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(54) METHOD AND APPARATUS FOR BATCH-FED MANUFACTURE OF NEEDLE COKE

(57) The present invention relates to a method and device for producing needle coke in batch feeding mode. According to the present invention, a needle coke with uniform product quality can be produced. The method for producing a needle coke according to the present invention comprises a step of sequentially adding n feedstock oils to a coking reaction at predetermined time intervals, wherein assuming that an i-th feedstock oil has an aromatic carbon ratio of A (in mol%), an i+1-th feedstock oil has an aromatic carbon ratio of B (in mol%), a first feedstock oil has an aromatic carbon ratio of A1 (in mol%), and a n-th feedstock oil has an aromatic carbon ratio of B1 (in mol%), then B≥A, and B1>A1.

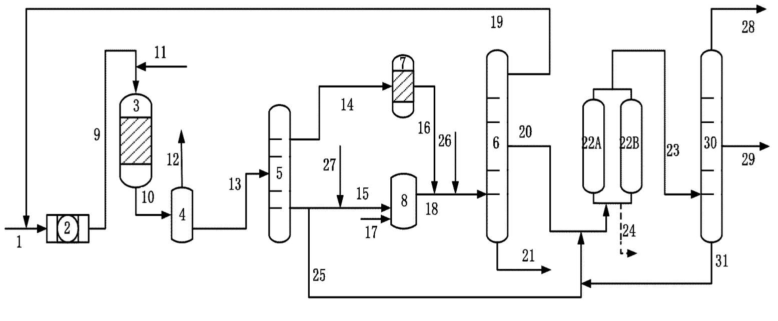

Fig.1

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Description

Technical Field

[0001] The invention belongs to the technical field of petrochemical industry, and particularly relates to a method and device for producing needle coke in batch feeding mode.

Background Art

[0002] In recent years, China's needle coke production technology has developed rapidly. In terms of production process, unlike conventional delayed coking, needle coke production are usually operated under pressure, at variable temperatures, and at large circulation ratio. That is to say, in one reaction period, feedstocks are continuously fed into the coking tower, and needle coke products are obtained by adjusting parameters such as pressure, temperature, and circulation ratio.

[0003] CN113004924A discloses a needle coke production process, wherein a feedstockoil is mixed with vacuum residue oil and then sent to a coking tower for coking reaction, during which the circulation ratio is controlled to be 0.15-0.20, so that needle coke with a high particle strength coefficient can be obtained.

[0004] CN103184057A discloses a method for producing needle coke, comprising three steps: (1) feeding fresh feedstocks into a coking tower at a relatively low temperature; (2) after the first step is completed, increasing the outlet temperature of the heating furnace, mixing the fresh feedstocks and coking heavy distillate oil and sending them to the coking tower; (3) when the solidification and coke-formation temperature is reached in the coking tower, sending the coking intermediate distillate oil generated in the first step to the coking tower at a higher temperature. This method can improve the uniformity of the properties of the needle coke in different parts of the coking tower.

Summary of the invention

[0005] After diligent research, the inventors of the present invention have found that the time required for the coking reaction to complete is different for coking feedstocks with different aromatic carbon ratios or different polymerization abilities. Therefore, needle coke with uniform product quality can be produced by making the feedstocks with different aromatic carbon ratios or different polymerization abilities stay in the coking tower for different times. According to the present invention, the microstructure of the needle coke product can be improved, the generation of short fibers, small pieces and other structures can be reduced, and high-quality needle coke can be obtained. The present invention has been completed on the basis of these discoveries.

[0006] In a first aspect, the present invention relates to a method for producing a needle coke, comprising a step of sequentially adding n feedstock oils (n is an integer equal to or greater than 2, preferably 2-15 or 3-5) to a coking reaction at predetermined time intervals, assuming that an i-th ($n-1 \geq i \geq 1$) feedstock oil has an aromatic carbon ratio of A (in mol%), an i+1-th feedstock oil has an aromatic carbon ratio of B (in mol%), a first feedstock oil has an aromatic carbon ratio of A1 (in mol%), and a n-th feedstock oil has an aromatic carbon ratio of B1 (in mol%), then $B \geq A$ (preferably $B-A \geq 5$mol% or $B-A \geq 10$mol%), and $B1 > A1$ (preferably $B1-A1 \geq 10$mol% or $B1-A1 \geq 20$mol%).

[0007] In a second aspect, the present invention relates to a device for producing a needle coke, comprising the following units:

a feedstock oil supplying unit, which is configured for providing n feedstock oils (n is an integer equal to or greater than 2, preferably 2-15 or 3-5), assuming that an i-th ($n-1 \geq i \geq 1$) feedstock oil has an aromatic carbon ratio of A (in mol%), an i+1-th feedstock oil has an aromatic carbon ratio of B (in mol%), a first feedstock oil has an aromatic carbon ratio of A1 (in mol%), and a n-th feedstock oil has an aromatic carbon ratio of B1 (in mol%), then $B \geq A$ (preferably $B-A \geq 5$mol% or $B-A \geq 10$mol%), and $B1 > A1$ (preferably $B1-A1 \geq 10$mol% or $B1-A1 \geq 20$mol%),
a coking unit, which is configured for receiving said n feedstock oils, and causing them to undergo a coking reaction to obtain a needle coke, and
a control unit, which is configured for allowing said n feedstock oils to enter the coking unit in sequence from said feedstock oil supplying unit at a predetermined time interval.

Technical Effects

[0008] Compared with the prior art, the present invention may have one or a combination of several or all of the following advantages:

(1) According to a preferable embodiment, the present invention divides the coking reaction period into three stages,

which can improve the performance of needle coke. In the first stage, the coking feedstock is a first feedstock (first heavier oil), which contains a large amount of hydrogenation products and has a low polymerization ability, and it has a long residence time in the coking tower, which can promote the conversion of the first feedstock into macromolecules; in the second stage, the coking feedstock is a second feedstock (intermediate distillate oil), which has an increased aromatic carbon ratio and has an enhanced polymerization ability because of the molecules undergoing cracking reactions such as side chain breaking, and the time required to form macromolecular structures is shorter than that of the first feedstock; and in the third stage, the coking feedstock is a third feedstock (third heavier oil), the third feedstock has undergone a delayed coking reaction and has a higher aromatic carbon ratio, which provides a strong heating capacity for the system and helps to improve the properties of needle coke. In view of the different molecular structures of the three feedstocks, the residence times in the coking tower are also different, which is conducive to the uniform quality of the needle coke products.

(2) According to a preferable embodiment, the inventors of the present invention found in the course of research that, while the catalytic slurry oil is being hydrodesulfurized, it is also accompanied by reactions such as C=C double bond saturation, aromatic ring saturation, and aromatic ring opening. Compared with the catalytic slurry oil, the hydrogenated catalytic slurry oil has an improved cracking activity but a deteriorated condensation reaction performance. In the subsequent preparation of needle coke, the period for condensing the hydrogenated slurry oil into macromolecules until the formation of a wide-area intermediate phase becomes longer, and this is not conducive to obtaining high-quality needle coke. In the needle coke preparation method and production system of the present invention, the heavy component (first heavier oil) obtained by separating the catalytic slurry oil obtained after hydrogenation is firstly subjected to a cracking reaction, and the aromatic hydrocarbons undergo a side chain breaking reaction and are converted into aromatic hydrocarbon structures with a small amount of short side chains. The cracked products are then fractionated, and the fraction enriched in three-ring and four-ring aromatic hydrocarbons is taken as the feedstock for preparing needle coke.

(3) According to a preferable embodiment, in the needle coke preparation method of the present invention, the aromatics in the catalytic slurry oil are fully utilized, and the aromatics are converted into three-ring and four-ring aromatic hydrocarbons suitable for preparing needle coke to the greatest extent, thereby improving the needle coke yield. All fractions of the catalytic slurry oil are hydrogenated, and five-ring and higher aromatic hydrocarbons contained in the catalytic slurry oil are successively subjected to hydrogenation, fractionation, and cracking reactions. These five-ring and higher aromatic hydrocarbons are converted into four-ring aromatic hydrocarbons with saturated side chains or even three-ring aromatic hydrocarbons with saturated side chains through hydrogenation reactions. These aromatic hydrocarbons are further converted into four-ring aromatic hydrocarbons or three-ring aromatic hydrocarbons with short side chains (ideal components of needle coke feedstocks) through cracking reactions, so that five-ring and higher aromatic hydrocarbons in the catalytic slurry oil can be effectively utilized to the greatest extent. In the prior art, the catalytic slurry oil is generally fractionated and then an appropriately-selected fraction is used for hydrogenation, or an appropriately-selected hydrogenated fraction is used as feedstock for producing needle coke, resulting in that the fraction containing five-ring and higher aromatic hydrocarbons of the catalytic slurry oil is not reasonably utilized and cannot be used as feedstock for producing needle coke. The method of the present invention can convert the fraction containing five-ring and higher aromatic hydrocarbons of the catalytic slurry oil into needle coke feedstock, thereby improving the effective utilization efficiency of the catalytic slurry oil, increasing the yields of needle coke feedstock and needle coke, and enhancing the economic value of the catalytic slurry oil. Moreover, two-ring aromatic hydrocarbons and a part of three-ring aromatic hydrocarbons contained in the first lighter oil can also be converted into three-ring and four-ring aromatic hydrocarbons through condensation reaction, and also become high-quality feedstocks for needle coke.

(4) According to a preferable embodiment, the needle coke preparation method of the present invention can reduce the heat load of the coking device. Under the conditions for preparing needle coke, the cracking reaction of the hydrogenated slurry oil, e.g. breaking side chains of aromatic hydrocarbons and the like, is an endothermic reaction, and the escape of the resulting small molecules will also take away a large amount of heat, resulting in a lower system temperature. In order to promote the condensation of aromatic hydrocarbon molecules into macromolecules, it is necessary to continuously increase the outlet temperature of the coking heating furnace to bring more heat into the coking tower. In the catalytic slurry oil treatment method and system of the present invention, a separate cracking reaction system is set. In the second stage of the coking reaction, the side chain breaking reaction of the hydrogenated catalytic slurry oil is transferred to the cracking reactor, and an aromatic hydrocarbon feedstock with a short side chain is obtained under suitable temperature, pressure and residence time conditions. In addition, by injecting steam into the cracking reactor, the small molecules generated by cracking can be quickly taken out of the reactor to avoid the residence in the cracking reactor for a secondary condensation reaction.

(5) According to a preferable embodiment, the needle coke preparation method of the present invention can expand the source of needle coke feedstocks by introducing a first auxiliary feedstock oil to mix with the first heavier oil to cause a molecular structure optimization reaction in a cracking reaction system, and remove saturated hydrocarbons and

aromatic hydrocarbon side chains in the first auxiliary feedstock oil in the cracking reaction system; and/or introducing a second auxiliary feedstock oil to blend with the cracked product to improve the aromatic hydrocarbon composition of the needle coke feedstock.

Brief description of the drawings

[0009]

Figure 1 is a schematic diagram of a needle coke preparation method and production system according to an embodiment of the present invention.

Figure 2 is a schematic diagram of the catalytic slurry oil treatment method in the comparative example.

Detailed description of the invention

[0010] The specific embodiments of the present invention are described in detail below, but it should be pointed out that the protection scope of the present invention is not limited by these specific embodiments, but is determined by the claims in the appendix.

[0011] All publications, patent applications, patents and other references mentioned in this specification are incorporated herein by reference. Unless otherwise defined, all technical and scientific terms used in this specification have the meanings conventionally understood by those skilled in the art. In the event of a conflict, the definitions in this specification shall prevail.

[0012] When this specification uses the prefix "well-known to those skilled in the art", "prior art" or similar expressions to introduce materials, substances, methods, steps, devices or components, the objects introduced by the prefix include those conventionally used in the field when this application is filed, but also include those that are not commonly used at present but will become generally recognized in the field to be suitable for similar purposes.

[0013] Unless explicitly stated otherwise, throughout the specification and claims, the terms "comprise/include/contain" or variations such as "comprises/includes/contains" or "comprising/including/containing", etc., will be understood to include the stated elements or components but not to exclude other elements or components.

[0014] In the context of the present specification, for the convenience of description, spatial relative terms such as "lower", "bottom", "below", "under", "upper", "top", "above", "on", etc. may be used to describe the relationship between one element or feature and another element or feature in the accompanying drawings. It should be understood that the spatial relative terms are intended to include different orientations of the object in use or operation in addition to the orientation depicted in figures. For example, if the object in the figure is turned over, the element described as being "below" or "under" another elements or features will be oriented "above" or "on" the other element or feature. Therefore, the exemplary term "below" can include two directions "below" and "above". Objects may also have other orientations (e.g., rotated 90 degrees or other orientations) and the spatial relative terms used herein should be interpreted accordingly.

[0015] In the context of the present specification, the terms "first", "second", etc. are used to distinguish two different elements or parts, but are not used to limit specific positions or relative relationships. In other words, in some embodiments, the terms "first", "second", etc. can also be interchangeable.

[0016] In the context of the present specification, all numerical values of parameters (e.g., amounts or conditions) are to be understood as being modified in all instances by the term "about", regardless of whether "about" actually appears before the numerical value or not.

[0017] In the context of the present specification, the catalytic slurry oil refers to a heavy distillate oil produced in the catalytic cracking reaction.

[0018] In the context of the present specification, the polarized light microstructure (coarse fiber, fine fiber, short fiber, large leaflet, small leaflet, mosaic) is determined by the YB/T 077 method.

[0019] In the context of the present specification, the ash content of the oil product is determined by the GB/T 508 method; the sulfur content of the oil product is determined by the SH/T 0689 method; the aromatic carbon ratio of the oil product is determined by the SH/T 0793 method; and the aromatic hydrocarbon content of the oil product is determined by the SH/T 0659 method.

[0020] In the context of the present specification, the ash content of the coke is determined by the GB/T 1429 method, and the sulfur content of the coke is determined by the GB/T 24526 method.

[0021] Unless otherwise specified, all percentages, parts, ratios, etc. mentioned in this specification are based on weight and the pressure refers to a gauge pressure.

[0022] In the context of the present specification, any two or more embodiments of the present invention may be arbitrarily combined, and the technical solutions thus formed belong to part of the original disclosure of this specification and also fall within the protection scope of the present invention.

[0023] According to one embodiment of the present invention, a method for producing a needle coke is provided.

According to the present invention, the method for producing a needle coke is carried out in the device for producing a needle coke described below. For this reason, the contents not described in detail in the preparation method section can be directly referred to the relevant contents described below for the device for producing a needle coke.

[0024] According to one embodiment of the present invention, the method for producing needle coke includes a step of sequentially adding (feeding) n feedstock oils to a coking reaction at a predetermined time interval. According to the present invention, the order of feeding these feedstock oils (described in detail below) is very critical for achieving the expected technical effect of the present invention and cannot be adjusted at will. In addition, the feeding can be carried out in an intermittent or continuous manner, preferably in a continuous manner. Moreover, the so-called predetermined time interval refers to feeding feedstock oil a period time after feeding the other feedstock oil, and the difference in the feeding timing of the two is the time interval. Preferably, the moment when one feedstock oil starts to be fed is the moment when the feeding of other feedstock oils (if any) is stopped. According to this preferred embodiment, in order to make the technical effect of the present invention more significant, said n feedstock oils are preferably added to the coking reaction separately at different times, and the feedings are basically not overlapped. Furthermore, the present invention does not particularly limit the specific value of the predetermined time interval, as long as the time interval can effectively separate the feeding timings of said n feedstock oils, but its preferred situation is described in detail below.

[0025] According to one embodiment of the present invention, n is an integer equal to or greater than 2, preferably 2-15 or 3-5.

[0026] According to one embodiment of the present invention, an i-th ($n-1 \geq i \geq 1$) feedstock oil has an aromatic carbon ratio of A(in mol%), an i+1-th feedstock oil has an aromatic carbon ratio of B (in mol%), then $B \geq A$. Preferably, $B-A \geq 5$mol% or $B-A \geq 10$mol%. If $B<A$, particularly if $B-A<5$ mol%, then the aromatic carbon contents of the two are similar, and the cracking/polymerization abilities are likely to be similar.

[0027] According to one embodiment of the present invention, a first feedstock oil has an aromatic carbon ratio of A1 (in mol%), a n-th feedstock oil has an aromatic carbon ratio of B1 (in mol%), then $B1>A1$. Preferably, $B1-A1 \geq 10$mol% or $B1-A1 \geq 20$mol%. When $B1-A1<10$mol%, the polymerization ability of B1 is insufficient, the process of forming the intermediate phase is slow, and the effect will deteriorate.

[0028] According to one embodiment of the present invention, said first feedstock oil has an aromatic carbon ratio of 40mol%-80mol% (preferably 55mol%-75mol%).

[0029] According to one embodiment of the present invention, the m-th feedstock oil has an aromatic carbon ratio of 60mol%-90mol% (preferably 70mol%-85mol%). Here, m is any integer greater than 1 and less than n.

[0030] According to one embodiment of the present invention, said n-th feedstock oil has an aromatic carbon ratio of greater than 75mol% (preferably 80mol%-95mol%).

[0031] According to one embodiment of the present invention, said i-th ($n-1 \geq i \geq 1$) feedstock oil has a sulfur content of not greater than 0.45wt% (preferably not greater than 0.37wt%), an ash content of not greater than 0.05wt% (preferably not greater than 0.01wt%), a 5% distillation temperature of 330°C-430°C (preferably 360°C-400°C), and a 95% distillation temperature of 470°C-530°C (preferably 485°C-510°C).

[0032] According to one embodiment of the present invention, said n-th feedstock oil has a sulfur content of not greater than 0.55wt% (preferably not greater than 0.5wt%), an ash content of not greater than 0.05wt% (preferably not greater than 0.01wt%), a 5% distillation temperature of 280°C-380°C (preferably 310°C-360°C), and a 95% distillation temperature of not greater than 480°C.

[0033] According to one embodiment of the present invention, said coking reaction has a reaction period of T (in hours), the predetermined time interval divides the coking reaction into n reaction sections. Preferably, in each reaction section, from the beginning to the end of the reaction time of the reaction section, the feedstock oil corresponding to the reaction section is continuously or intermittently added. According to one embodiment of the present invention, in each reaction section, from the beginning to the end of the reaction time of the reaction section, no feedstock oil other than that corresponding to the reaction section is added.

[0034] According to one embodiment of the present invention, said coking reaction has a reaction period of T (in hours), the predetermined time interval divides the coking reaction into n reaction sections. To this end, the first reaction section has a reaction time of T1 (in hours), the m-th reaction section (m is any integer greater than 1 and less than n) has a reaction time of Tm (in hours), the n-th reaction section has a reaction time of Tn (in hours), then $T1/T=5\%-40\%$ (preferably 10%-25%), $Tm/T=15\%-85\%$ (preferably 25%-70%), $Tn/T=15\%-80\%$ (preferably 25%-55%).

[0035] According to one embodiment of the present invention, among said n feedstock oils, said first feedstock oil is a hydrogenated product of the catalytic slurry oil, said n-th feedstock oil is a heavier fraction of the coker oil gas, and any one of the other feedstock oils is a cracked product of the hydrogenation product of the catalytic slurry oil.

[0036] According to one embodiment of the present invention, n = 3. To this end, the number of the feedstock oils is 3, namely the first feedstock oil, the second feedstock oil and the third feedstock oil. Moreover, the reaction period T of said coking reaction is divided into three reaction sections, namely the first reaction section, the second reaction section and the third reaction section, wherein in the first reaction section, the first feedstock oil is added to the coking reaction, in the second reaction section, the second feedstock oil is added to the coking reaction, and in the third reaction section, the third feedstock oil is added to the coking reaction.

[0037] According to one embodiment of the present invention, the method for producing the first feedstock oil comprises: the catalytic slurry oil is purified to obtain a purified slurry oil, which is sent to a hydrotreating system, a hydrogenation reaction is carried out in the presence of hydrogen and a hydrogenation catalyst, a gas phase stream and a liquid phase stream are obtained after separation of the hydrogenation product, the liquid phase stream is sent to a first separation system to obtain a first lighter oil and a first heavier oil, wherein the first heavier oil is used as the first feedstock oil.

[0038] According to one embodiment of the present invention, the catalytic slurry oil has an ash content of generally higher than 0.01wt%, a sulfur content of generally higher than 0.5wt%, sometimes higher than 0.8wt%. To this end, if the ash and sulfur content in the catalytic slurry oil cannot meet the requirements for the needle coke feedstock, it needs to be processed.

[0039] According to one embodiment of the present invention, said purified slurry oil has an ash content of ≯0.008wt%, preferably ≯0.005wt%.

[0040] According to one embodiment of the present invention, said purification treatment is generally solid removing treatment. Here, the solid removing treatment can be carried out by any one or more of the treament manners such as filtration, centrifugal sedimentation, and flocculation sedimentation, preferably by filtration.

[0041] According to one embodiment of the present invention, the core equipment of the filtration treatment is a filter, and the filter element can be one of or a combination of some of sintered metal powder filter element, metal mesh filter element, ceramic membrane filter element, etc., preferably ceramic membrane filter element.

[0042] According to one embodiment of the present invention, the hydrogenation reaction is carried out in a hydrotreating system. To this end, said hydrotreating system includes a reaction unit and a separation unit. The reaction unit is provided with at least one hydrogenation reactor. The hydrogenation reactor can be selected from one of or a combination of some of ebullated bed reactor, suspended bed reactor, slurry bed reactor, fixed bed reactor, preferably fixed bed reactor; the separation unit includes a high-temperature & high-pressure separator, a low-temperature & high-pressure separator, a high-temperature & low-pressure separator, a low-temperature & low-pressure separator, and can also comprise a stripping column, a fractionation column and the like.

[0043] According to one embodiment of the present invention, the hydrogenation catalyst can be prepared by existing methods in the art, or by using existing commercial catalysts, such as the FZC series hydrogenation catalysts developed by Dalian Petroleum&Chemical Research Institute of SINOPEC. In the hydrogenation catalyst, alumina is generally used as support, and the active component is an oxide of a metal of Group VIB and/or Group VIII, such as one of or a combination of some of oxides of metals such as Mo, W, Co and Ni.

[0044] According to one embodiment of the present invention, the operation conditions of said hydrogenation reaction are as follows: the reaction temperature is 310°C-450°C, preferably 340°C-390°C, the reaction pressure is 2MPa-20MPa, preferably 4MPa-8MPa, the hydrogen/oil volume ratio is 100-2500, preferably 800-1800, the LHSV by volume is 0.1h^{-1}-2.0h^{-1}, preferably 0.6h^{-1}-1.2h^{-1}. According to one embodiment of the present invention, the liquid phase stream is a liquid phase stream from which non-condensable gas is separated, preferably a liquid phase stream from which non-condensable gas and a naphtha fraction are separated.

[0045] According to one embodiment of the present invention, said liquid phase stream has a sulfur content of ≯0.4wt%, preferably ≯0.35wt%.

[0046] According to one embodiment of the present invention, said first heavier oil has a 5% distillation temperature of 330°C-420°C, preferably 360°C-400°C. Correspondingly, said first lighter oil has a 95% distillation temperature of 310°C-420°C, preferably 340°C-400°C.

[0047] According to one embodiment of the present invention, said first lighter oil is discharged from the device, or sent to a condensation reaction system for treatment, or a part thereof is discharged from the device, and a part thereof is sent to the condensation reaction system for treatment.

[0048] According to one embodiment of the present invention, the operation conditions of said condensation reaction system are: the reaction temperature is 350°C-530°C, preferably 380°C-450°C, the reaction pressure is 0.01MPa-5MPa, preferably 1MPa-3MPa, the residence time is 0.1h-15h, preferably 0.5h-6h. Preferably, said condensation reaction system is provided with at least one fixed bed reactor, the reactor includes at least one feeding inlet and one discharging outlet.

[0049] According to one embodiment of the present invention, the reaction time of said first reaction section comprises 5%-40%, preferably 10%-25% of said reaction period T. That is, in the first stage, the coking system feed is said first feedstock oil, and its feeding time comprises 5%-40%, preferably 10%-25% of said reaction period.

[0050] According to one embodiment of the present invention, the reaction time of said second reaction section comprises 15%-85%, preferably 25%-70% of said reaction period T. That is, in the second stage, the coking system feed is said second feedstock oil, and its feeding time comprises 15%-85%, preferably 25%-70% of said reaction period.

[0051] According to one embodiment of the present invention, in the third stage, the coking system feed is said third feedstock oil, and its feeding time comprises the balance of said reaction period. According to one embodiment of the present invention, the reaction period of said coking reaction is 24-92 hrs (preferably 36-60 hrs).

[0052] According to one embodiment of the present invention, the method for producing the second feedstock oil comprises: the first feedstock oil (e.g., the first heavier oil) is sent to a cracking reaction system, a cracking reaction is carried out in the presence of a carrier gas, and the obtained cracked product is sent to a second separation system, and after separation, a second lighter oil, an intermediate distillate oil and a second heavier oil are obtained, wherein the intermediate distillate oil is used as the second feedstock oil.

[0053] According to one embodiment of the present invention, the cracking reaction is carried out in a cracking reaction system. To this end, the cracking reaction system is provided with at least one reactor, and the reactor type can be one of or a combination of some of tubular reactor, column reactor, tank reactor, preferably column reactor. The reactor comprises at least two feeding inlets and one discharging outlet, wherein one feeding inlet is used to feed the first heavier oil, and the other feeding inlet is used to feed the carrier gas.

[0054] According to one embodiment of the present invention, said carrier gas can be one or more of water vapor, nitrogen gas, inert gas (e.g., helium gas, neon gas, argon gas and the like), preferably water vapor.

[0055] According to one embodiment of the present invention, the operation conditions of the cracking reaction are as follows: the reaction temperature is 380°C-520°C, preferably 420°C-490°C, the reaction pressure is 0.1MPa-5MPa, preferably 0.2MPa-1.0MPa, the residence time 0.01h-30h, preferably 0.1h-3h, the oil-to-steam mass ratio is 100:0.1-100:20, preferably 100:1-100:8.

[0056] According to one embodiment of the present invention, said intermediate distillate oil has a 5% distillation temperature of 340°C-430°C, preferably 360°C-400°C, a 95% distillation temperature of 470°C-530°C, preferably 485°C-510°C, a sulfur content of ≯0.43wt%, preferably ≯0.37wt%, an ash content of ≯0.006wt%, preferably ≯0.004wt%. Correspondingly, said second lighter oil has a 95% distillation temperature of 330°C-430°C, preferably 350°C-400°C, or said second heavier oil has a 5% distillation temperature of 470°C-540°C, preferably 485°C-520°C.

[0057] According to one embodiment of the present invention, said first feedstock oil is sent together with the first auxiliary feedstock oil to said cracking reaction system. Preferably, said first auxiliary feedstock oil has an ash content of not greater than 0.02wt%, preferably not greater than 0.01wt%, a sulfur content of not greater than 0.4wt%, preferably not greater than 0.35wt%, a three-ring and higher aromatic hydrocarbon content of not less than 40wt%, an aromatic carbon ratio of not less than 40mol%, preferably 55mol%-80 mol%, and a distillation range of 300°C-550°C, preferably 330°C-510°C.

[0058] According to one embodiment of the present invention, said first auxiliary feedstock oil is one or more of catalytic slurry oil, ethylene tar, vacuum gas oil, coker gas oil, deasphalted oil, and hydrogenated oil.

[0059] According to one embodiment of the present invention, the mass ratio of said first auxiliary feedstock oil to said first feedstock oil is 0:100-50:100, preferably 5:100-20:100.

[0060] According to one embodiment of the present invention, said cracked product is sent together with the second auxiliary feedstock oil to said second separation system. Preferably, said second auxiliary feedstock oil has an ash content of not greater than 0.02wt%, preferably not greater than 0.01wt%, a sulfur content of not greater than 0.4wt%, preferably not greater than 0.35wt%, an aromatic hydrocarbon content of 50wt%-95wt%, preferably 65wt%-90wt%, a three-ring and higher aromatic hydrocarbon content of not less than 40wt%, an aromatic carbon ratio of not less than 50mol%, preferably not less than 75 mol%.

[0061] According to one embodiment of the present invention, said second auxiliary feedstock oil is one or more of catalytic slurry oil, ethylene tar, vacuum gas oil, coker gas oil, and deasphalted oil.

[0062] According to one embodiment of the present invention, the mass ratio of said second auxiliary feedstock oil to said cracked product is 0:100-100:10, preferably 5:100-20:100.

[0063] According to one embodiment of the present invention, said cracked product is sent together with a condensation reaction product of said first lighter oil to said second separation system for separation. According to one embodiment of the present invention, the mass ratio of said cracked product to a condensation reaction product of said first lighter oil is 100:0-100:20, preferably 100:0-100:5.

[0064] According to one embodiment of the present invention, the method for producing the third feedstock oil comprises: the coker oil gas generated by the coking reaction is sent to a third separation system, and after separation, a coker gas, a third lighter oil and a third heavier oil are obtained, wherein said third heavier oil is used as said third feedstock oil.

[0065] According to one embodiment of the present invention, said third heavier oil has a 5% distillation temperature of 280°C-380°C, preferably 310°C-360°C. Correspondingly, said third lighter oil has a 95% distillation temperature of 270°C-380°C, preferably 300°C-360°C.

[0066] According to one embodiment of the present invention, the operation conditions of said coking reaction include: the outlet temperature of the heating furnace is 420°C-560°C, preferably 440°C-530°C, the heating rate is 0.5°C/h-30°C/h, preferably 3°C/h-7°C/h; the coking tower top pressure is 0.01MPa-2.5MPa, preferably 0.2MPa-1.3MPa. The coking reaction can be carried out under a constant pressure or a changing pressure. If the changing pressure operation is adopted, the changing pressure rate is 0.1MPa/h-5MPa/h. The reaction period of the coking reaction is generally 24h-92h, preferably 36h-60h.

[0067] According to one embodiment of the present invention, said coking reaction is carried out in a coking system. As an example, the coking system generally includes at least one heating furnace and two coking towers. At least one of the coking towers is always in a reaction stage and at least one is in a purge and decoking stage. The reaction conditions of the coking system are: the outlet temperature of the heating furnace is 420°C-560°C, preferably 440°C-530°C, the heating rate is 0.5°C/h-30°C/h, preferably 3°C/h-7°C/h; the coking tower top pressure is 0.01MPa-2.5MPa, preferably 0.2MPa-1.3MPa, and it can be carried out under a constant pressure or a changing pressure, if the changing pressure operation is adopted, the changing pressure rate is 0.1MPa/h-5MPa/h; the reaction period is 10h-72h, preferably 32h-54h; the needle coke generated by the reaction is deposited at the bottom of the coking tower, and the generated coker oil gas is discharged from the top of the coking tower.

[0068] According to one embodiment of the present invention, the aforementioned condensation reaction is carried out in a condensation reaction system. As an example, the reaction conditions of said condensation reaction system include: the reaction temperature is 350°C-530°C, preferably 380°C-450°C, the reaction pressure is 0.01MPa-5MPa, preferably 1MPa-3MPa, the residence time is 0.1h-15h, preferably 0.5h-6h. said condensation reaction system is provided with at least one fixed bed reactor, the reactor includes at least one feeding inlet and one discharging outlet.

[0069] According to one embodiment of the present invention, the condensation reaction can be carried out in the presence of a condensation catalyst. The condensation catalyst comprises a support and an active component, wherein the support is one of or a combination of two or more of kaolin, montmorillonite, alumina, silicon-containing alumina, preferably alumina, and the active component is at least one of the oxides of Group IVB and/or Group VIB metals, e.g. the oxide of metal such as zirconium, tungsten, and molybdenum. Based on the weight of the catalyst, the content of the active component is 0.1wt%-50wt%, preferably 5wt%-25wt%. The shape of the condensation catalyst can be one of or a combination of some of spheres, cylinders, three-leaf clover, four-leaf clover, Raschig rings, etc.

[0070] According to one embodiment of the present invention, a device for producing a needle coke is also provided. According to the present invention, the device for producing a needle coke is specifically used to implement the needle coke preparation method described above. For this reason, the contents not described in detail in the section of the device for producing a needle coke can be directly referred to the relevant contents described in the full text for the preparation method.

[0071] According to one embodiment of the present invention, said device for producing a needle coke comprises the following units:

a feedstock oil supplying unit, which is configured for providing n (n is an integer equal to or greater than 2) feedstock oil, wherein an i-th ($n-1 \geq i \geq 1$) feedstock oil has an aromatic carbon ratio of A (in mol%), an i+1-th feedstock oil has an aromatic carbon ratio of B (in mol%), a first feedstock oil has an aromatic carbon ratio of A1 (in mol%), and a n-th feedstock oil has an aromatic carbon ratio of B1 (in mol%), then $B \geq A$, and $B1 > A1$,
a coking unit, which is configured for receiving said n feedstock oils, and causing them to undergo a coking reaction to obtain a needle coke,
a control unit, which is configured for allowing said n feedstock oils to enter the coking unit in sequence from said feedstock oil supplying unit at a predetermined time interval.

[0072] According to one embodiment of the present invention, preferably $B-A \geq 5$mol% or $B-A \geq 10$mol%.

[0073] According to one embodiment of the present invention, preferably $B1-A1 \geq 10$mol% or $B1-A1 \geq 20$mol%.

[0074] According to one embodiment of the present invention, in said device for producing a needle coke, n=3, and it comprises:

a purification system, which is used to receive and purify the catalytic slurry oil to obtain a purified slurry oil;
a hydrotreating system, which is used to receive hydrogen and the purified slurry oil from the purification system, and to carry out a hydrogenation reaction in the presence of a hydrogenation catalyst, and to obtain a gas phase stream and a liquid phase stream after separation of the hydrogenation product;
a first separation system, which is used to receive a liquid phase stream from the hydrotreating system and obtain a first lighter oil and a first heavier oil after separation;
a cracking reaction system, which is used to receive the first heavier oil from the first separation system and optionally a first auxiliary feedstock oil, and carry out a reaction in the presence of a carrier gas;
a second separation system, which is used to receive a reaction effluent from the cracking reaction system and optionally a second auxiliary feedstock oil, and obtain a second lighter oil, an intermediate distillate oil and a second heavier oil after separation;
a coking unit, which is used to receive a first heavier oil from the first separation system (the first feedstock oil), an intermediate distillate oil from the second separation system (the second feedstock oil) and a third heavier oil from a third separation system (the third feedstock oil), and to perform the reaction to obtain the coker oil gas and the needle coke;

a third separation system, which is used for receiving the coker oil gas obtained after the reaction from the coking unit, and obtaining a coker gas, a third lighter oil and a third heavier oil after separation.

[0075] According to one embodiment of the present invention, the device for producing a needle coke also includes a condensation reaction system, which is used to receive the first lighter oil from the first separation system. The first lighter oil is sent to the condensation reaction system and undergoes a condensation reaction in the presence of a condensation catalyst. The reaction effluent obtained from the condensation reaction is sent to the second fractionation unit and is separated together with the cracking reaction effluent.

[0076] According to one embodiment of the present invention, said first separation system can be one of or a combination of some of stripping column, flash column, fractionation column and the like, preferably fractionation column.

[0077] According to one embodiment of the present invention, said condensation reaction system is provided with at least one fixed bed reactor, and the reactor includes at least one feeding inlet and one discharging outlet.

[0078] According to one embodiment of the present invention, in the device for producing a needle coke, the purification system uses any one or more of filtration device, centrigual sedimentation device, flocculation sedimentation device, and the like, preferably filtration device; the core equipment of filtration device is a filter, and the filter element can be one of or a combination of some of sintered metal powder filter element, metal mesh filter element, ceramic membrane filter element, etc., preferably ceramic membrane filter element.

[0079] According to one embodiment of the present invention, in the device for producing a needle coke,the hydrotreating system includes a reaction unit and a separation unit, and the reaction unit is provided with at least one hydrogenation reactor. The hydrogenation reactor can be selected from one of or a combination of some of ebullated bed reactor, suspended bed reactor, slurry bed reactor, fixed bed reactor, and the like, preferably fixed bed reactor. The separation unit includes a high-temperature & high-pressure separator, a low-temperature & high-pressure separator, a high-temperature & low-pressure separator, a low-temperature & low-pressure separator, and can also comprise a stripping column, a fractionation column and the like.

[0080] According to one embodiment of the present invention, in the device for producing a needle coke, the first separation system can be one of or a combination of some of stripping column, flash column, fractionation column and the like, preferably fractionation column.

[0081] According to one embodiment of the present invention, in the device for producing a needle coke, the cracking reaction system is provided with at least one reactor. The reactor can be at least one of tubular reactor, column reactor, and tank reactor, preferably column reactor. The reactor includes at least two feeding inlets and one discharging outlet, wherein one feeding inlet is used for feeding the first heavier oil, and the other feeding inlet is used for feeding the carrier gas.

[0082] According to one embodiment of the present invention, in the device for producing a needle coke, said second separation system can be one of or a combination of some of stripping column, flash column, fractionation column and the like, preferably fractionation column.

[0083] According to one embodiment of the present invention, in the device for producing a needle coke, the coking system includes at least one heating furnace, two coking towers, and one fractionation column.

[0084] At least one of the coking towers is always in a reaction stage and at least one is in a purge and decoking stage.

[0085] A specific implementation of the present invention is described in detail below in conjunction with the accompanying drawings.

[0086] As shown in Figure 1, the specific procedure of the method for producing a needle coke provided by the present invention is as follows: a catalytic slurry oil 1 is firstly sent to a purification system 2 for purification treatment for removing solids. After the treatment, the resulting purified slurry oil 9 is mixed with a hydrogen gas 11 and the mixture is sent to a hydrotreating system 3 to react in the presence of the hydrogenation catalyst; the resulting hydrogenation product 10 is sent to a hydrogenation separation unit 4 for separation, and after separation, a gas phase stream 12 and a liquid phase stream 13 are obtained. The liquid phase stream 13 is sent to a first separation system 5, and after separation, a first lighter oil 14 and a first heavier oil 15 are obtained; wherein the first lighter oil 14 can be directly discharged from the device, or sent to a condensation reaction system 7 for condensation reaction, and the resulting condensation reaction product 16 is sent to a second separation system 6; in the first stage of the coking reaction, the first heavier oil 15 is sent to the coking system 22A/22B as the first feedstock 25, and in the remaining stages of the coking reaction, the first heavier oil 15 and optionally a first auxiliary feedstock oil 27 are sent to a cracking reaction system 8, and a cracking reaction is carried out in the presence of a carrier gas 17, and the resulting reaction effluent 18 from the cracking reaction and optionally a second auxiliary feedstock oil 26 are sent to a second separation system 6, and after separation, a second lighter oil 19, an intermediate distillate oil 20 and a second heavier oil 21 are obtained, wherein the second lighter oil 19 is discharged from the device, or is sent to the purification system 2 as a diluent to be mixed with the catalytic slurry oil 1 for purification treatment; and the second heavier oil 21 is discharged from the device. In the second stage of the coking reaction, the intermediate distillate oil 20 is sent to the coking system 22A/22B as the second feedstock for producing a needle coke, and after the reaction, a coker oil gas 23 and a needle coke product 24 are obtained, wherein the coker oil gas 23 is sent to the third separation system 30, and after separation, coker gas 28, third lighter oil 29 and third heavier oil 30 are obtained. In the third stage of the coking reaction, the third heavier oil 30 is sent to the coking system 22A/22B as the third feedstock for producing a needle coke.

Examples

[0087] The present invention is further described in detail below using examples, but the present invention is not limited to these examples.

[0088] The feedstock properties of the catalytic slurry oil, the first auxiliary feedstock oil, and the second auxiliary feedstock oil used in the examples of the present invention and the comparative examples are shown in Table 1. The hydrogenation catalyst used is the FZC-34BT hydrogenation catalyst developed by Dalian Petroleum&Chemical Research Institute of SINOPEC. The purification system uses a filter, and water vapor is used as carrier gas.

Example 1

[0089] After purification, the catalytic slurry oil was sent to the hydrotreating system. A liquid phase stream obtained by separating the hydrogenation product was sent to the first separation system, and a first lighter oil and a first heavier oil were obtained by separation.

[0090] A part of the first heavier oil was used as the first feedstock oil and sent to the coking tower in the first stage of the coking reaction; a part of the first heavier oil was sent to the cracking reaction system, and the resulting cracking reaction effluent was sent to the second separation system, and a second lighter oil, an intermediate distillate oil and a second heavier oil were obtained by separation.

[0091] The intermediate distillate oil was used as the second feedstock oil and sent to the coking tower in the second stage of the coking reaction; the needle coke generated in the coking reaction deposited at the bottom of the drum; and the coker oil gas was sent to the third separation system, and a coker gas, a third lighter oil and a third heavier oil were obtained by separation. The third heavier oil was used as the third feedstock oil and sent to the coking tower in the third stage of the coking reaction. The conditions of the hydrogenation reaction, cracking reaction and coking reaction were listed in Table 2, and the feed properties of the three-stage coking system were listed in Table 3.

[0092] The needle coke yields based on the catalytic slurry oil were listed in Table 4.

[0093] The microstructural statistics of the obtained needle coke were listed in Table 5.

Example 2

[0094] Example 2 was carried out in the same manner as in Example 1 except that the first feedstock oil was sent to the coking tower throughout the entire coking reaction period, the second feedstock oil was sent to the coking tower in the second stage of the coking reaction, and the third feedstock oil was sent to the coking tower in the third stage of the coking reaction. The conditions of the hydrogenation reaction, cracking reaction and coking reaction were listed in Table 2, and the feed properties of the three-stage coking system were listed in Table 6.

[0095] The needle coke yields based on the catalytic slurry oil were listed in Table 4.

[0096] The microstructural statistics of the obtained needle coke were listed in Table 5.

Example 3

[0097] Example 3 was carried out in the same manner as in Example 1 except for some operation parameters. The conditions of the hydrogenation reaction, cracking reaction and coking reaction were listed in Table 2, and the feed properties of the three-stage coking system were listed in Table 7.

[0098] The needle coke yields based on the catalytic slurry oil were listed in Table 4.

[0099] The microstructural statistics of the obtained needle coke were listed in Table 5.

Example 4

[0100] Example 4 was carried out in the same manner as in Example 1 except for some operation parameters. The conditions of the hydrogenation reaction, cracking reaction and coking reaction were listed in Table 2, and the feed properties of the three-stage coking system were listed in Table 8.

[0101] The needle coke yields based on the catalytic slurry oil were listed in Table 4.

[0102] The microstructural statistics of the obtained needle coke were listed in Table 5.

Example 5

[0103] Example 5 was carried out in the same manner as in Example 4 except that the first lighter oil was sent to the condensation reaction system, the condensation reaction conditions included: the reaction temperature was 405°C, the reaction pressure was 1.2MPa, the residence time 2.5h; the condensation catalyst: alumina as support, 8wt% ZrO2-3.5wt%MoO2 as active component, three-leaf clover structure. The condensation reaction product was sent to the second separation system, the mass ratio of the cracked product to the condensation reaction product was 100:9. The conditions of the hydrogenation reaction, cracking reaction and coking reaction were listed in Table 2, and the feed properties of the three-stage coking system were listed in Table 9.

[0104] The needle coke yields based on the catalytic slurry oil were listed in Table 4.

[0105] The microstructural statistics of the obtained needle coke were listed in Table 5.

Example 6

[0106] Example 6 was carried out in the same manner as in Example 1 except that the first auxiliary feedstock and the first heavier oil at a mass ratio of 7:100 were sent to the cracking reaction system. The conditions of the hydrogenation reaction, cracking reaction and coking reaction were listed in Table 2, and the feed properties of the three-stage coking system were listed in Table 10.

[0107] The needle coke yields based on the catalytic slurry oil and the first auxiliary feedstock were listed in Table 4.

[0108] The microstructural statistics of the obtained needle coke were listed in Table 5.

Example 7

[0109] Example 7 was carried out in the same manner as in Example 1 except that the second auxiliary feedstock and the cracked product at a mass ratio of 9:100 were sent to the cracking reaction system. The conditions of the hydrogenation reaction, cracking reaction and coking reaction were listed in Table 2, and the feed properties of the three-stage coking system were listed in Table 11.

[0110] The needle coke yields based on the catalytic slurry oil and the second auxiliary feedstock were listed in Table 4.

[0111] The microstructural statistics of the obtained needle coke were listed in Table 5.

Comparative Example 1

[0112] The specific procedure of Comparative Example 1 was shown in Figure 2.

[0113] After purification, the catalytic slurry oil was sent to the vacuum distillation device, and a first intermediate distillate oil was obtained by separation. The first intermediate distillate oil was sent to the hydrotreating system, and the resulting hydrogenation product was separated to obtain a liquid phase stream, which was sent to the hydrogenation separation system to obtain a second intermediate distillate oil by separation. The second intermediate distillate oil was sent to the coking tower as the first feedstock oil, and the needle coke generated by the reaction deposited at the bottom of the drum. The resulting coker oil gas was sent to the coking separation system, and the separated coking heavier oil was used as the second feedstock oil. The second feedstock oil and the first feedstock oil at a mass ratio of 1:1 returned to the coking tower. The conditions of the hydrogenation reaction and the coking reaction were listed in Table 12, and the feed properties of the coking system were listed in Table 13. The needle coke yields based on the catalytic slurry oil were listed in Table 14.

[0114] The microstructural statistics of the obtained needle coke were listed in Table 15.

Comparative Example 2

[0115] After purification, the catalytic slurry oil was sent to the hydrotreating system. The hydrogenation product was separated to obtain a liquid phase stream, which was sent to the first separation system, in which a first lighter oil and a first heavier oil were obtained by separation. A part of the first heavier oil was used as the first feedstock oil; and a part of the first heavier oil was sent to the cracking reaction system. The resulting cracking reaction effluent was sent to the second separation system, in which a second lighter oil, an intermediate distillate oil and a second heavier oil were obtained by separation. The intermediate distillate oil was used as the second feedstock oil. The coker oil gas generated by the coking reaction was sent to the third separation system, in which a coker gas, a third lighter oil and a third heavier oil were obtained by separation. The third heavier oil was used as the third feedstock oil. The first feedstock oil, the second feedstock oil and the third feedstock oil were sent to the coking tower at a mass ratio of 2:4:4, and the needle coke generated by the coking reaction deposited at the bottom of the drum. The conditions of the hydrogenation reaction, the cracking reaction and the coking reaction were listed in Table 12, and the feed properties of the coking system were listed in Table 16.

[0116] The needle coke yields based on the catalytic slurry oil were listed in Table 14.

[0117] The microstructural statistics of the obtained needle coke were listed in Table 15.

Comparative Example 3

[0118] Three feedstock oils were obtained in the same way as those in Comparative Example 2 except for the stages of feeding to the coking tower, wherein the third feedstock oil was sent to the coking tower in the first stage of the coking reaction, the second feedstock oil was sent to the coking tower in the second stage of the coking reaction, and the first feedstock oil was sent to the coking tower in the third stage of the coking reaction.

[0119] The conditions of the hydrogenation reaction, the cracking reaction, and the coking reaction were listed in Table 12, and the feed properties of the coking system were listed in Table 17.

[0120] The needle coke yields based on the catalytic slurry oil were listed in Table 14.

[0121] The microstructural statistics of the obtained needle coke were listed in Table 15.

Table 1 Feedstock properties

Item	Catalytic slurry oil	First auxiliary feedstock oil	Second auxiliary feedstock oil
Sulfur content, wt%	0.97	0.12	0.27
Ash, wt%	0.23	0.006	0.008
Three-ring and higher aromatic hydrocarbons, wt%	53.7	51.3	49.5
Aromatic carbon ratio, mol%	80.4	63.2	78.8
5% distillation temperature/°C	308	353	329
95% distillation temperature/°C	571	502	542

Table 2 Conditions of hydrogenation reaction, cracking reaction and coking reaction in Examples

Reaction conditions	Example 1	Example 2	Example 3	Example 4	Example 5	Example 6	Example 7
Hydrogenation reaction							
Temperature/°C	373	366	366	368	367	368	366
Pressure/MPa	6.2	5.8	6.0	5.8	5.6	5.8	5.8
Hydrogen/oil volume ratio	1100	1100	1200	1100	1200	1200	1100
LHSV/h^{-1}	0.8	0.8	0.9	1.0	1.0	1.0	1.0
Cracking reaction							
Temperature/°C	425	472	470	465	448	446	437
Pressure/MPa	0.5	0.35	0.53	0.50	0.55	0.35	0.50
Residence time/h	1.0	1.2	1.2	1.0	1.8	0.7	0.8
Mass ratio of first heavier oil to water vapor	100:6						
Coking reaction							
Heating furnace temperature/°C	450-505						
Heating rate/°C-h^{-1}	5						
Coking tower top pressure/MPa	0.8						
Reaction period/h	42	56	52	48	42	44	48
First stage, %	20	20	45	20	15	15	20
Second stage, %	40	40	20	40	35	45	40

(continued)

Coking reaction							
Third stage, %	40	40	35	40	50	40	40

Table 3 Properties of three feedstock oils in Example 1

Item	First feedstock	Second feedstock	Third feedstock
Sulfur content, wt%	0.29	0.33	0.41
Ash, wt%	0.003	0.004	-
Three-ring and higher aromatic hydrocarbons, wt%	48.3	50.1	53.8
Aromatic carbon ratio, mol%	61.5	65.3	70.8
5% distillation temperature/°C	376	375	312
95% distillation temperature/°C	552	502	458

Table 4 Needle coke yield in Examples

Yield, wt%	Example 1	Example 2	Example 3	Example 4	Example 5	Example 6	Example 7
Needle coke	32.6	34.3	35.6	37.8	38.0	38.2	38.8

Table 5 Microstructural statistics of needle coke in Examples

Microstructure, %	Example 1	Example 2	Example 3	Example 4	Example 5	Example 6	Example 7
Coarse fiber	24.3	25.3	23.7	20.1	22.8	21.4	20.6
Fine fiber	36.5	36.1	38.2	43.2	42.6	43.8	43.0
Short fiber	9.8	11.4	12.7	11.8	8.4	12.2	12.8
Large leaflet	16.5	16.3	14.6	13.7	15.1	14.7	13.4
Small leaflet	11.9	9.8	9.7	10.6	10.3	6.8	8.9
Mosaic	1.0	1.1	1.1	0.6	0.8	1.1	1.3

[0122] In Table 5, the proportions of coarse fiber and fine fiber in Examples were more than 60%.

Table 6 Properties of three feedstock oils in Example 2

Item	First feedstock	Second feedstock	Third feedstock
Sulfur content, wt%	0.33	0.36	0.44
Ash, wt%	0.005	0.004	-
Three-ring and higher aromatic hydrocarbons, wt%	51.6	54.2	58.7
Aromatic carbon ratio, mol%	64.7	76.4	83.6
5% distillation temperature/°C	378	383	336
95% distillation temperature/°C	558	501	465

Table 7 Properties of three feedstock oils in Example 3

Item	First feedstock	Second feedstock	Third feedstock
Sulfur content, wt%	0.35	0.37	0.46
Ash, wt%	0.004	0.005	-
Three-ring and higher aromatic hydrocarbons, wt%	52.1	54.7	58.1

(continued)

Item	First feedstock	Second feedstock	Third feedstock
Aromatic carbon ratio, mol%	65.6	76.0	82.6
5% distillation temperature/°C	378	375	323
95% distillation temperature/°C	559	498	466

Table 8 Properties of three feedstock oils in Example 4

Item	First feedstock	Second feedstock	Third feedstock
Sulfur content, wt%	0.33	0.37	0.43
Ash, wt%	0.003	0.004	-
Three-ring and higher aromatic hydrocarbons, wt%	51.74	54.0	57.7
Aromatic carbon ratio, mol%	64.5	75.9	89.4
5% distillation temperature/°C	375	374	319
95% distillation temperature/°C	551	502	464

Table 9 Properties of three feedstock oils in Example 5

Item	First feedstock	Second feedstock	Third feedstock
Sulfur content, wt%	0.33	0.36	0.43
Ash, wt%	0.005	0.004	-
Three-ring and higher aromatic hydrocarbons, wt%	51.4	53.1	57.2
Aromatic carbon ratio, mol%	64.0	73.7	87.3
5% distillation temperature/°C	373	372	320
95% distillation temperature/°C	548	495	463

Table 10 Properties of three feedstock oils in Example 6

Item	First feedstock	Second feedstock	Third feedstock
Sulfur content, wt%	0.34	0.35	0.42
Ash, wt%	0.003	0.004	-
Three-ring and higher aromatic hydrocarbons, wt%	52.3	53.5	56.8
Aromatic carbon ratio, mol%	63.7	70.2	86.4
5% distillation temperature/°C	367	363	318
95% distillation temperature/°C	544	507	459

Table 11 Properties of three feedstock oils in Example 7

Item	First feedstock	Second feedstock	Third feedstock
Sulfur content, wt%	0.34	0.36	0.42
Ash, wt%	0.003	0.002	-
Three-ring and higher aromatic hydrocarbons, wt%	51.2	51.8	57.3
aromatic carbon ratio, mol%	63.6	69.1	90.5
5% distillation temperature/°C	362	365	315
95% distillation temperature/°C	549	506	462

Table 12 Conditions of hydrogenation reaction, cracking reaction and coking reaction in Comparative Examples

Reaction conditions	Comparative Example 1	Comparative Example 2	Comparative Example 3
Hydrogenation reaction			
Temperature/°C	365	368	370
Pressure/MPa	5.7	6.0	5.9
Hydrogen/oil volume ratio	1100	1100	1200
LHSV/h^{-1}	0.9	1.0	1.0
cracking reaction			
Temperature/°C		462	470
Pressure/MPa		0.55	0.5
Residence time/h		1.2	1.0
Mass ratio of first heavier oil to water vapor		100:6	100:6
coking reaction			
Heating furnace temperature/°C	450-505		
Heating rate/°C·h^{-1}	5		
Coking tower top pressure/MPa	0.8		
Reaction period/h	52		
First stage, %	-	-	23
Second stage, %	-	-	45
Third stage, %	-	-	32

Table 13 Comparative Properties of three feedstock oils in Example 1

Item	First feedstock	Second feedstock
Sulfur content, wt%	0.34	0.46
Ash, wt%	0.004	-
Three-ring and higher aromatic hydrocarbons, wt%	52.9	56.8
Aromatic carbon ratio, mol%	64.7	83.2
5% distillation temperature/°C	372	328
95% distillation temperature/°C	506	461

Table 14 Needle coke yield in Comparative Examples

Yield, wt%	Comparative Example 1	Comparative Example 2	Comparative Example 3
Needle coke	29.8	31.3	30.5

Table 15 Microstructural statistics of needle coke in Comparative Examples

Microstructure, %	Comparative Example 1	Comparative Example 2	Comparative Example 3
Coarse fiber	27.5	25.3	21.8
Fine fiber	22.7	28.2	17.3
Short fiber	11.6	15.8	13.3
Large leaflet	24.1	17.5	29.6
Small leaflet	12.9	12.2	15.6

(continued)

Microstructure, %	Comparative Example 1	Comparative Example 2	Comparative Example 3
Mosaic	1.2	1	2.4

[0123] In Table 5, the proportions of coarse fiber and fine fiber in Comparative Examples were less than 55%.

Table 16 Properties of three feedstock oils in Comparative Example 2

Item	First feedstock	Second feedstock	Third feedstock
Sulfur content, wt%	0.32	0.36	0.48
Ash, wt%	0.003	0.004	
Three-ring and higher aromatic hydrocarbons, wt%	50.7	53.1	64.0
Aromatic carbon ratio, mol%	62.3	73.5	84.3
5% distillation temperature/°C	368	377	331
95% distillation temperature/°C	547	499	464

Table 17 Properties of three feedstock oils in Comparative Example 3

Item	First feedstock	Second feedstock	Third feedstock
Sulfur content, wt%	0.32	0.35	0.47
Ash, wt%	0.004	0.003	
Three-ring and higher aromatic hydrocarbons, wt%	51.3	53.8	64.7
Aromatic carbon ratio, mol%	62.8	72.2	84.4
5% distillation temperature/°C	375	370	326
95% distillation temperature/°C	551	503	461

Claims

1. A method for producing a needle coke, comprising a step of sequentially adding n feedstock oils (n is an integer equal to or greater than 2, preferably 2-15 or 3-5) to a coking reaction at predetermined time intervals, wherein assuming that an i-th (n-1≥i≥1) feedstock oil has an aromatic carbon ratio of A (in mol%), an i+1-th feedstock oil has an aromatic carbon ratio of B (in mol%), a first feedstock oil has an aromatic carbon ratio of A1 (in mol%), and a n-th feedstock oil has an aromatic carbon ratio of B1 (in mol%), then B≥A (preferably B-A≥5mol% or B-A≥10mol%), and B1>A1 (preferably B1-Al≥10mol% or B1-A1≥20mol%).

2. The method according to claim 1, wherein said first feedstock oil has an aromatic carbon ratio of 40mol%-80mol% (preferably 55mol%-75mol%), an m-th (m is any integer greater than 1 and less than n) feedstock oil has an aromatic carbon ratio of 60mol%-90mol% (preferably 70mol%-85mol%), said n-th feedstock oil has an aromatic carbon ratio of greater than 75mol% (preferably 80mol%-95mol%).

3. The method according to claim 1, wherein said i-th (n-1≥i≥1) feedstock oil has a sulfur content of not greater than 0.45wt% (preferably not greater than 0.37wt%), an ash content of not greater than 0.05wt% (preferably not greater than 0.01wt%), a 5% distillation temperature of 330°C-430°C (preferably 360°C-400°C), a 95% distillation temperature of 470°C-530°C (preferably 485°C-510°C), a three-ring and higher aromatic hydrocarbon content of greater than 35wt% (preferably 38-60wt%), said n-th feedstock oil has a sulfur content of not greater than 0.55wt% (preferably not greater than 0.5wt%), an ash content of not greater than 0.05wt% (preferably not greater than 0.01wt%), a 5% distillation temperature of 280°C-380°C (preferably 310°C-360°C), a 95% distillation temperature of not greater than 480°C, and a three-ring and higher aromatic hydrocarbon content of greater than 40wt% (preferably 45-65wt%).

4. The method according to claim 1, wherein assuming that said coking reaction has a reaction period of T (in hours), then

the predetermined time interval divides the coking reaction into n reaction sections, and in each reaction section, from the beginning to the end of the reaction time of the reaction section, the feedstock oil corresponding to the reaction section is continuously or intermittently added.

5. The method according to claim 4, wherein to each reaction section, from the beginning to the end of the reaction time of this reaction section, any feedstock oil other than that corresponding to this reaction section is not added.

6. The method according to claim 1, wherein assuming that said coking reaction has a reaction period of T (in hours), then the predetermined time interval divides the coking reaction into n reaction sections, and the first reaction section has a reaction time of T1 (in hours), the m-th reaction section (m is any integer greater than 1 and less than n) has a reaction time of Tm (in hours), the n-th reaction section has a reaction time of Tn (in hours), then T1/T=5%-40% (preferably 10%-25%), Tm/T=15%-85% (preferably 25%-70%), Tn/T=15%-80% (preferably 25%-55%).

7. The method according to claim 1, wherein among said n feedstock oils, said first feedstock oil is a hydrogenated product of a catalytic slurry oil, said n-th feedstock oil is a heavier fraction of a coker distillates, and any one of other feedstock oils is a cracked product of a hydrogenation product of a catalytic slurry oil.

8. The method according to claim 1, wherein n=3, the number of the feedstock oil is 3, corresponding to the first feedstock oil, the second feedstock oil and the third feedstock oil, the reaction period T of said coking reaction is divided into three reaction sections, corresponding to the first reaction section, the second reaction section and the third reaction section, wherein in the first reaction section, the first feedstock oil is added to the coking reaction, in the second reaction section, the second feedstock oil is added to the coking reaction, and in the third reaction section, the third feedstock oil is added to the coking reaction.

9. The method according to claim 8, wherein the method for producing the first feedstock oil comprises: a catalytic slurry oil is purified to obtain a purified slurry oil, which is then sent to a hydrotreating system, wherein a hydrogenation reaction is carried out in the presence of hydrogen gas and a hydrogenation catalyst, then the hydrogenation product is separated to obtain a gas phase stream and a liquid phase stream, wherein the liquid phase stream is sent to a first separation system to obtain a first lighter oil and a first heavier oil, wherein the first heavier oil is used as the first feedstock oil.

10. The method according to claim 9, wherein said catalytic slurry oil has an ash content of higher than 0.01wt%, and a sulfur content of higher than 0.5wt%.

11. The method according to claim 9, wherein said purified slurry oil has an ash content of ≯ 0.008wt%, preferably ≯0.005wt%.

12. The method according to claim 9, wherein said purification is a solid removing treatment, and wherein the solid removing treatment is carried out by any one or more of filtration, centrifugal sedimentation, and flocculation sedimentation, preferably filtration.

13. The method according to claim 9, wherein the operation conditions of said hydrogenation reaction are as follows: the reaction temperature is 310°C-450°C, preferably 340°C-390°C, the reaction pressure is 2MPa-20MPa, preferably 4MPa-8MPa, the hydrogen/oil volume ratio is 100-2500, preferably 800-1800, the LHSV by volume is $0.1h^{-1}$-$2.0h^{-1}$, preferably $0.6h^{-1}$-$1.2h^{-1}$.

14. The method according to claim 9, wherein said liquid phase stream is one from which a non-condensable gas has been separated, preferably one from which a non-condensable gas and a naphtha fraction have been separated, and/or, said liquid phase stream has a sulfur content of ≯ 0.4wt%, preferably ≯0.35wt%.

15. The method according to claim 9, wherein said first heavier oil has a 5% distillation temperature of 330°C-420°C, preferably 360°C-400°C, and/or, said first lighter oil has a 95% distillation temperature of 310°C-420°C, preferably 340°C-400°C.

16. The method according to claim 9, wherein said first lighter oil is discharged from the device or sent to a condensation reaction system for treatment, or alternatively, a part thereof is discharged from the device and other part thereof is sent to the condensation reaction system for treatment.

17. The method according to claim 16, wherein the operation conditions of said condensation reaction system are: the reaction temperature is 350°C-530°C, preferably 380°C-450°C, the reaction pressure is 0.01MPa-5MPa, preferably 1MPa-3MPa, the residence time is 0.1h-15h, preferably 0.5h-6h.

18. The method according to claim 8, wherein the reaction time of said first reaction section comprises 5%-40%, preferably 10%-25% of said reaction period T, and/or, the reaction time of said second reaction section comprises 15%-85%, preferably 25%-70% of said reaction period T.

19. The method according to claim 1, wherein the reaction period of said coking reaction is 24-92 hrs (preferably 36-60 hrs).

20. The method according to claim 8, wherein said method for producing the second feedstock oil comprises: the first feedstock oil (e.g., the first heavier oil) is sent to a cracking reaction system wherein a cracking reaction is carried out in the presence of a carrier gas, and the obtained cracked product is sent to a second separation system, and after separation, a second lighter oil, an intermediate distillate oil and a second heavier oil are obtained, wherein the intermediate distillate oil is used as the second feedstock oil.

21. The method according to claim 20, wherein the operation conditions of the cracking reaction are as follows: the reaction temperature is 380°C-520°C, preferably 420°C-490°C, the reaction pressure is 0.1MPa-5MPa, preferably 0.2MPa-1.0MPa, the residence time 0.01h-30h, preferably 0.1h-3h, the oil-to-steam mass ratio is 100:0.1-100:20, preferably 100:1-100:8.

22. The method according to claim 20, wherein said intermediate distillate oil has a 5% distillation temperature of 340°C-430°C, preferably 360°C-400°C, a 95% distillation temperature of 470°C-530°C, preferably 485°C-510°C, a sulfur content of ≯ 0.43wt%, preferably ≯ 0.37wt%, an ash content of ≯ 0.006wt%, preferably ≯ 0.004wt%, and/or, said second lighter oil has a 95% distillation temperature of 330°C-430°C, preferably 350°C-400°C, and/or, said second heavier oil has a 5% distillation temperature of 470°C-540°C, preferably 485°C-520°C.

23. The method according to claim 20, wherein said first feedstock oil is sent together with a first auxiliary feedstock oil to said cracking reaction system, wherein the first auxiliary feedstock oil has an ash content of not greater than 0.02wt%, preferably not greater than 0.01wt%, a sulfur content of not greater than 0.4wt%, preferably not greater than 0.35wt%, a three-ring and higher aromatic hydrocarbon content of not less than 40wt%, an aromatic carbon ratio of not less than 40mol%, preferably 55mol%-80 mol%, and a distillation range of 300°C-550°C, preferably 330°C-510°C.

24. The method according to claim 23, wherein said first auxiliary feedstock oil is one or more of a catalytic slurry oil, an ethylene tar, a vacuum gas oil, a coker gas oil, a deasphalted oil, and a hydrogenated oil.

25. The method according to claim 23, wherein the mass ratio of said first auxiliary feedstock oil to said first feedstock oil is 0:100-50:100, preferably 5:100-20:100.

26. The method according to claim 20, wherein said cracked product is sent together with a second auxiliary feedstock oil to said second separation system, wherein the second auxiliary feedstock oil has an ash content of not greater than 0.02wt%, preferably not greater than 0.01wt%, a sulfur content of not greater than 0.4wt%, preferably not greater than 0.35wt%, an aromatic hydrocarbon content of 50wt%-95wt%, preferably 65wt%-90wt%, a three-ring and higher aromatic hydrocarbon content of not less than 40wt%, an aromatic carbon ratio of not less than 50mol%, preferably not less than 75 mol%.

27. The method according to claim 26, wherein said second auxiliary feedstock oil is one or more of catalytic slurry oil, ethylene tar, vacuum gas oil, coker gas oil, and deasphalted oil.

28. The method according to claim 26, wherein the mass ratio of said second auxiliary feedstock oil to said cracked product is 0:100-100:10, preferably 5:100-20:100.

29. The method according to claim 20, wherein said cracked product is sent together with a condensation reaction product of said first lighter oil to said second separation system for separation.

30. The method according to claim 29, wherein the mass ratio of said cracked product to the condensation reaction product of said first lighter oil is 100:0-100:20, preferably 100:0-100:5.

31. The method according to claim 8, wherein the method for producing the third feedstock oil comprises: the coker oil gas generated by the coking reaction is sent to a third separation system, and after separation, a coker gas, a third lighter oil and a third heavier oil are obtained, wherein said third heavier oil is used as said third feedstock oil.

32. The method according to claim 31, wherein said third heavier oil has a 5% distillation temperature of 280°C-380°C, preferably 310°C-360°C, and/or, said third lighter oil has a 95% distillation temperature of 270°C-380°C, preferably 300°C-360°C.

33. The method according to claim 1, wherein the operation conditions of said coking reaction include: the outlet temperature of the heating furnace is 420°C-560°C, preferably 440°C-530°C, the heating rate is 0.5°C/h-30°C/h, preferably 3°C/h-7°C/h; the coking tower top pressure is 0.01MPa-2.5MPa, preferably 0.2MPa-1.3MPa, the coking reaction is carried out under a constant pressure or a changing pressure, wherein if a changing pressure operation is used, the pressure changing rate is 0.1MPa/h-5MPa/h; the reaction period is 24h-92h (preferably 36h-60h).

34. A device for producing a needle coke, which comprises the following units:

a feedstock oil supplying unit, which is configured for providing n feedstock oils (n is an integer equal to or greater than 2, preferably 2-15 or 3-5), assuming that an i-th ($n-1 \geq i \geq 1$) feedstock oil has an aromatic carbon ratio of A (in mol%), an i+1-th feedstock oil has an aromatic carbon ratio of B (in mol%), a first feedstock oil has an aromatic carbon ratio of A1 (in mol%), and a n-th feedstock oil has an aromatic carbon ratio of B1 (in mol%), then $B \geq A$ (preferably $B-A \geq 5$mol% or $B-A \geq 10$mol%), and $B1 > A1$ (preferably $B1-A1 \geq 10$mol% or $B1-A1 \geq 20$mol%),
a coking unit, which is configured for receiving said n feedstock oils, and causing them to undergo a coking reaction to obtain a needle coke,
a control unit, which is configured for feeding said n feedstock oils to the coking unit in sequence from said feedstock oil supplying unit at a predetermined time interval.

35. The device according to claim 34, wherein n=3, and it comprises:

a purification system, which is used to receive and purify a catalytic slurry oil to obtain a purified slurry oil;
a hydrotreating system, which is used to receive hydrogen gas and the purified slurry oil from the purification system, and to carry out a hydrogenation reaction in the presence of a hydrogenation catalyst, and to obtain a gas phase stream and a liquid phase stream after separation of the hydrogenation product;
a first separation system, which is used to receive the liquid phase stream from the hydrotreating system and obtain a first lighter oil and a first heavier oil after separation;
a cracking reaction system, which is used to receive the first heavier oil from the first separation system and optionally a first auxiliary feedstock oil, and carry out a cracking reaction in the presence of a carrier gas;
a second separation system, which is used to receive the reaction effluent from the cracking reaction system and optionally a second auxiliary feedstock oil, and obtain a second lighter oil, an intermediate distillate oil and a second heavier oil after separation;
a coking unit, which is used to receive the first heavier oil from the first separation system (i.e. the first feedstock oil), the intermediate distillate oil from the second separation system (i.e. the second feedstock oil) and the third heavier oil from a third separation system (i.e. the third feedstock oil), and to conduct a coking reaction to obtain a coker oil gas and a needle coke;
a third separation system, which is used for receiving the coker oil gas obtained from the coking unit, and then obtaining a coker gas, a third lighter oil and a third heavier oil after separation.

36. The device according to claim 35, which further comprises a condensation reaction system, which is used to receive the first lighter oil from the first separation system, wherein the first lighter oil is sent to the condensation reaction system and undergoes a condensation reaction in the presence of a condensation catalyst, and then the reaction effluent obtained from the condensation reaction is sent to the second separation unit and is subjected to separation together with the reaction effluent from the cracking reaction system.

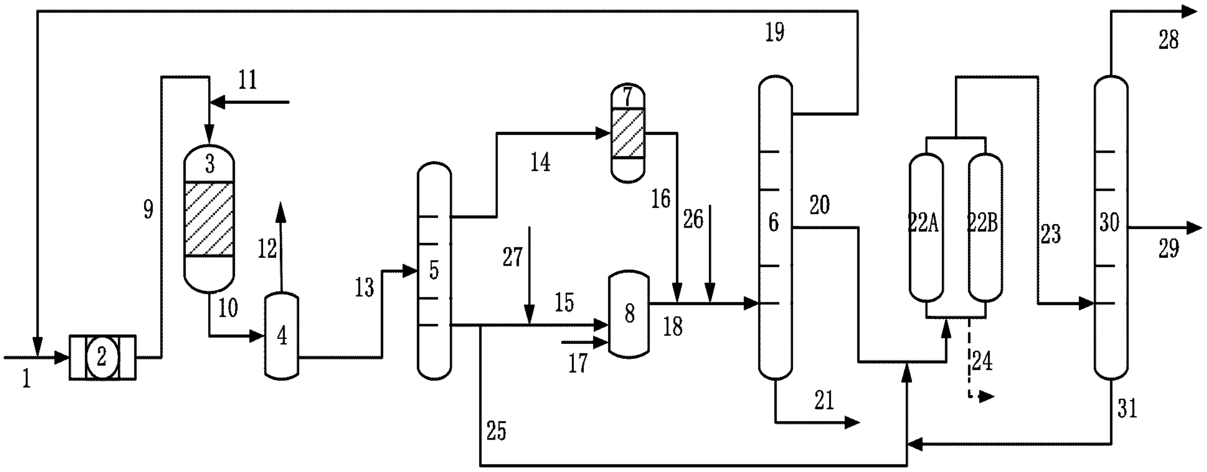
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Fig.1

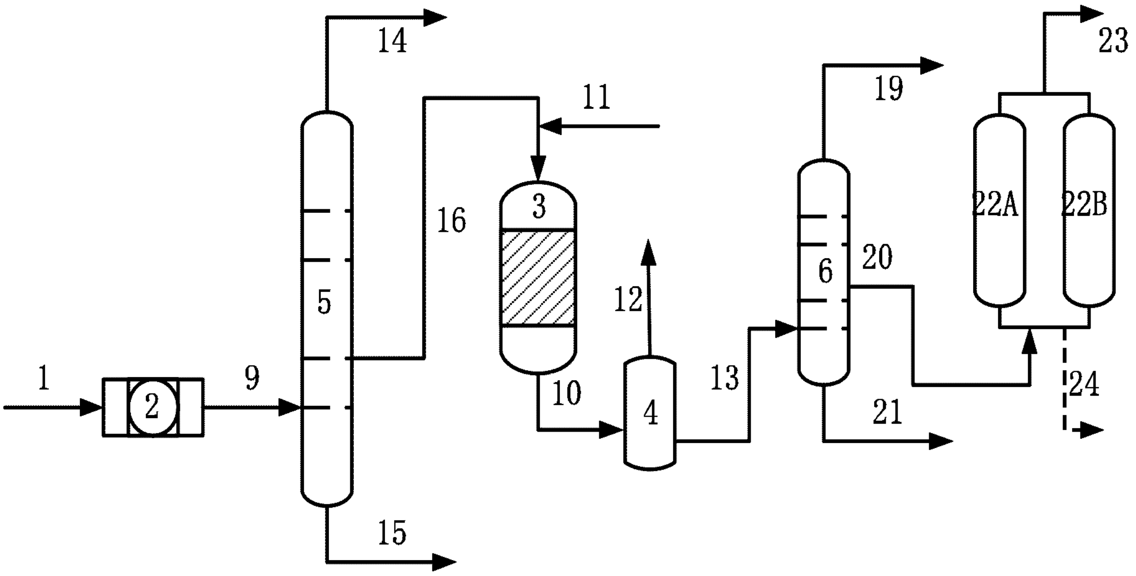
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Fig. 2

INTERNATIONAL SEARCH REPORT

International application No.
PCT/CN2023/098774

A. CLASSIFICATION OF SUBJECT MATTER

C10B55/00(2006.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C10B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

CNTXT, VEN, CJFD: 针状焦, 原料油, 芳碳率, 焦化反应, 加氢催化, needle coke, feed oil, aromatic carbon ratio, coking reation, catalytic hydrogeneration

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	CN 107987880 A (CHINA PETROCHEMICAL CO., LTD. et al.) 04 May 2018 (2018-05-04) description, paragraphs 5-19	1-36
A	CN 112745916 A (CHINA PETROCHEMICAL CO., LTD. et al.) 04 May 2021 (2021-05-04) entire document	1-36
A	CN 114479906 A (CHINA PETROCHEMICAL CO., LTD. et al.) 13 May 2022 (2022-05-13) entire document	1-36
A	KR 20140072761 A (SEMES CO., LTD.) 13 June 2014 (2014-06-13) entire document	1-36

☐ Further documents are listed in the continuation of Box C. ☑ See patent family annex.

* Special categories of cited documents:

"A"	document defining the general state of the art which is not considered to be of particular relevance	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"D"	document cited by the applicant in the international application	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E"	earlier application or patent but published on or after the international filing date	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&"	document member of the same patent family
"O"	document referring to an oral disclosure, use, exhibition or other means		
"P"	document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search **15 August 2023**	Date of mailing of the international search report **09 September 2023**
Name and mailing address of the ISA/CN **China National Intellectual Property Administration (ISA/CN)** **China No. 6, Xitucheng Road, Jimenqiao, Haidian District, Beijing 100088**	Authorized officer Telephone No.

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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/CN2023/098774

Patent document cited in search report	Publication date (day/month/year)	Patent family member(s)	Publication date (day/month/year)
CN 107987880 A	04 May 2018	None	
CN 112745916 A	04 May 2021	None	
CN 114479906 A	13 May 2022	None	
KR 20140072761 A	13 June 2014	KR 101559027 B1	13 October 2015

Form PCT/ISA/210 (patent family annex) (July 2022)

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- CN 113004924 A **[0003]**
- CN 103184057 A **[0004]**