

METHOD AND SYSTEM FOR PRODUCING SOLVENT OIL FROM RAFFINATE OIL

TECHNICAL FIELD

5 [0001] The present invention relates to the technical field of treatment of a reforming raffinate oil, and in particular to a method and a system for producing a solvent oil from a reforming raffinate oil.

BACKGROUND ART

10 [0002] Reforming raffinate oil is a by-product of the production of aromatic hydrocarbons and is a good petrochemical raw material due to its low contents of impurities such as sulfur, nitrogen, and heavy metals. It can be fractionated into different high-value-added components according to different boiling points and is suitable for the production of high-quality solvent oil and high-value-added hexane oil, isohexane oil, etc.

15 [0003] Reforming raffinate oil contains a small amount of unsaturated components such as olefins and aromatic hydrocarbons, which seriously affect the properties of the raffinate oil as a high-value-added solvent oil. For example, n-hexane is mainly used as a solvent for the polymerization of olefins such as propylene, an extractant for edible vegetable oil, a solvent for rubber and coatings, a pigment diluent, etc., so there are clear restrictions on unsaturated hydrocarbons such as benzene; a 6# solvent oil is an organic solvent used for producing edible
20 oils and fats. When it is used in the production of edible fats and oils, there will be some residues in edible oils and fats, and the carcinogenic aromatic hydrocarbons in solvent oil will also remain in edible oils and fats, which is harmful to human health. Therefore, the aromatic hydrocarbon content in the 6# solvent oil must be strictly controlled; and a pentane foaming agent is mainly used as a solvent to make synthetic ice, anesthetics, etc., and the bromine
25 index is clearly required to be ≤ 100 mg Br/100 g. Therefore, in order to rationally utilize a reforming raffinate oil and give it a higher economic value, it is necessary to carry out hydrodeolefin and dearomatization treatment to remove unsaturated hydrocarbons therein. Currently, representative catalysts used in hydrogenation for removing olefins and aromatic hydrocarbons are mainly classified into two categories: precious metals and non-precious
30 metals, among which Ni, Pt and Pd are the three most widely used metal catalysts. Although the hydrogenation performance K_{Pd} of Pd is 1/7 of that of Ni metal and the activity K_{Pt} of Pt is 2.5 times that of Ni, the prices of palladium and platinum are several hundred times higher than that of nickel, and the requirements on sulfur, arsenic and other toxic substances in raw materials are higher.

[0004] Currently, the process flow of a reforming raffinate oil to produce high value-added products varies according to the properties of the raw materials and product requirements, mainly including hydrogenation followed by fractionation and fractionation followed by hydrogenation. When the content of benzene and olefins is high, the process flow of hydrogenation followed by fractionation is generally used to ensure that the benzene content in the product meets the standard requirements; when the content of benzene and olefins is low, the process flow of fractionation followed by hydrogenation is generally used, in which the hydrogenation operation load is low, but the requirement on the purity of hydrogen is high. During the fractionation process, due to the azeotropic phenomenon of components, the requirements on the number of plates and columns are different. Moreover, nickel-based catalysts used in hydrogenation for removing olefins and benzene have poor thermal stability at a high temperature, NiO particles are prone to agglomeration and sintering, resulting in problems such as poor dispersion and utilization rate. In addition, since impurities such as sulfur, nitrogen and heavy metals in raw materials easily cause catalyst poisoning, which affects the service life of the catalyst and increases the operating cost, so it is necessary to pretreat the raw materials. Therefore, the existing process flow often has problems such as low utilization rate of a reforming raffinate oil, single processed products, low product yield, short operating cycle of a hydrogenation catalyst, and insensitivity to temperature increase. It is necessary to comprehensively consider multiple factors such as raw material properties, product types, stability and sulfur resistance of a catalyst, and distillation accuracy to achieve an efficient utilization of the reforming raffinate oil.

[0005] For the process of fractionation followed by hydrogenation, C5 or lighter components are prone to benzene and bromine index failure without hydrogenation saturation treatment, which cannot meet the requirements of the pentane foaming agent and is not suitable for raw materials with high benzene content; the material stream II is a C6 mixture, which has the problem of low isomerization conversion rate; the hydrogenation and isomerization products have not undergone gas-liquid separation, resulting in a higher content of light hydrocarbon components in isohexane during the subsequent fractionation process; and the raw materials entering a hydrogenation reactor have not been desulfurized, which can easily lead to poisoning and deactivation of the hydrogenation catalyst.

[0006] For the process of hydrogenation followed by fractionation, during the rectification treatment, sulfolane, water and impurities are discharged from the bottom of the column, which can easily cause the loss of some heavy fractions and affect the yield of a 120# solvent oil. In addition, the C6 product at the top of the rectification column is not rectified and separated, which can easily lead to a low yield of n-hexane and it is impossible to produce high-purity n-hexane with price lower than that of a 6# solvent oil, and the efficient utilization of the raffinate oil is not realized.

[0007] In addition, it has been reported in literature or publicity that a two-stage hydrogenation process flow is used for removing benzene by means of hydrogenation during the production of a solvent oil from a reforming raffinate oil, wherein in the first stage, a hydrodesulfurization catalyst is used to remove sulfolane to protect subsequent catalysts, and in the second stage, a high-nickel hydrogenation catalyst is used to remove benzene. However, due to the fact that the hydrodesulfurization catalyst needs to be pre-sulfurized first, the catalyst in the second stage needs to be pre-reduced first, and they cannot be operated simultaneously, the start-up process is cumbersome, and the residual sulfurized oil from the first stage will inevitably affect the catalyst in the second stage, so a large amount of raw oil is required for flushing, which will affect the start-up cycle of a device.

SUMMARY OF THE INVENTION

[0008] In order to solve the above problems, an object of the present invention is to provide a method and a system for producing a solvent oil from a reforming raffinate oil. The method is suitable for the separation and utilization of a reforming raffinate oil with high contents of benzene and olefins and can be used to produce various solvent oils from the reforming raffinate oil, thereby effectively improving the added value of the reforming raffinate oil.

[0009] In order to achieve the above object, the present invention provides a hydrogenation catalyst comprising a carrier, and a first active metal component and a second active metal component which are loaded on the carrier, wherein the metal element of the first active metal component comprises nickel, and with the total weight of the catalyst being 100%, the content of the first active metal component in the catalyst is 40-70% by weight, and the content of the carrier (in oxide) in the catalyst is 20-59% by weight, with the balance being the second active metal component.

[0010] In a specific embodiment of the present invention, compared with existing nickel-based catalysts and hydrogenation catalysts, the hydrogenation catalyst provided by the present invention has a higher nickel content, a higher dispersion of Ni metal, which can reach 10% or more, and more hydrogenation active centers. Therefore, the hydrogenation catalyst has a better and more thorough removal effect on benzene and olefins.

[0011] In the above hydrogenation catalyst, the weight of the first active metal component in the catalyst is generally controlled to be 40-70%, for example, 40%, 45%, 50%, 55%, 60%, 65%, 70%, or a range composed of any two thereof.

[0012] In the above hydrogenation catalyst, the content of the carrier in the catalyst is 20-59% by weight, for example, 20%, 25%, 30%, 35%, 40%, 45%, 50%, 55%, 59%, or a range composed of any two thereof.

[0013] In a specific embodiment of the present invention, the hydrogenation catalyst generally has a specific surface area of 200-500 m²/g, for example, 200 m²/g, 250 m²/g, 300 m²/g, 350 m²/g, 400 m²/g, 450 m²/g, 500 m²/g, or a range composed of any two thereof.

[0014] In a specific embodiment of the present invention, the hydrogenation catalyst generally has a pore volume of 0.3-0.6 cm³/g, for example, 0.3 cm³/g, 0.35 cm³/g, 0.4 cm³/g, 0.45 cm³/g, 0.5 cm³/g, 0.55 cm³/g, 0.6 cm³/g, or a range composed of any two thereof.

[0015] In a specific embodiment of the present invention, the carrier is generally an oxide, and may comprise, for example, one of aluminum oxide, silicon oxide, titanium oxide and cerium oxide, or a mixture of aluminum oxide and at least one of silicon oxide, titanium oxide and cerium oxide. That is, the carrier may comprise one of or a combination of two or more of aluminum oxide, silicon oxide, titanium oxide, and cerium oxide, and the content of aluminum oxide is not 0.

[0016] In a specific embodiment of the present invention, the first active metal component and the second active metal component in the above catalyst are generally present in the form of metal oxides.

[0017] In a specific embodiment of the present invention, the metal element of the second active metal component may comprise one of or a combination of two or more of copper, lanthanum and magnesium, etc. In a specific embodiment of the present invention, by controlling the coprecipitation process and pH value during precipitation of the metal active components during the catalyst preparation process, the content of nickel, the dispersion of nickel, and the content of hydrogenation active centers in the catalyst can be increased.

[0018] The present invention further provides a preparation method for the above hydrogenation catalyst, the preparation method comprising:

bringing a slurry of a carrier precursor to a temperature at which a precipitation reaction occurs, and adjusting the pH value of the slurry of the carrier precursor to an alkaline pH value (which may be achieved by adding a precipitant), so as to obtain a first mixed system;

simultaneously adding a precursor of the first active metal component, a precursor of the second active metal component, and a precipitant to the first mixed system, and maintaining the pH of the system at an alkaline pH value to obtain a second mixed system; and

subjecting the second mixed system to an aging treatment, and roasting the product after aging to obtain the hydrogenation catalyst.

[0019] In the above preparation method, the carrier precursor is converted into the carrier of the hydrogenation catalyst after being dried and roasted as described above. In a specific embodiment, the carrier precursor may comprise pseudo-boehmite, which is converted into aluminum oxide after being dried and roasted.

[0020] In the above preparation method, by adjusting the type of the precursor of the first active metal component, the type of the precursor of the second active metal component, and the type of the precipitant precursor, the content of nickel, the dispersion of nickel, and the content of hydrogenation active centers in the catalyst can be increased.

[0021] In the above preparation method, the precipitant can be used to not only adjust the pH value, but also precipitate the metal element of precursor of the first active metal component and the metal element of the precursor of the second active metal component. Specifically, the precipitant may comprise an alkaline precipitant, preferably a soluble carbonate, for example, potassium carbonate and/or sodium carbonate.

[0022] In the above preparation method, the amount of the precipitant can be determined according to the amount required to adjust the pH value and precipitate the metal element of the precursor of the first active metal component and the metal element of the precursor of the second active metal component.

[0023] In the above preparation method, the precursor of the first active metal component may be a compound of the metal element of the first active metal component, for example, a metal salt of the metal element of the first active metal component, preferably a soluble metal salt of the metal element of the first active metal component, for example, a nitrate of the metal element of the first active metal component, such as nickel nitrate.

[0024] In the above preparation method, the precursor of the second active metal component may be a compound of the metal element of the second active metal component, for example, a metal salt of the metal element of the second active metal component, preferably a soluble metal salt of the metal element of the second active metal component, for example, a nitrate of the metal element of the second active metal component, such as magnesium nitrate.

[0025] In the above preparation method, the amounts of the carrier precursor, the precursor of the first active metal component, and the precursor of the second active metal component correspond to the weight contents of the carrier, the first active metal component, and the second active metal component in the hydrogenation catalyst.

[0026] In a specific embodiment of the invention, the precursor of the first active metal component and the precursor of the second active metal component may be added to the first mixed system in the form of a mixed solution of the two; and the precipitant is also generally added to the first mixed reaction system in the form of a solution. By adding the mixed solution of the precursor of the first active metal component and the precursor of the second active metal component and the precipitant solution in a parallel flow manner and controlling the dropwise addition rates of the two mixed solutions, the content of nickel, the dispersion of nickel, and the content of hydrogenation active centers in the catalyst can be effectively controlled. In a specific embodiment, the dropwise addition rate of the mixed solution of the precursor of the first active metal component and the precursor of the second active metal component is generally controlled to be 20-100 ml/min, and the dropwise addition rate of the precipitant solution is generally controlled to be 10-300 ml/min.

[0027] In the above preparation method, the alkaline pH value is 8-11, for example, 8, 9, 10, 11, or a range composed of any two thereof.

[0028] In the above preparation method, the precipitation reaction is carried out at a temperature of 40-90°C, for example, 40°C, 50°C, 60°C, 70°C, 80°C, 90°C, or a range composed of any two thereof.

[0029] In the above preparation method, the temperature of the aging treatment and the temperature of the precipitation reaction may be the same or different. The aging treatment is generally carried out at a temperature of 40-90°C, for example, 40°C, 50°C, 60°C, 70°C, 80°C, 90°C, or a range composed of any two thereof.

[0030] In the above preparation method, the duration of the aging treatment is generally controlled to be 1-5 h, for example, 1 h, 2 h, 3 h, 4 h, 5 h, or a range composed of any two thereof.

[0031] In the above preparation method, the temperature of the roasting may be generally controlled to be 300-600°C, for example, 300°C, 350°C, 400°C, 450°C, 500°C, 550°C, 600°C, or a range composed of any two thereof.

[0032] In the above preparation method, the duration of the roasting is generally 1-5 h, for example, 1 h, 2 h, 3 h, 4 h, 5 h, or a range composed of any two thereof.

[0033] In a specific embodiment of the present invention, the preparation method generally further comprises filtering, washing and drying operations in sequence after the aging treatment and before roasting.

[0034] In the above preparation method, the washing is generally stopped when the filtrate becomes neutral. The resulting cake is subsequently dried and roasted.

[0035] In the above preparation method, the drying may be carried out at a temperature of 100-130°C, for example, 100°C, 110°C, 120°C, 130°C, or a range composed of any two thereof.

[0036] In the above preparation method, the drying is generally carried out for 1-5 h, for example, 1 h, 2 h, 3 h, 4 h, 5 h, or a range composed of any two thereof.

[0037] According to a specific embodiment of the present invention, a method for preparing the above hydrogenation catalyst may comprise:

heating a slurry formed by a carrier precursor and water to a precipitation reaction temperature of 40-90°C under stirring, and adding a precipitant aqueous solution to the slurry to allow the pH value of the system to be 8-11, so as to obtain a first mixed system; keeping stirring, simultaneously adding an aqueous mixed solution of the precursor of the first active metal component and the precursor of the second active metal component (the aqueous mixed solution may be formed by mixing an aqueous solution of the precursor of the first active metal component with an aqueous solution of the precursor of the second active metal component) and the precipitant aqueous solution to the first mixed system, and maintaining the pH value of the system at 8-11 to obtain a second mixed system; and subjecting the second mixed system to an aging treatment at 40-90°C for 1-5 h, filtering same, and washing same

until the filtrate is neutral, and drying the resulting cake and roasting it at 300-600°C for 1-5 h to obtain the hydrogenation catalyst.

[0038] The present invention further provides a method for producing a solvent oil from a reforming raffinate oil, the method comprising:

- 5 S2, subjecting a desulfurized and dehydrated reforming raffinate oil to a hydrogenation reaction to remove benzene and olefins under the catalysis of a hydrogenation catalyst, so as to a reaction product; wherein the hydrogenation catalyst comprises the above hydrogenation catalyst;
- S3, subjecting the reaction product obtained in S2 to gas-liquid separation;
- S4, rectifying the separated liquid to distill off a C5 component, a C6 component, and a C7+
10 component, respectively;
- S5, rectifying the C6 component to distill off cyclohexane, and a mixture of n-hexane and isohexane, respectively; and
- S6, rectifying the mixture of n-hexane and isohexane to distill off isohexane and n-hexane, respectively, thereby completing the production of solvent oils.

15 [0039] In a specific embodiment of the present invention, in the reforming raffinate oil that has not been desulfurized and dehydrated, the sulfur content is 20 mg/kg or less, the benzene content is 3-5 v%, the olefin content is 1-3 v%, and the total content of n-hexane and isohexane is greater than 50 v% in percentages by volume.

[0040] In a specific embodiment of the present invention, the above method further
20 comprises: S1, desulfurizing and dehydrating a reforming raffinate oil to obtain a product with $S \leq 1$ mg/kg.

[0041] In a specific embodiment of the present invention, the desulfurization and dehydration process in S1 is carried out at a space velocity of $1-10 \text{ h}^{-1}$.

25 [0042] In a specific embodiment of the present invention, an adsorbent used during the desulfurization and dehydration process in S1 comprises a molecular sieve adsorbent, for example, one of or a combination of two or more of a 3A molecular sieve, a 4A molecular sieve, a 5A molecular sieve, and a 13A molecular sieve.

[0043] In a specific embodiment of the present invention, the molecular sieve adsorbent used in S1 generally has a specific surface area of 400-700 m^2/g . The molecular sieve adsorbent
30 generally has a pore volume of 0.05-0.30 cm^3/g .

[0044] In a specific embodiment of the present invention, the hydrogenation catalyst in S2 can effectively remove benzene and olefins from the reforming raffinate oil. According to a specific embodiment of the present invention, the reaction product obtained in S2 has a benzene content $\leq 0.01\%$ and a bromine index $\leq 50 \text{ mg Br}/100 \text{ g}$.

[0045] In a specific embodiment of the present invention, the conditions of the hydrogenation reaction to remove benzene and olefins in S2 may generally be controlled as follows: a temperature of 90-200°C, a reaction pressure of 1.0-3.0 MPa, a volume ratio of hydrogen to the oil of 100-300 : 1, and a volume hourly space velocity of 1.0-3.0 h⁻¹.

5 [0046] In a specific embodiment of the present invention, the rectification in S4 is generally carried out at a pressure of 0-0.2 MPa.

[0047] In a specific embodiment of the present invention, the rectification process in S4 may be completed in a rectification column, with the temperature at the top of the rectification column being 30-50°C, the temperature at the bottom of the column being 90-110°C, and the
10 pressure in the column being 0-0.2 MPa.

[0048] In a specific embodiment of the present invention, the rectification in S5 is generally carried out at a pressure of 0-0.1 MPa.

[0049] In a specific embodiment of the present invention, the rectification process in S5 may be completed in a rectification column, with the temperature at the top of the rectification
15 column being 55-75°C, the temperature at the bottom of the column being 70-90°C, and the pressure in the column being 0-0.1 MPa.

[0050] In a specific embodiment of the present invention, the rectification in S6 is carried out at a pressure of 0-0.1 MPa.

[0051] In a specific embodiment of the present invention, the rectification process in S6 may
20 be completed in a rectification column, with the temperature at the top of the rectification column being 50-70°C, the temperature at the bottom of the column being 60-80°C, and the pressure in the column being 0-0.1 MPa.

[0052] In a specific embodiment of the present invention, the isohexane obtained in S6 can be directly output as a 6# solvent oil. According to actual needs, the isohexane obtained in S6 can
25 also be converted into n-hexane by means of a normalization reaction, and the purity of the n-hexane product is $\geq 80\%$.

[0053] In a specific embodiment of the present invention, the method further comprises: S7, converting the isohexane obtained in S6 into n-hexane by means of a normalization reaction.

[0054] In a specific embodiment of the present invention, the normalization reaction in S7 is
30 carried out under the following conditions: a reaction temperature of 200-400°C, a reaction pressure of 1.0-3.0 MPa, a volume ratio of hydrogen to the oil of 100-300 : 1, and a volume hourly space velocity of 1.0-3.0 h⁻¹.

[0055] In a specific embodiment of the present invention, a catalyst used in the normalization reaction in S7 may be a molecular sieve catalyst. Specifically, the molecular sieve catalyst
35 may comprise a third active metal component, a non-molecular sieve carrier and a molecular sieve carrier.

[0056] For the above molecular sieve catalyst, the molecular sieve carrier comprises one of or a combination of two or more of MOR, MCM-41, ZSM-22, and SAPO-11.

[0057] For the above molecular sieve catalyst, the metal element of the third active metal component may comprise an element of group VIB and/or group VIII. In a specific embodiment, the third active metal component is generally present in the form of a metal oxide.

[0058] For the above molecular sieve catalyst, the non-molecular sieve carrier comprises aluminum oxide.

[0059] For the above molecular sieve catalyst, with the total weight of the molecular sieve catalyst being 100%, the weight of the molecular sieve carrier accounts for 10-80% of the total weight of the catalyst, and the weight of the third active metal component (in oxide) accounts for 0.01-5% (e.g., 0.1-0.5%) of the total weight of the catalyst, with the balance being the non-molecular sieve carrier.

[0060] In a specific embodiment of the present invention, the raw material of isohexane for the normalization reaction in S7 has a purity of 90% or more, preferably 95% or more.

[0061] In a specific embodiment of the present invention, the method for producing a solvent oil from a reforming raffinate oil may specifically comprise:

S1, desulfurizing and dehydrating a reforming raffinate oil by using a molecular sieve adsorbent;

S2, subjecting a desulfurized and dehydrated reforming raffinate oil to a hydrogenation reaction to remove benzene and olefins under the catalysis of a hydrogenation catalyst, so as to a reaction product; wherein the hydrogenation catalyst comprises the above hydrogenation catalyst;

S3, subjecting the reaction product obtained in S2 to gas-liquid separation to output hydrogen-rich gas and liquid;

S4, rectifying the separated liquid to distill off a C5 component (which can be used as a pentane foaming agent), a C6 component, and a C7+ component (which can be used as a 120# solvent oil), respectively;

S5, rectifying the C6 component to distill off cyclohexane, and a mixture of n-hexane and isohexane, respectively;

S6, rectifying the mixture of n-hexane and isohexane to distill off isohexane and n-hexane, respectively; and

S7, converting isohexane obtained in S6 into n-hexane by means of a normalization reaction, thus completing the production of solvent oils.

[0062] The present invention further provides a system for producing a solvent oil from a reforming raffinate oil, which system can realize the above method for producing a solvent oil from a reforming raffinate oil.

[0063] In a specific embodiment of the present invention, the system for producing a solvent oil from a reforming raffinate oil comprises a desorption desulfurization reactor, a
5 hydrogenation reactor, a first gas-liquid separator, a first rectification column, a second rectification column, and a third rectification column, which are connected in sequence.

[0064] The connection relationships of the devices in the above system may be: the inlet of the desorption desulfurization reactor is used to receive a reforming raffinate oil, and the inlet
10 is generally located at the top of the reactor;

the outlet at the bottom of the desorption desulfurization reactor is connected to the inlet (at the top) of the hydrogenation reactor;

the outlet at the bottom of the hydrogenation reactor is connected to the inlet (at the side line) of the first gas-liquid separator;

15 the outlet at the bottom of the first gas-liquid separator is connected to the inlet (at the side line) of the first rectification column;

the outlet at the side line of the first rectification column is connected to the inlet of the second rectification column;

20 the outlet at the top of the second rectification column is connected to the inlet of the third rectification column; and

the outlet at the top of the third rectification column is used to output isohexane.

[0065] In the above system, the outlet at the top of the first gas-liquid separator is used to output hydrogen; the outlet at the top of the first rectification column is used to output a C5 component; the outlet at the bottom of the first rectification column is used to output a C7+
25 component, and the outlet at the side line of the first rectification column is used to output a C6 component; the outlet at the top of the second rectification column is used to output a mixture of n-hexane and isohexane, and the outlet at the bottom of the second rectification column is used to output cyclohexane; and the outlet at the bottom of the third rectification column is used to output n-hexane, and the outlet at the top of the third rectification column is
30 used to output isohexane.

[0066] In a specific embodiment of the present invention, the system for producing a solvent oil from a reforming raffinate oil further comprises a normalization reactor and a second gas-liquid separator, wherein the inlet of the normalization reactor is connected to the outlet at the top of the third rectification column, the outlet of the normalization reactor is connected to the
35 inlet (at the side line) of the second gas-liquid separator, the outlet at the top of the second gas-

liquid separator is used to output hydrogen, and the outlet at the bottom of the second gas-liquid separator is used to output n-hexane.

[0067] In a specific embodiment of the present invention, the above system may further comprise a hydrogen pipeline for supplementing hydrogen to the hydrogenation reactor and/or the normalization reactor. The hydrogen pipeline may be provided with a circulating hydrogen compressor, the inlet of which may be connected to the gas outlet of the first gas-liquid separator and/or the second gas-liquid separator, that is the compressor may be supplied with gas by the first gas-liquid separator and the second gas-liquid separator.

[0068] The beneficial effects of the present invention are as follows:

1. By pretreating the raw material by means of filling an adsorption reactor with a molecular sieve adsorbent, followed by desulfurization, dehydration and impurity removal, the method provided by the present invention solves the problem of subsequent catalyst poisoning during hydrogenation for benzene removal caused by sulfolane in the raw material of a reforming raffinate oil in the prior art, effectively guarantees the service life of the subsequent high-nickel hydrogenation catalyst in a hydrogenation unit for removing olefins and benzene, prolongs the operation cycle of the device, reduces the increase in operation costs caused by frequent replacement of the catalyst, and enables the separated a C7+ component meeting the sulfur content requirement of a 120# solvent oil; moreover, the method avoids the problem of cumbersome start-up processes of the device caused by the need for pre-sulfurization of a hydrodesulfurization catalyst in the prior art, and the difficulty in replacing residual sulfurized oil, which affects the start-up cycle of the device.
2. The method provided by the present invention can arrange rectification units step by step from the perspective of molecular refining according to the composition of the raw material and the difference in the boiling points thereof, improve the purity and yield of n-hexane by utilizing the normalization reaction of isohexane, and can produce n-hexane, a pentane foaming agent, and a 120# solvent oil, thereby achieving the efficient utilization of a reforming raffinate oil. Problems such as low utilization rate of a reforming raffinate oil, single processed product, and relatively low product yield are effectively solved.
3. The nickel-based hydrogenation catalyst provided by the present invention can realize high dispersion of high content of a nickel active component on the carrier of aluminum oxide and guarantee the operation cycle of a hydrogenation device when the catalyst is used in the hydrogenation reaction of a reforming raffinate oil to remove olefins and benzene.

BRIEF DESCRIPTION OF THE DRAWINGS

[0069] Fig. 1 shows a process flow diagram of the method for producing a solvent oil from a reforming raffinate oil and a schematic diagram of connection of the system of the present invention.

[0070] Description of reference signs of main components:

adsorption desulfurization reactor 1, hydrogenation reactor 2, first gas-liquid separator 3, first rectification column 4, second rectification column 5, third rectification column 6, normalization reactor 7, second gas-liquid separator 8, circulating hydrogen compressor 9.

5 DETAILED DESCRIPTION OF EMBODIMENTS

[0071] In order to understand the technical features, object and beneficial effects of the present invention more clearly, then the technical solution of the present invention is described in detail as below, but it cannot be construed as a limitation for the implementable scope of the present invention.

10 [0072] In the following examples and comparative examples, the dispersion of metal in the hydrogenation catalyst was measured by using a static chemical adsorption instrument, with H₂ as an adsorbed gas. The specific measuring method was as follows:

a sample was degassed at 130°C, then reduced with H₂ at 400°C, cooled to 35°C, and then subjected to first saturation adsorption, and after vacuuming, a second saturated adsorption
15 was performed. The difference between the two saturation adsorptions was the volume of chemically adsorbed hydrogen.

[0073] Calculation formula of dispersion of metal:

$$\text{Dispersion of metal} = \frac{\text{Number of Ni atoms on surface of catalyst}}{\text{Total number of Ni atoms in catalyst}} = \frac{V_{H_2} / 22.414}{W \times P / M_{Ni}}$$

20 In the formula, V_{H₂} is the volume of chemically adsorbed hydrogen, in L; W is the total mass of the catalyst, in g; P is the percentage content of Ni; and M_{Ni} is the molecular mass of Ni.

Example 1a

[0074] A hydrogenation catalyst was provided in this example, the preparation method therefor comprising:

25 step 1 of mixing 11.50 g of a pseudo-boehmite powder (containing 70 wt% of Al₂O₃) with 40 ml of deionized water under stirring until uniform to obtain a first slurry;

dissolving 58.16 g of nickel nitrate hexahydrate in deionized water, and adjusting same to a constant volume of 200 ml to prepare a 1 mol/L nickel nitrate solution; dissolving 12.82 g of magnesium nitrate hexahydrate in deionized water, and adjusting same to a constant volume of 50 ml to prepare a 1 mol/L magnesium nitrate solution; metering 184.7 ml of the 1 mol/L
30 nickel nitrate solution and 28.5 ml of the 1 mol/L magnesium nitrate solution and mixing same until uniform to obtain a second solution; and

dissolving 207.32 g of anhydrous potassium carbonate in deionized water, adjusting same to a constant volume of 1000 ml to prepare a 1.5 mol/L potassium carbonate solution, and metering 665.3 ml of the 1.5 mol/L potassium carbonate solution as a third solution;

step 2 of adding the first slurry to a reaction kettle, starting stirring at a speed of 200 rpm, heating same to a reaction temperature of 60°C, and adding 1.3 ml of the third solution to the reaction kettle to adjust the pH of the first slurry to 10, so as to form a first mixed system; and

under stirring, adding the second solution and the third solution to the first mixed system in a parallel flow manner at 35 ml/min and 109.2 ml/min, respectively, and controlling the pH value to be constant at 10, so as to obtain a second mixed system after the dropwise addition of the second solution and the third solution was completed; and

step 3 of aging the second mixed system under stirring at 60°C for 2 h, filtering same after aging to obtain a cake and washing same until neutral, placing the cake in an oven and drying same at 120°C for 4 h, grinding same, and then roasting same in a muffle furnace at 500°C for 5 h to obtain a nickel hydrogenation catalyst.

[0075] For the above hydrogenation catalyst, the content of a nickel oxide was 60% by mass, and the content of a magnesium oxide was 5% by mass.

[0076] After the catalyst in this example was tested, it was found that the dispersion of Ni metal was 15.08%, the specific surface area was 251 m²/g, and the pore volume of the hydrogenation catalyst was 0.41 cm³/g.

Example 1b

[0077] A hydrogenation catalyst was provided in this example, the preparation method therefor comprising:

step 1 of mixing 16.10 g of a pseudo-boehmite powder (containing 70 wt% of Al₂O₃) and 2.30 g of silicon oxide with 55 ml of deionized water under stirring until uniform to obtain a first slurry;

dissolving 72.70 g of nickel nitrate hexahydrate in deionized water, and adjusting same to a constant volume of 500 ml to prepare a 0.5 mol/L nickel nitrate solution; dissolving 4.33 g of lanthanum nitrate hexahydrate in deionized water, and adjusting same to a constant volume of 20 ml to prepare a 0.5 mol/L lanthanum nitrate solution; metering 246.3 ml of the 0.5 mol/L nickel nitrate solution and 2.8 ml of the 0.5 mol/L lanthanum nitrate solution and mixing same until uniform to obtain a second solution;

dissolving 15.81 g of ammonium bicarbonate in deionized water, and adjusting same to a constant volume of 200 ml to prepare a 1 mol/L ammonium bicarbonate solution; and metering 191.1 ml of the 1 mol/L ammonium bicarbonate solution as a third solution;

step 2 of adding the first slurry to a reaction kettle, starting stirring at a speed of 200 rpm, heating same to a reaction temperature of 80°C, and adding 1.2 ml of the third solution to the reaction kettle to adjust the pH of the first slurry to 8, so as to form a first mixed system; and

under stirring, adding the second solution and the third solution to the first mixed system in a parallel flow manner at 20 ml/min and 15 ml/min, respectively, and controlling the pH value to be constant at 8, so as to obtain a second mixed system after the dropwise addition of the second solution and the third solution was completed; and

step 3 of aging the second mixed system under stirring at 80°C for 3 h, filtering same after aging to obtain a cake and washing same until neutral, placing the cake in an oven and drying same at 120°C for 4 h, grinding same, and then roasting same in a muffle furnace at 500°C for 5 h to obtain a nickel hydrogenation catalyst.

[0078] For the above hydrogenation catalyst, the content of a nickel oxide was 40% by mass, and the content of a lanthanum oxide was 1% by mass.

[0079] After the catalyst in this example was tested, it was found that the dispersion of Ni metal was 16.18%, the specific surface area was 246 m²/g, and the pore volume of the hydrogenation catalyst was 0.40 cm³/g.

Example 1c

[0080] A hydrogenation catalyst was provided in this example, the preparation method therefor comprising:

step 1 of mixing 11.50 g of a pseudo-boehmite powder (containing 70 wt% of Al₂O₃) with 40 ml of deionized water under stirring until uniform to obtain a first slurry;

dissolving 58.16 g of nickel nitrate hexahydrate in deionized water, and adjusting same to a constant volume of 200 ml to prepare a 1 mol/L nickel nitrate solution; dissolving 4.83 g of copper nitrate trihydrate in deionized water, and adjusting same to a constant volume of 20 ml to prepare a 1 mol/L copper nitrate solution; metering 184.7 ml of the 1 mol/L nickel nitrate solution and 14.5 ml of the 1 mol/L copper nitrate solution and mixing same until uniform to obtain a second solution; and

dissolving 207.32 g of anhydrous potassium carbonate in deionized water, adjusting same to a constant volume of 1000 ml to prepare a 1.5 mol/L potassium carbonate solution, and metering 621.4 ml of the 1.5 mol/L potassium carbonate solution as a third solution;

step 2 of adding the first slurry to a reaction kettle, starting stirring at a speed of 100 rpm, heating same to a reaction temperature of 60°C, and adding 1.3 ml of the third solution to the reaction kettle to adjust the pH of the first slurry to 10, so as to form a first mixed system; and

under stirring, adding the second solution and the third solution to the first mixed system in a parallel flow manner at 35 ml/min and 109 ml/min, respectively, and controlling the pH value to be constant at 10, so as to obtain a second mixed system after the dropwise addition of the second solution and the third solution was completed; and

step 3 of aging the second mixed system under stirring at 60°C for 2 h, filtering same after aging to obtain a cake and washing same until neutral, placing the cake in an oven and drying same at 120°C for 4 h, grinding same, then roasting same in a muffle furnace at 500°C for 5 h, and reducing same with high-purity H₂ at 400°C for 10 h to obtain a nickel hydrogenation catalyst.

[0081] For the above hydrogenation catalyst, the content of a nickel oxide was 60% by mass, and the content of a copper oxide was 5% by mass.

[0082] After the catalyst in this example was tested, it was found that the dispersion of Ni metal was 14.74%, the specific surface area was 248 m²/g, and the pore volume of the hydrogenation catalyst was 0.42 cm³/g.

[0083] The methods for producing a solvent oil from a reforming raffinate oil in examples 2a to 2e were carried out in a system as shown in Fig. 1. The system included a desorption desulfurization reactor 1, a hydrogenation reactor 2, a first gas-liquid separator 3, a first rectification column 4, a second rectification column 5, a third rectification column 6, a normalization reactor 7, a second gas-liquid separator 8, and a circulating hydrogen compressor 9.

[0084] The desorption desulfurization reactor 1 was provided with an inlet at the top and an outlet at the bottom; the hydrogenation reactor 2 was provided with an inlet at the top and an outlet at the bottom; the first gas-liquid separator 3 was provided with an inlet at the side line thereof and outlets at the bottom and the top thereof respectively; the first rectification column 4 was provided with an inlet at the side line thereof and outlets at the top and the bottom thereof respectively; the second rectification column 5 was provided with an inlet at the side line thereof and outlets at the top and the bottom thereof respectively; the third rectification column 6 was provided with an inlet at the side line thereof and outlets at the top and the bottom thereof respectively; the normalization reactor 7 was provided with an inlet at the top and an outlet at the bottom; the second gas-liquid separator 8 was provided with an inlet at the side line thereof and outlets at the top and the bottom thereof respectively; and the circulating hydrogen compressor 9 was provided with an inlet and an outlet.

[0085] Specifically, the connection relationship between the devices were that the outlet at the bottom of the desorption desulfurization reactor 1 was connected to the inlet (at the top) of the hydrogenation reactor 2; the outlet at the bottom of the hydrogenation reactor 2 was connected to the inlet of the first gas-liquid separator 3; the outlet at the bottom of the first gas-liquid separator 3 was connected to the inlet of the first rectification column 4; the outlet at the side line of the first rectification column 4 was connected to the inlet of the second

rectification column 5; the outlet at the top of the second rectification column 5 was connected to the inlet of the third rectification column 6; and the outlet at the top of the third rectification column 6 was connected to the inlet of the normalization reactor 7; the outlet at the bottom of the normalization reactor 7 was connected to the inlet of the second gas-liquid separator 8, and the outlet at the top of the second gas-liquid separator 8 and the outlet at the top of the first gas-liquid separator 3 were separately connected to the inlet of the circulating hydrogen compressor 9; and the outlet of the circulating hydrogen compressor 9 was separately connected to the inlet of the hydrogenation reactor 2 and the inlet of the normalization reactor 7.

[0086] The process flow of the method for producing a solvent oil from a reforming raffinate oil used in examples 2a to 2e was shown in Fig. 1, specifically comprising:

S1, conveying a reforming raffinate oil to an adsorption reactor for desulfurization and dehydration;

S2, mixing the product obtained after desulfurization and dehydration with hydrogen, and feeding same into a hydrogenation reactor to remove benzene and olefins, wherein the hydrogenation reactor was filled with a hydrogenation catalyst provided by the present invention;

S3, conveying the resulting hydrogenation reaction product to a gas-liquid separator for gas-liquid separation, with the separated liquid product being discharged from the bottom of the gas-liquid separator, and the separated hydrogen-rich gas being discharged from the top of the gas-liquid separator, wherein the hydrogen-rich gas can be mixed with fresh hydrogen and used as circulating hydrogen after being pressurized by means of a circulating hydrogen compressor;

S4, feeding the liquid product after gas-liquid separation into a first rectification column, thereby obtaining a C5 component (a pentane foaming agent) at the top of the column, a C6 component at the side line of the column, and a C7+ component (a 120# solvent oil) at the bottom of the column;

S5, feeding the C6 component from the side line of the first rectification column into the second rectification column for fractionation, thereby obtaining a mixture of n-hexane and isohexane at the top of the column, and cyclohexane at the bottom of the column;

S6, then feeding the mixture of n-hexane and isohexane into a third rectification column for fractionation, thereby obtaining isohexane at the top of the column, and n-hexane at the bottom of the column; and

S7, feeding the isohexane into a normalization reactor for a reaction, feeding the resulting product to a separator for gas-liquid separation to obtain a product of high-concentration n-hexane at the bottom of the separator, and then mixing same with the n-hexane product from the bottom of the third rectification column, thereby further improving the yield of n-hexane.

The composition of the raw materials of reforming raffinate oil in the following examples 2a to 2e and comparative examples 1 and 2 below was shown in Table 1.

Table 1

Analysis item		Unit	Reforming raffinate oil
Density		g/cm ³	0.682
Distillation range	IFP	°C	53.9
	10%		65.1
	50%		71.1
	70%		76.3
	90%		83.1
	FBP		98.8
Paraffins, olefins, naphthenes, and aromatics (PONA)	n-alkanes	v%	23.6
	iso-alkanes		66.02
	Olefins		1.02
	Naphthenes		6.05
	Aromatics		3.31 (all being benzene)
Sulfur content		mg/kg	15.3
Bromine index		mg Br/100 g	1785

Example 2a

- 5 [0087] A method for producing a solvent oil from a reforming raffinate oil was provided in this example, the method comprising:

S1, using the reforming raffinate oil in Table 1 as a raw material, and feeding the reforming raffinate oil into an adsorption reactor for desulfurization and dehydration, wherein the catalyst used was an adsorbent of an industrial 5A molecular sieve;

- 10 S2, mixing the product obtained after desulfurization and dehydration with hydrogen, and feeding same into a hydrogenation reactor to remove benzene and olefins, wherein the catalyst used was a high-nickel hydrogenation catalyst (with a dispersion of Ni metal greater than 10%) prepared in example 1a;

15 the reaction conditions of the adsorptive desulfurization were: room temperature, normal pressure, and a space velocity of 3 h⁻¹, so as to obtain a product with S ≤ 1 mg/kg;

S3, feeding the product from the hydrogenation reactor into a separator for gas-liquid separation, thereby discharging a liquid product from the bottom of the separator, and discharging a hydrogen-rich gas from the top, wherein the hydrogen-rich gas can be mixed with fresh

hydrogen from a reforming device and used as circulating hydrogen after being pressurized by means of a circulating hydrogen compressor; and

the reaction conditions of the fixed-bed hydrogenation reactor were: a reaction temperature of 120°C, a reaction pressure of 1.0 MPa, a volume ratio of hydrogen to the oil of 100 : 1, a volume hourly space velocity of 3.0 h⁻¹, and the measured removal rate of benzene being 100%;

S4, feeding the liquid product from the bottom of the separator into a first rectification column, thereby obtaining a C5 component at the top of the column and a C7+ component at the bottom of the column, and a C6 component was discharged from the side line of the column;

the operating conditions of the first rectification column were: the pressure in the column was 0.1 MPa, the temperature at the top of the column was 35°C, the temperature at the bottom of the column was 95°C, the C5 component at the top of the column was a pentane foaming agent, the C7+ component at the bottom of the column was the 120# solvent oil, and the C6 component was discharged from the side line of the column; and the bromine index of the C5 component was 5.1 mg Br/100 g, and the bromine index of the C7+ component was 9.8 mg Br/100 g, as determined by using a bromine number and bromine index tester based on the principle of microcoulometric titration;

S5, feeding the C6 component discharged from the side line of the column into a second rectification column for fractionation, thereby obtaining a mixture of n-hexane and isohexane at the top of the column, and cyclohexane at the bottom of the column;

the operating conditions of the second rectification column were: the pressure at the top of the column being 0.1 MPa, the temperature at the top of the column being 60°C, the temperature at the bottom of the column being 72°C, and the purity of cyclohexane at the bottom of the column being 97 wt%;

S6, then feeding the mixture of n-hexane and isohexane into a third rectification column for fractionation, thereby obtaining isohexane at the top of the column, and n-hexane at the bottom of the column;

the operating conditions of the third rectification column were: the pressure at the top of the column being 0.1 MPa, the temperature at the top of the column being 55°C, the temperature at the bottom of the column being 65°C, and the purity of n-hexane at the bottom of the column being 87 wt%; and

S7, feeding the product of isohexane from the top of the column into a normalization reactor for a reaction, feeding the resulting product to a separator for gas-liquid separation to obtain a product of high-concentration n-hexane at the bottom of the separator, and then mixing same

with the n-hexane product from the bottom of the third rectification column, thereby further improving the yield of n-hexane.

[0088] The reaction conditions of the normalization reactor were: a reaction temperature of 380°C, a reaction pressure of 2.0 MPa, a volume ratio of hydrogen to the oil of 200 : 1, a

[0089] The catalyst used in the normalization reaction was a molecular sieve catalyst, which was composed of a molecular sieve carrier, a non-molecular sieve carrier, and a third active metal component, wherein the molecular sieve carrier was a mercerized molecular sieve MOR, and the content thereof in the catalyst was 80% by weight; and the third active metal component was a palladium oxide, and the weight percentage thereof in the catalyst was 0.35%; with the balance being aluminum oxide as a non-molecular sieve catalyst.

[0090] As for the products obtained in this example, the purity of n-hexane was 83 wt%, and the yield was 54%; the purity of cyclohexane was > 97 wt%; the C5 component met the standard requirements of a pentane foaming agent; and the C7+ component met the standard requirements of a 120# solvent oil.

[0091] The above benzene removal rate, the conversion rate, the selectivity, and the purity and yield of each product component were all obtained by PONA analysis of the raw material and the products by means of gas chromatography.

Example 2b

[0092] A method for producing a solvent oil from a reforming raffinate oil was provided in this example, which was exactly the same as in example 2a in terms of the raw material used, the process flow, and the conditions of the adsorptive desulfurization reaction, hydrogenation reaction and normalization reaction, except that the operating conditions of the three rectification columns were changed.

The operating conditions of the first rectification column were: the pressure in the column being 0.1 MPa, the temperature at the top of the column being 40°C, and the temperature at the bottom of the column being 102°C; the C5 component from the top of the column being a pentane foaming agent with a bromine index of 5.8 mg Br/100 g, and the C7+ component from the bottom of the column being a 120# solvent oil with a bromine index of 8.3 mg Br/100 g;

the operating conditions of the second rectification column were: the pressure at the top of the column being 0.1 MPa, the temperature at the top of the column being 66°C, the temperature at the bottom of the column being 78°C, and the purity of cyclohexane at the bottom of the column being 99 wt%;

the operating conditions of the third rectification column were: the pressure at the top of the column being 0.1 MPa, the temperature at the top of the column being 60°C, the temperature

at the bottom of the column being 71°C, and the purity of n-hexane at the bottom of the column being 91 wt%.

As for the products obtained in this example, the purity of n-hexane was 88 wt%, and the yield was 53%; the purity of cyclohexane was > 99 wt%; the C5 component met the standard requirements of a pentane foaming agent; and the C7+ component met the standard requirements of a 120# solvent oil.

Example 2c

[0093] A method for producing a solvent oil from a reforming raffinate oil was provided in this example, which was exactly the same as in example 2b in terms of the raw material used, the process flow, and the conditions of the adsorptive desulfurization reaction, hydrogenation reaction and normalization reaction, except that the operating conditions of the three rectification columns were changed.

The operating conditions of the first rectification column were: the pressure in the column being 0.1 MPa, the temperature at the top of the column being 50°C, and the temperature at the bottom of the column being 110°C; the C5 component from the top of the column being a pentane foaming agent with a bromine index of 7.8 mg Br/100 g, and the C7+ component from the bottom of the column being a 120# solvent oil with a bromine index of 8.9 mg Br/100 g;

the operating conditions of the second rectification column were: the pressure at the top of the column being 0.1 MPa, the temperature at the top of the column being 75°C, the temperature at the bottom of the column being 90°C, and the purity of cyclohexane at the bottom of the column being 98 wt%;

the operating conditions of the third rectification column were: the pressure at the top of the column being 0.1 MPa, the temperature at the top of the column being 65°C, the temperature at the bottom of the column being 78°C, and the purity of n-hexane at the bottom of the column being 88 wt%.

As for the products obtained in this example, the purity of n-hexane was 85 wt%, and the yield was 51%; the purity of cyclohexane was > 98 wt%; the C5 component met the standard requirements of a pentane foaming agent; and the C7+ component met the standard requirements of a 120# solvent oil.

Example 2d

[0094] A method for producing a solvent oil from a reforming raffinate oil was provided in this example, which was exactly the same as in example 2b in terms of the raw material used, the process flow, the operation conditions of the rectification columns, and the conditions of

the adsorptive desulfurization reaction and normalization reaction, except for the fixed-bed hydrogenation reaction conditions.

The reaction conditions of the fixed-bed hydrogenation reactor were: a reaction temperature of 180°C, a reaction pressure of 1.0 MPa, a volume ratio of hydrogen to the oil of 100 : 1, a volume hourly space velocity of 3.0 h⁻¹, and the removal rate of benzene being 100%.

As for the products from the first rectification column, the C5 component from the top of the column had a bromine index of 1.2 mg Br/100 g and met the requirements of a pentane foaming agent, and the C7+ component from the bottom of the column had a bromine index of 3.5 mg Br/100 g and met the requirements of a 120# solvent oil.

As for the resulting products: the purity of n-hexane was 88 wt%, and the yield was 53%; the purity of cyclohexane was > 99 wt%; the C5 component met the standard requirements of a pentane foaming agent; and the C7+ component met the standard requirements of a 120# solvent oil.

Example 2e

[0095] A method for producing a solvent oil from a reforming raffinate oil was provided in this example, which was exactly the same as in example 2b in terms of the raw material used, the process flow, the operation conditions of the rectification columns, and the conditions of the adsorptive desulfurization reaction and fixed-bed hydrogenation reaction, except for the normalization reaction conditions.

The reaction conditions of the normalization reactor were: a reaction temperature of 300°C, a reaction pressure of 2.0 MPa, a volume ratio of hydrogen to the oil of 200 : 1, and a volume hourly space velocity of 1.5 h⁻¹, a conversion rate of 73%, and a selectivity > 99 wt%.

As for the resulting products: the purity of n-hexane was 82 wt%, and the yield was 52%; the purity of cyclohexane was > 99 wt%; the C5 component met the standard requirements of a pentane foaming agent; and the C7+ component met the standard requirements of a 120# solvent oil.

Comparative example 1

[0096] A method for producing a solvent oil from a reforming raffinate oil was provided in this comparative example, which was exactly the same as in example 2b in terms of the raw material used, the process flow, the operation conditions of the rectification columns, and the conditions of the adsorptive desulfurization reaction and normalization reaction, except for the fixed-bed hydrogenation reaction conditions.

The reaction conditions of the fixed-bed hydrogenation reactor were: a reaction temperature of 80°C, a reaction pressure of 1.0 MPa, a volume ratio of hydrogen to the oil of 100 : 1, a volume hourly space velocity of 3.0 h⁻¹, and the removal rate of benzene being 83%.

As for the products from the first rectification column, the C5 component from the top of the column had a bromine index of 121.2 mg Br/100 g and did not meet the requirements of a pentane foaming agent, and the C7+ component from the bottom of the column had a bromine index of 133.7 mg Br/100 g and did not meet the requirements of a 120# solvent oil.

As for the products obtained in this comparative example: the purity of n-hexane was 76 wt%, and the yield was 53%; the purity of cyclohexane was > 99 w%.

Comparative example 2

[0097] A method for producing a solvent oil from a reforming raffinate oil was provided in this comparative example, wherein the raw materials used were the same as those in example 2b, the method comprising:

1. first removing benzene and olefins from the raw material of a reforming raffinate oil in a hydrogenation reactor, wherein the catalyst used was a conventional hydrogenation catalyst for removing olefins;

the reaction conditions of the hydrogenation reactor were: a reaction temperature of 120°C, a reaction pressure of 1.0 MPa, a volume ratio of hydrogen to the oil of 100 : 1, a volume hourly space velocity of 3.0 h⁻¹, and the removal rate of benzene being 82%;

the catalyst was prepared by the following method: weighing 82.9 g of aluminum nitrate nonahydrate, and adjusting same to a constant volume of 240 ml to prepare a 1 mol/L aluminum nitrate solution; metering 190 ml of a 1 mol/L nickel nitrate solution, 30 ml of a 1 mol/L magnesium nitrate solution, and 170 ml of the 1 mol/L aluminum nitrate solution, and mixing same until uniform to obtain a metal mixed solution for later use; metering 1000 ml of a 1.5 mol/L potassium carbonate as a precipitant solution for later use; adding 40 ml of purified water to a reaction kettle, starting stirring at a speed of 250 rmp, and heating same to a reaction temperature of 50°C; under stirring, adding the metal mixed solution and the precipitant solution in a parallel flow manner at 35 ml/min and 71 ml/min, respectively, with the pH value being controlled to be constant at 9; after the dropwise addition of the solutions, aging same under stirring at 50°C for 2 h; filtering the resulting material and washing same until the filtrate was neutral; and placing the cake in an oven and drying same at 120°C for 4 h, grinding same, then roasting same in a muffle oven at 500°C for 5 h, and grinding same to obtain the catalyst;

2. feeding the hydrogenation reaction product into a separator for gas-liquid separation, thereby discharging a liquid product from the bottom, and a hydrogen-rich gas from the top, which was mixed with fresh hydrogen from a reforming device and used as circulating hydrogen after being pressurized by means of a circulating hydrogen compressor;

5 3. feeding the liquid product from the bottom of the separator into a first rectification column for fractionation, thereby discharging a C5 component from the top of the column, a C6 component from the side line of the column, and a C7+ component from the bottom of the column;

10 the operating conditions of the first rectification column were: the pressure in the column being 0.1 MPa, the temperature at the top of the column being 40°C, and the temperature at the bottom of the column being 102°C; the C5 component from the top of the column being a pentane foaming agent, which had a bromine index of 131.1 mg Br/100 g and did not meet the requirements of the pentane foaming agent, and the C7+ component from the bottom of the column having a bromine index of 138.9 mg Br/100 g, which did not meet the requirements of
15 a 120# solvent oil;

4. feeding the C6 component into a second rectification column for fractionation, thereby obtaining a mixture of n-hexane and isohexane at the top of the column, and cyclohexane at the bottom of the column;

20 the operating conditions of the second rectification column were: the pressure at the top of the column being 0.1 MPa, the temperature at the top of the column being 66°C, the temperature at the bottom of the column being 78°C, and the purity of cyclohexane at the bottom of the column being 98 wt%;

25 5. then feeding the mixture of n-hexane and isohexane into a third rectification column for fractionation, thereby obtaining isohexane at the top of the column, and n-hexane at the bottom of the column;

the operating conditions of the third rectification column were: the pressure at the top of the column being 0.1 MPa, the temperature at the top of the column being 60°C, and the temperature at the bottom of the column being 71°C.

30 As for the products obtained in this comparative example: the purity of n-hexane was 88 wt%, and the yield was 31%; the purity of isohexane was 91 wt% (which can be used as a 6# solvent oil), and the purity of cyclohexane was > 99 wt%.

The evaluation results of the products of examples 2a to 2e and comparative examples 1 to 2 are shown in Table 2.

Table 2

Item	Example 2a	Example 2b	Example 2c	Example 2d	Example 2e	Comparative example 1	Comparative example 2
Pentane foaming agent	√	√	√	√	√	/	/
120# solvent oil	√	√	√	√	√	/	/
Purity of n-hexane, %	83	88	85	88	82	76	88
Yield of n-hexane, %	54	53	51	53	52	51	31
Purity of isohexane, %	/	/	/	/	/	/	91
Purity of cyclohexane, %	> 97	> 99	> 99	> 99	> 99	> 98	> 99
Removal rate of benzene, %	100	100	100	100	100	83	82
Conversion rate of isohexane, %	91	91	91	91	73	91	/

[0098] As can be seen from Table 2, the evaluation results of examples 2a to 2e are

significantly better than the evaluation results of comparative examples 1 and 2. The reasons are as follows:

[0099] for comparative example 2 where a process flow of hydrogenation followed by cutting is used and the reforming raffinate oil is treated with a conventional hydrogenation catalyst, since the catalyst has a slightly poor hydrogenation performance, the removal rates of olefins and benzene are low, such that the C5 component cannot meet the standard requirements on the bromine index of a pentane foaming agent due to the presence of olefins, and the C7+ component cannot meet the requirements on the sulfur content of a 120# solvent oil because sulfolane is not removed; moreover, due to the absence of an isohexane normalization reaction unit, isohexane cannot be converted into n-hexane, which reduces the yield of n-hexane, failing to achieve the efficient utilization of the reforming raffinate oil.

[0100] By contrast, for examples 2a to 2e where the reforming raffinate oil is treated by means of the process flow of the present invention, the efficient utilization of the reforming raffinate oil is achieved by adding an adsorptive desulfurization unit and a normalization reaction unit,

[0101] wherein for examples 2a to 2c, the purity and yield of n-hexane can be adjusted and controlled by adjusting the operating temperatures at the top and bottom of the rectification columns; for examples 2b and 2d, benzene and olefins can be removed to different degrees by changing the operating temperature of the hydrogenation catalyst. In contrast, the operating temperature of the hydrogenation catalyst in comparative example 1 does not reach 90°C-200°C, resulting in incomplete removal of benzene and olefins; and for examples 2b and 2e, by changing the normalization reaction conditions, isohexane can be normalized to different degrees to produce n-hexane, and the purity of n-hexane can be adjusted.

[0102] The above results show that the method for producing a solvent oil from a reforming raffinate oil provided by the invention is suitable for the separation and utilization of a reforming raffinate oil with high contents of benzene and olefins, and the produced solvent oil has high purity and yield and good utilization effect, and the added value of the reforming raffinate oil can be effectively improved.

Claims

1. A method for producing a solvent oil from a reforming raffinate oil, comprising:

S2: subjecting a desulfurized and dehydrated reforming raffinate oil to a hydrogenation reaction to remove benzene and olefins under the catalysis of a hydrogenation catalyst, so as to obtain a reaction product;

S3: subjecting the reaction product obtained in S2 to gas-liquid separation;

S4: rectifying the separated liquid to distill off a C5 component, a C6 component, and a C7+ component, respectively;

S5: rectifying the C6 component to distill off cyclohexane, and a mixture of n-hexane and isohexane, respectively; and

S6: rectifying the mixture of n-hexane and isohexane to distill off isohexane and n-hexane, respectively, thereby completing the production of the solvent oil;

wherein the hydrogenation catalyst comprises a carrier, and a first active metal component and a second active metal component which are supported on the carrier, wherein the metal element of the first active metal component comprises nickel, and the content of the first active metal component in the catalyst is 40-70% by weight, and the content of the carrier in the catalyst is 20-59% by weight, with the balance being the second active metal component, based on 100% of the total weight of the catalyst.

2. The method according to claim 1, wherein in S2, the hydrogenation reaction to remove benzene and olefins is carried out under the following conditions: a temperature of 90-200°C, a reaction pressure of 1.0-3.0 MPa, a volume ratio of hydrogen to oil of 100-300 : 1, and a volume hourly space velocity of 1.0-3.0 h⁻¹;

in S4, the rectification is carried out at a pressure of 0-0.2 MPa;

in S5, the rectification is carried out at a pressure of 0-0.1 MPa; and

in S6, the rectification is carried out at a pressure of 0-0.1 MPa.

3. The method according to claim 1 or 2, wherein the reaction product in S2 has a benzene content of ≤0.01% and a bromine index of ≤50 mg Br/100 g.

4. The method according to claim 1 or 2, wherein the rectification process in S4 is completed in a rectification column with a column top temperature of 30-50°C, and a column bottom temperature of 90-110°C.

5. The method according to claim 1 or 2, wherein the rectification process in S5 is completed in a rectification column with a column top temperature of 55-75°C, and a column bottom temperature of 70-90°C.

6. The method according to claim 1 or 2, wherein the rectification process in S6 is completed in a rectification column with a column top temperature of 50-70°C, and a column bottom temperature of 60-80°C.

7. The method according to any one of claims 1-6, wherein in a reforming raffinate oil that has not been desulfurized and dehydrated, the sulfur content is 20 mg/kg or less, the benzene content is 3-5 v%, the olefin content is 1-3 v%, and the total content of n-hexane and isohexane is greater than 50 v%.

8. The method according to claim 1, wherein the dispersion of Ni metal in the hydrogenation catalyst is 10% or more;

the metal element of the second active metal component comprises one of or a combination of two or more of copper, lanthanum and magnesium; and

the carrier comprises one of aluminum oxide, silicon oxide, titanium oxide and cerium oxide, and/or a mixture of aluminum oxide and at least one of silicon oxide, titanium oxide and cerium oxide.

9. The method according to claim 1, wherein the hydrogenation catalyst has a specific surface area of 200-500 m²/g and a pore volume of 0.3-0.6 cm³/g.

10. The method according to any one of claims 1 and 8-9, wherein the hydrogenation catalyst is prepared by a process comprising:

bringing a slurry of a carrier precursor to a temperature for precipitation reaction, and adjusting the pH value of the slurry of the carrier precursor to an alkaline pH value, so as to obtain a first mixture system;

adding a precursor of the first active metal component, a precursor of the second active metal component, and a precipitant to the first mixture system in a parallel flow manner, and maintaining the pH of the system at an alkaline pH value to obtain a second mixture system; and

subjecting the second mixture system to an aging treatment, and roasting the product after aging to obtain the hydrogenation catalyst.

11. The method according to claim 10, wherein the alkaline pH value is 8-11.

12. The method according to claim 10, wherein the precipitation reaction is carried out at a temperature of 40-90°C.

13. The method according to claim 10, wherein the aging treatment is carried out at a temperature of 40-90°C.

5 14. The method according to claim 10, wherein the roasting is carried out at a temperature of 300-600°C.

15. The method according to claim 10, wherein the precursor of the first active metal component is a compound of the metal element of the first active metal component;

10 the precursor of the second active metal component is a compound of the metal element of the second active metal component; and

the precipitant comprises an alkaline precipitant.

16. The method according to claim 10, wherein the precursor of the first active metal component comprises a metal salt of the metal element of the first active metal component.

15 17. The method according to claim 10, wherein the precursor of the second active metal component comprises a metal salt of the metal element of the second active metal component.

18. The method according to claim 10, wherein the precipitant comprises a soluble carbonate.

19. The method according to any one of claims 1-18, wherein the method further comprises S1: desulfurizing and dehydrating a reforming raffinate oil to obtain a product with $S \leq 1$ mg/kg.

20 20. The method according to claim 19, wherein the desulfurization and dehydration process in S1 is carried out at a space velocity of 1-10 h⁻¹.

21. The method according to claim 19, wherein an adsorbent comprising a molecular sieve adsorbent is used for the desulfurization and dehydration in S1.

25 22. The method according to claim 21, wherein the molecular sieve adsorbent comprises one of or a combination of two or more of a 3A molecular sieve, a 4A molecular sieve, a 5A molecular sieve, and a 13A molecular sieve.

23. The method according to claim 21 or 22, wherein the molecular sieve adsorbent has a specific surface area of 400-700 m²/g and a pore volume of 0.05-0.30 cm³/g.

24. The method according to any one of claims 1-23, wherein the method further comprises S7: converting the isohexane obtained in S6 into n-hexane by means of a normalization reaction.

30 25. The method according to claim 24, wherein the normalization reaction in S7 is carried out under the following conditions: a reaction temperature of 200-400°C, a reaction pressure of 1.0-

3.0 MPa, a volume ratio of hydrogen to oil of 100-300 : 1, and a volume hourly space velocity of 1.0-3.0 h⁻¹.

26. The method according to claim 24, wherein the isohexane in S7 has a purity of 90% or more.

27. The method according to claim 24, wherein the isohexane in S7 has a purity of 95% or more.

5 28. The method according to any one of claims 24-27, wherein a catalyst for the normalization reaction comprises a molecular sieve catalyst, which comprises a third active metal component, a molecular sieve carrier and a non-molecular sieve carrier.

29. The method according to claim 28, wherein the molecular sieve carrier comprises one of or a combination of two or more of MOR, MCM-41, ZSM-22, and SAPO-11.

10 30. The method according to claim 28, wherein the metal element of the third active metal component comprises an element of group VIB and/or group VIII.

31. The method according to claim 28, wherein the non-molecular sieve carrier comprises aluminum oxide.

15 32. The method according to claim 28, wherein the weight of the molecular sieve carrier accounts for 10-80% of the total weight of the catalyst, and the weight of the third active metal component accounts for 0.01-5% of the total weight of the catalyst, with the balance being a non-metal carrier, based on 100% of the total weight of the molecular sieve catalyst.

33. The method according to claim 28, wherein the weight of the third active metal component accounts for 0.1-0.5% of the total weight of the catalyst.

20 34. A system for producing a solvent oil from a reforming raffinate oil, which system is capable of implementing a method for producing a solvent oil from a reforming raffinate oil according to any one of claims 1-33.

25 35. The system according to claim 34, wherein the system for producing a solvent oil from a reforming raffinate oil comprises a desorption and desulfurization reactor, a hydrogenation reactor, a gas-liquid separator, a first rectification column, a second rectification column, and a third rectification column, which are connected in sequence.

30 36. The system according to claim 35, wherein the system for producing a solvent oil from a reforming raffinate oil further comprises a normalization reactor and a gas-liquid separator, wherein the inlet of the normalization reactor is connected to the outlet of the third rectification column, and the outlet of the normalization reactor is connected to the inlet of the gas-liquid separator.