

LIQUID-PHASE HYDROGENATION REACTION METHOD

WITH MULTI-STAGE HYDROGEN DISSOLUTION

FIELD OF THE INVENTION

The present invention relates to a liquid-phase hydrogenation reaction method with multi-stage hydrogen dissolution, especially to a process of product circulation and liquid-phase hydrogenation treatment.

BACKGROUND OF ART

With increasingly reinforced environmental consciousness, many countries have limited sulfur content of diesel fuel to a quite low level (10 to 15 $\mu\text{g/g}$), to reduce the emission of harmful gases, and improve air quality by means of environmental legislation. The sulfur content of diesel fuel was decreased to 15 $\mu\text{g/g}$ in 2006 in USA. The sulfur content of diesel fuel was decreased to 10 $\mu\text{g/g}$ in January, 2003 in Germany. The sulfur content of diesel fuel was decreased to 10 $\mu\text{g/g}$ in 2008 in other countries of European Union (EU) and Japan. The national standard on the urban automotive diesel fuel of China, *GB 19147-2009* was formulated according to the Europe's category III standard, which requires the sulfur content to be less than 350 $\mu\text{g/g}$. In the discharging index of the fifth stage for the automotive gasoline and diesel oil, issued by the State Ministry of Environmental Protection of China, it is required that the sulfur content in the diesel oil should be less than 10 $\mu\text{g/g}$.

The requirement for the diesel oil in the international market has been increasing constantly. However, the supply amount of high-grade feedstock oil has been decreasing. How to utilize the low-grade feedstock oil to manufacture diesel with ultralow sulfur content to meet the increasing demand has been a big challenge that the refineries have to face. To meet the challenge, on one hand, it needs to resolve the key technological difficulties, and newly construct hydrogenation apparatuses to conduct deep hydrodesulfurization for diesel; on the other hand, it needs to reduce

risks and repeated investments in order to guarantee economic benefits. In the traditional hydrogenation process using a trickle bed, it is necessary to transfer hydrogen gas from gas phase to liquid phase, then the reaction between the dissolved hydrogen and sulfur compound occurs at an active centre of catalysts, thereby achieving the desulfuration purpose. During the process, the required volume of hydrogen gas is much greater than that consumed in the hydrogenation reaction. This is because, on one hand, the hydrogenation reaction is a strong exothermic reaction, which, for controlling the reaction temperature, needs a large amount of hydrogen and feedstock oil to pass through catalyst beds to bring away reaction heat; on the other hand, in the reaction related to three phases of gas, liquid and solid, maintaining a high hydrogen partial pressure is helpful for the hydrogenation reaction, inhibiting the production of coke and prolonging catalyst life. In addition, the hydrogen not reacted in the reaction may be retransferred to the reactor for reaction after the pressure thereof is increased by passing through a circulating hydrogen compressor. As key equipment for the hydrogenation process, the circulating hydrogen compressor has a high cost in investment and operation. In order to eliminate the circulating hydrogen and the circulating hydrogen compressor so as to reduce the investment cost of the apparatus, a liquid-phase hydrogenation technology was proposed. In the liquid-phase circulation hydrogenation process, the hydrogen gas is premixed with the feedstock oil, so that the hydrogen gas is dissolved in the feedstock oil, then the mixture is introduced into the reactor for reaction. The hydrogen gas needed during the reaction are entirely from the dissolved hydrogen without additional supplement of cool hydrogen. The liquid-phase circulation hydrogenation process possesses advantages of small reactor, low investment cost, easy control of the reaction temperature and the like. However, this liquid-phase circulation hydrogenation process also has one problem, that is, in order to meet the hydrogen gas volume needed in the hydrogenation reaction, it is necessary to use a large amount of circulation oil or additionally add a solvent to dissolve the hydrogen gas, which results in the reduction of the hydrogenation efficiency.

Generally, for raw materials containing simple sulfide, the reaction rate of its

hydrodesulfurization in a trickle bed hydrogenation reactor is not only related with the concentration of organic sulfide, but also affected by the factors such as wetting situation of the catalyst, concentrations of organic nitride and H_2S in the reactor system, and the like. The wetting factor of the catalyst is a measurement of the infiltration degree of the catalyst surface by a liquid reactant under the condition of hydrogenation reaction. The higher is the infiltration degree of the catalyst, the higher the wetting factor of the catalyst will be, that is to say, the higher the effective availability of the catalyst will be. Under the condition that the factors including the catalyst and the like have been defined, the main factor affecting the wetting factor of the catalyst is the flow rate of the liquid in the reactor and the ratio of the flow rate of the gas to that of the liquid (the ratio of hydrogen to oil). It is generally considered that the increase in the flow rate of the liquid enhances the wetting effect of the catalyst, while the conventional hydrogenation process mostly utilizes a high ratio of hydrogen to oil much more than the need of the reaction, thereby decreasing the wetting effect of the catalyst, and having an adverse influence on the wetting factors. In addition, the investment of the section of hydrogen circulation during petroleum refining occupies a large proportion of the cost of the whole process.

Organic nitride is poison for the hydrogenation catalyst, which has an obvious inhibition effect on the reaction of hydrodenitrification, hydrodesulfurization, and hydrodearomatization. This inhibition effect is mainly caused by the very strong adsorption energy of some nitrides and most of the intermediate reaction product of nitrides to the active centre for hydrogenation reaction of the catalyst, which inhibits occurrence of the other hydrogenation reaction from a viewpoint of competitive adsorption. However, the impurity content of the raw material will be decreased greatly by circulating the hydrogenated product, which helps to exert the performance of the catalyst.

The hydrodesulfurized byproduct, H_2S also has an obvious inhibition effect on the reaction of hydrodenitrification, hydrodesulfurization, and hydrodearomatization. In the literature *Reaction order and role of hydrogen sulfide in deep hydrodesulfurization of gas oil: consequences for industrial reactor configuration,*

Fuel Processing Technology, 1999, 61(1-2) : 149-171, Sie S T.[J], it is considered that one of the influences of H_2S on the hydrodesulfurization reaction is to increase the activation energy of the hydrodesulfurization reaction. Take toluene hydrogenation as an example, when the partial pressure of hydrogen sulfide is equal to zero, the activation energy of the reaction is equal to 16kcal/mol; when the partial pressure of hydrogen sulfide reaches 42kPa, the activation energy rises to 20kcal/mol; another influence is that the hydrodesulfurization rate is decreased enormously if a small amount of H_2S exists, and the adsorption of H_2S on the catalyst surface is monolayer adsorption, so once the adsorption center is engaged by H_2S , the reaction rate might no longer decrease with the increase in the partial pressure of H_2S . Therefore, the elimination of the influence of H_2S with effective means is the key problem to resolve the deep desulfurization.

United State patent US20060144756A1 discloses a control system method and apparatus for two phase hydroprocessing. In a continuous liquid phase hydroprocessing, the circulating hydrogen is eliminated, and all the hydrogen needed by the hydrogenation reaction comes from the hydrogen dissolved in the liquid phase without the need of additional hydrogen gas. However, it needs to utilize a solvent or diluent with a high hydrogen solubility to dissolve hydrogen, which influences the subsequent hydrogenation efficiency.

US6213835, US6428686, and CN200680018017.3 discloses a hydrogenation process with dissolving hydrogen in advance, which controls the volume of liquid or the air pressure in the reactor by controlling the hydrogen gas amount contained in liquid feed. But these patents have not totally resolved the problem of removing the detrimental impurity such as H_2S and NH_3 produced in the hydrorefining reaction process, which results in a continuous accumulation of these impurities in the reactor, thereby greatly reducing the reaction efficiency, and failing to effectively handle raw material with high sulphur and nitrogen content. The above literatures do not disclose the specific structure of the reactor, either.

SUMMARY OF THE INVENTION

The purpose of the present invention is to provide a liquid-phase hydrogenation reaction method with multi-stage hydrogen dissolution.

The liquid-phase hydrogenation reaction method with multi-stage hydrogen dissolution of the present invention includes: circulating a portion of liquid material, which has passed through a stripping tower for hydrogen mixing, and mixing it with a fresh feedstock oil into a liquid-phase material, which is introduced into a heating furnace to be heated; dividing hydrogen gas into n routes and then introducing into the heating furnace to be heated, or heating hydrogen gas in the heating furnace and then dividing it into n routes, where n is the number of catalyst beds in a reactor or the number of multi-stage reactors; mixing one route of hydrogen gas with the liquid-phase material in a mixer for a first stage hydrogen dissolution, and introducing the remaining $(n-1)$ routes of hydrogen gas into a component for hydrogen-oil mixing inside said component via an inlet between beds in the reactor to be mixed with a mixture from a reaction in the preceding bed for a second stage hydrogen dissolution, while stripping the reaction byproduct, hydrogen sulfide and ammonia, wherein one stage hydrogen dissolution is added by provision of every one bed or one reactor, a reaction pressure control system is arranged on the top of the reactor, an exhaust system is arranged at each section of the reactor, and the liquid level at each section of the reactor is accomplished by controlling the discharge of gas to be generated in the next stage and the redundant hydrogen gas; introducing the reaction product into the stripping tower provided with a hydrogen-oil mixer, to strip the byproduct, hydrogen sulfide and ammonia from the product, while increasing the hydrogen dissolution capability; introducing a portion of oil product from the stripping tower into a product tank, and recirculating another portion.

In the method of the present invention, the number of catalyst beds in the reactor or the number of multi-stage reactors, n , is 3 to 5.

In the method of the present invention, the liquid-phase material flow after hydrogen dissolution is introduced into the reactor from the top of the liquid-phase circulation hydrogenation reactor, and discharged from the bottom of the reactora liquid-phase; or the liquid-phase material flow is introduced into the reactor from the

bottom of the liquid-phase circulation hydrogenation reactor, and discharged from the top of the reactor.

In the method of the present invention, a component for hydrogen-oil mixing is arranged in the reactor.

In the method of the present invention, a hydrogen-oil mixer or a component for hydrogen-oil mixing is arranged in the stripping tower.

In the method of the present invention, the volume ratio of hydrogen to oil on the catalyst bed is from 2:1 to 10:1.

In the method of the present invention, the mixing ratio of the circulating oil to the raw materials is determined according to the volume of hydrogen required in the reaction and the stability of the catalyst beds, so as to ensure the volume of hydrogen dissolved in the mixed material. The temperature of the material entering the reactor is controlled by using the ratio of the feedstock oil to the circulating oil. When the chemical hydrogen consumption is high and the reaction heat is high, the amount of circulating oil is increased appropriately; on the contrary, the amount of circulating oil is decreased. The volume ratio of the circulating oil to the feedstock is from 0.1:1 to 5:1, and the volume ratio of hydrogen to oil on the catalyst bed is from 2:1 to 10:1.

The liquid-phase hydrogenation reaction method and reaction system with multi-stage hydrogen dissolution system according to the present invention is to carry out a two-phase hydrogenation reaction in an immobilized bed reactor, and the hydrogen required by the reaction is provided by the excessive hydrogen gas dissolved in the feedstock oil. The hydrogenation process condition is determined according to the nature of the raw materials, and the quality requirements of final product. In general, the reaction temperature is at 220 to 420°C, the hydrogen partial pressure in the reaction is from 0.5 to 15 MPa, and the volumetric space velocity is 0.8 to 15 h⁻¹.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a flow chart of the liquid-phase hydrogenation method and reaction system with multi-stage hydrogen dissolution system according to the present

invention.

In the figure, 1 - feedstock oil, 2 - circulating oil, 3 - hydrogen gas, 4 - heating furnace, 5 - mixer, 6 - reactor, 7 - pressure control valve, 8/13/14/15/18 - gas-phase product, 9/10/11/12 - liquid level control valve, 16 - liquid-phase reaction product, 17 - stripping tower, 19 - stripping gas, 20 - circulating pump, and 21 - product.

DETAILED DESCRIPTION OF THE EMBODIMENTS

As shown in Figure 1, after being heated in the heating furnace 4, the fresh feedstock oil 1 and the circulating oil 2 are introduced into the mixer 5, and mixed with the hydrogen gas 3 discharged from the heating furnace 4 to form the presaturated liquid-phase material flow, which then flows into a single-stage multi-bed reactor or a multi-stage hydrogenation reactor 6 to carry out the hydrogenation reaction. The gas phase products 8/13/14/15/18 in the reaction are discharged from the reactor. The liquid-phase reaction product 16 is introduced into the stripping tower 17, and stripped by the stripping gas 19, then the gas-phase product 18 is discharged through the top of the tower, and a portion of the liquid-phase product after stripping is introduced through the circulating pump 20 into the heating furnace 4 as the circulating oil 2. Another portion of the liquid-phase product is introduced into the product tank in the form of the product 21. A pressure control valve 7 is provided at the top of the reactor, and liquid level control valves 9/10/11/12 for the exhaust system are provided at each section of the reactor.

The present invention will be further explained by the following examples.

The catalyst used in the experiment is an industrially applicable hydrogenation catalyst, including PHF-101 diesel hydrosulfurization catalyst, PHT-01 heavy oil hydrogenation pretreatment catalyst, SD-2 paraffin hydrogenation catalyst, which are developed and produced by Research Institute of Petroleum Processing of PetroChina. The physical and chemical property indexes thereof are shown in table 1.

Example 1

When the mixed diesel oil passed through the heating furnace to reach the required temperature and was sufficiently mixed with hydrogen gas for dissolution in

a gas-liquid mixer, the mixture was introduced into the hydrogenation reactor under the reaction conditions of the hydrogen partial pressure at 6.5 MPa, the reaction temperature at 310°C, and the volume ratio of hydrogen to oil at 300:1. The liquid-phase product was introduced into the stripping tower to be stripped, a portion of the stripped liquid-phase product was introduced through the circulation pump into the heating furnace as the circulating oil, and another portion of the liquid-phase product was introduced into the product tank in the form of product. The properties of the feedstock oil and the properties of the products are listed in table 2.

As seen from table 2, the sulfur and nitrogen content in the diesel oil can be reduced remarkably by the use of this technology.

Example 2

When the heavy wax oil feedstock passed through the heating furnace to reach the required temperature and was sufficiently mixed with hydrogen gas for dissolution in a gas-liquid mixer, the mixture was introduced into the hydrogenation reactor under the reaction conditions of the hydrogen partial pressure at 12.0 MPa, the reaction temperature at 365°C, and the volume ratio of hydrogen to oil at 800:1. The liquid-phase product was introduced into the stripping tower to be stripped, a portion of the stripped liquid-phase product was introduced through the circulation pump into the heating furnace as the circulating oil, and another portion of the liquid-phase product was introduced into the product tank in the form of product. The properties of the feedstock oil and the properties of the products are listed in table 3.

As seen from table 3, the content of sulfur and nitrogen impurities in the heavy wax oil can be reduced remarkably by the use of this technology.

Example 3

When the crude paraffin feedstock passed through the heating furnace to reach the required temperature and was sufficiently mixed with hydrogen gas for dissolution in a gas-liquid mixer, the mixture was introduced into the hydrogenation reactor under the reaction conditions of the hydrogen partial pressure at 7.0 MPa, the reaction

temperature at 240°C, and the volume ratio of hydrogen to oil at 400:1. The liquid-phase product was introduced into the stripping tower to be stripped, a portion of the stripped liquid-phase product was introduced through the circulation pump into the heating furnace as the circulating oil, and another portion of the liquid-phase product was introduced into the product tank in the form of product. The properties of the feedstock oil and the properties of the products are listed in table 4.

As seen from table 4, the color and light stability of the paraffin product can be improved by the use of this technology.

Comparison example 1

The mixed diesel oil having the same properties was treated. The data for comparison using this method and the conventional method are shown in table 5. As seen from table 5, the reaction temperature in this method is 16°C lower than that of the conventional method, the ratio of hydrogen to oil is 300, which is only 3/5 of that of the conventional method, but the properties of the product are superior to those of the conventional method.

Table 1 Physical and chemical property indexes of catalysts

Catalyst No.	PHF-101	PHT-01	SD-2
Metal composition			
WO ₃	25.1	---	26.4
MoO ₃	---	20 to 30	---
NiO	3.2	3 to 10	3.3
Pore volume, mL/g	✧ 0.37	✧ 0.33	✧ 0.35
Specific surface area, m ² /g	✧ 150	✧ 160	✧ 190
Shape	trefoil	trefoil	trefoil

Table 2 Properties of the feedstock oil and the experimental result of Example 1

Item	mixed diesel oil	mixed diesel oil (160 to 230°C)	mixed diesel oil (>230°C)	Generated oil (160 to 230°C)	Generated oil (>230°C)
Density (20°C), g/cm ³	0.8350	0.8110	0.8731	0.8130	0.8501
Sulphur content,	1020.0	541.8	1602.1	1.5	40.0

$\mu\text{g/g}$					
Nitrogen content, $\mu\text{g/g}$	881.8	267.7	1330.6	7.9	48.0

Table 3 Properties of the feedstock oil and the experimental result of Example 2

Item	Heavy wax oil	Generated oil
Density (20°C), g/cm^3	0.8559	0.8498
Sulphur content, $\mu\text{g/g}$	780.0	4.2
Nitrogen content, $\mu\text{g/g}$	697.0	6.3

Table 4 Properties of the feedstock oil and the experimental result of Example 3

Item	Crude paraffin	Paraffin product
Melting point, °C	58.6	---
Oil content, wt%	1.37	1.33
Color, (Saybolt) number	3	30
Light stability, number	8	4

Table 5 Properties of the feedstock oil and the experimental result of
Comparative Example 1

Item			Comparative Example 1	Example 1
Reaction temperature, °C			326	310
Hydrogen partial pressure, MPa			6.5	6.5
Volume ratio of hydrogen to oil,v/v			500:1	300:1
Properties of oil product	Mixed diesel oil	Mixed diesel oil (>230°C)	Generated oil by conventional method (>230°C)	Generated oil by the liquid-phase hydrogenation method (>230°C)
Density, (20°C), g/cm3	0.8350	0.8731	0.8501	0.8547
Sulphur content, µg/g	1020.0	1602.1	40.0	8.0
Nitrogen content, µg/g	881.8	1330.6	48.0	7.1

Industrial applicability

The hydrogenation reactor used in the present invention has functions both of catalyzing the hydrogenation reaction and discharging the byproducts hydrogen sulfide and ammonia from the reaction system, wherein the solid catalyst comes in contact with liquid-phase reaction materials, thereby enhancing the efficiency of

hydrogenation reaction.

The present invention is mainly used for the deep desulfurization, denitrification and dearomatization of inferior diesel oil components, the production of clean diesel oil, and the hydrorefining of naphtha, jet fuel, lubricating oil, paraffin and the like to produce high-quality oil products, and the process of manufacturing high-quality clean jet fuel and diesel oil by means of mild hydrocracking of wax oil feedstock.

What is claimed is:

1. A liquid-phase hydrogenation reaction method with multi-stage hydrogen dissolution, characterized in that the method comprises: circulating a portion of liquid material, which has passed through a stripping tower for hydrogen mixing, and mixing it with a fresh feedstock oil into a liquid-phase material, which is introduced into a heating furnace to be heated; dividing hydrogen gas into n routes and then introducing into the heating furnace to be heated, or heating hydrogen gas in the heating furnace and then dividing it into n routes, where n is the number of catalyst beds in a reactor or the number of multi-stage reactors; mixing one route of hydrogen gas with the liquid-phase material in a mixer for a first stage hydrogen dissolution, and introducing the remaining $(n-1)$ routes of hydrogen gas into a component for hydrogen-oil mixing inside said component via an inlet between beds in the reactor to be mixed with a mixture from a reaction in the preceding bed for a second stage hydrogen dissolution, while stripping the reaction byproduct, hydrogen sulfide and ammonia, wherein one stage hydrogen dissolution is added by provision of every one bed or one reactor, a reaction pressure control system is arranged on the top of the reactor, an exhaust system is arranged at each section of the reactor, and the liquid level at each section of the reactor is accomplished by controlling the discharge of gas to be generated in the next stage and the redundant hydrogen gas; introducing the reaction product into the stripping tower provided with a hydrogen-oil mixer, to strip the byproduct, hydrogen sulfide and ammonia, while increasing the hydrogen dissolution capability; introducing a portion of oil product from the stripping tower into a product tank, and recirculating another portion.

2. The liquid-phase hydrogenation reaction method with multi-stage hydrogen dissolution according to claim 1, characterized in that, n is 3 to 5 stages.

3. The liquid-phase hydrogenation reaction method with multi-stage hydrogen dissolution according to claim 1, characterized in that, the liquid-phase material flow after hydrogen dissolution is introduced into the reactor from the top of the liquid-phase circulation hydrogenation reactor, and discharged from the bottom of the

reactor.

4. The liquid-phase hydrogenation reaction method with multi-stage hydrogen dissolution according to claim 1, characterized in that, the liquid-phase material flow is introduced into the reactor from the bottom of the liquid-phase circulation hydrogenation reactor, and discharged from the top of the reactor.

5. The liquid-phase hydrogenation reaction method with multi-stage hydrogen dissolution according to claim 1, characterized in that, a component for hydrogen-oil mixing is arranged in the reactor.

6. The liquid-phase hydrogenation reaction method with multi-stage hydrogen dissolution according to claim 1, characterized in that, a hydrogen-oil mixer is arranged in the stripping tower.

7. The liquid-phase hydrogenation reaction method with multi-stage hydrogen dissolution according to claim 1, characterized in that, a component for hydrogen-oil mixing is arranged in the stripping tower.

8. The liquid-phase hydrogenation reaction method with multi-stage hydrogen dissolution according to claim 1, characterized in that, the volume ratio of hydrogen to oil on the catalyst bed is from 2:1 to 10:1.

9. The liquid-phase hydrogenation reaction method with multi-stage hydrogen dissolution according to claim 1, characterized in that, the volume ratio of the circulated oil to the fresh feedstock oil is from 0.1:1 to 5:1.

10. The liquid-phase hydrogenation reaction method with multi-stage hydrogen dissolution according to claim 1, characterized in that, the reaction temperature is at 220 to 420°C.

11. The liquid-phase hydrogenation reaction method with multi-stage hydrogen dissolution according to claim 1, characterized in that, the hydrogen partial pressure in the reaction is from 0.5 to 15 MPa.

12. The liquid-phase hydrogenation reaction method with multi-stage hydrogen dissolution according to claim 1, characterized in that, the volumetric space velocity is from 0.8 to 15 h⁻¹.