenation reactor (1) and the two-phase hydrogenation reactor (4) communicate with a separate fresh feedstock feeding device respectively, the liquid phase outlet pipeline of the high-pressure separator (2) communicates with the two-phase hydrogenation unit, and a circulating oil system is canceled in the two-phase hydrogenation unit.
18. The apparatus according to claim 17, wherein, a first heat exchanger (11) is arranged between the gas-phase circulating hydrogenation reactor (1) and the high-pressure separator (2), to accomplish heat exchange between the feedstocks and effluents of the gas-phase circulating hydrogenation reactor (1).
19. The apparatus according to claim 18, wherein, the gas-phase circulating hydrogenation reactor (1) further communicates directly with the high-pressure separator (2) through another pipeline.
20. The apparatus according to claim 18 or 19, wherein, a heating device (10) is arranged between the gas-phase circulating hydrogenation reactor (1) and the first heat exchanger (11).
21. The apparatus according to claim 20, wherein, the hydrogen dissolving device (3) for the feedstocks to be processed by two-phase hydrogenation is arranged between the high-pressure separator (2) and the two-phase hydrogenation reactor (4).
22. The apparatus according to any of previous claims, wherein, the two-phase

hydrogenation unit further comprises a second heat exchanger (12), to accomplish heat exchange between the feedstocks and the effluents of the two-phase hydrogenation unit.