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(54) **METHOD AND DEVICE FOR PRODUCING LOW-CARBON OLEFINS AND BTX BY CATALYTICALLY CRACKING HYDROCARBON-CONTAINING RAW OIL**

(57) A process and apparatus for producing lower carbon olefins and BTX by catalytic pyrolysis of hydrocarbon-containing feedstock oil, and the process comprises the steps: cutting the hydrocarbon-containing feedstock oil into a light distillate oil and a heavy distillate oil; introducing the light distillate oil and a first catalyst into a down-flow reactor to perform a catalytic pyrolysis to produce a stream after the first catalytic pyrolysis; subjecting the stream after the first catalytic pyrolysis to a gas-solid separation to produce a first reaction hydrocarbon product and a first spent catalyst; or, introducing the stream after the first catalytic pyrolysis into a fluidized bed reactor to perform a catalytic pyrolysis, and then subjecting to a gas-solid separation to produce a second reaction hydrocarbon product and a second spent cata-

lyst; introducing a continuous catalyst, the heavy distillate oil and a second catalyst into an up-flow reactor to perform a catalytic pyrolysis, and then subjecting to a gas-solid separation to produce a third reaction hydrocarbon product and a third spent catalyst; separating out lower carbon olefins and light aromatics from reaction hydrocarbon products, and separating out a light olefin fraction, and returning the light olefin fraction to the fluidized bed reactor or the up-flow reactor. The process can significantly increase the yields of lower carbon olefins and light aromatics as well as the economy of the apparatus.

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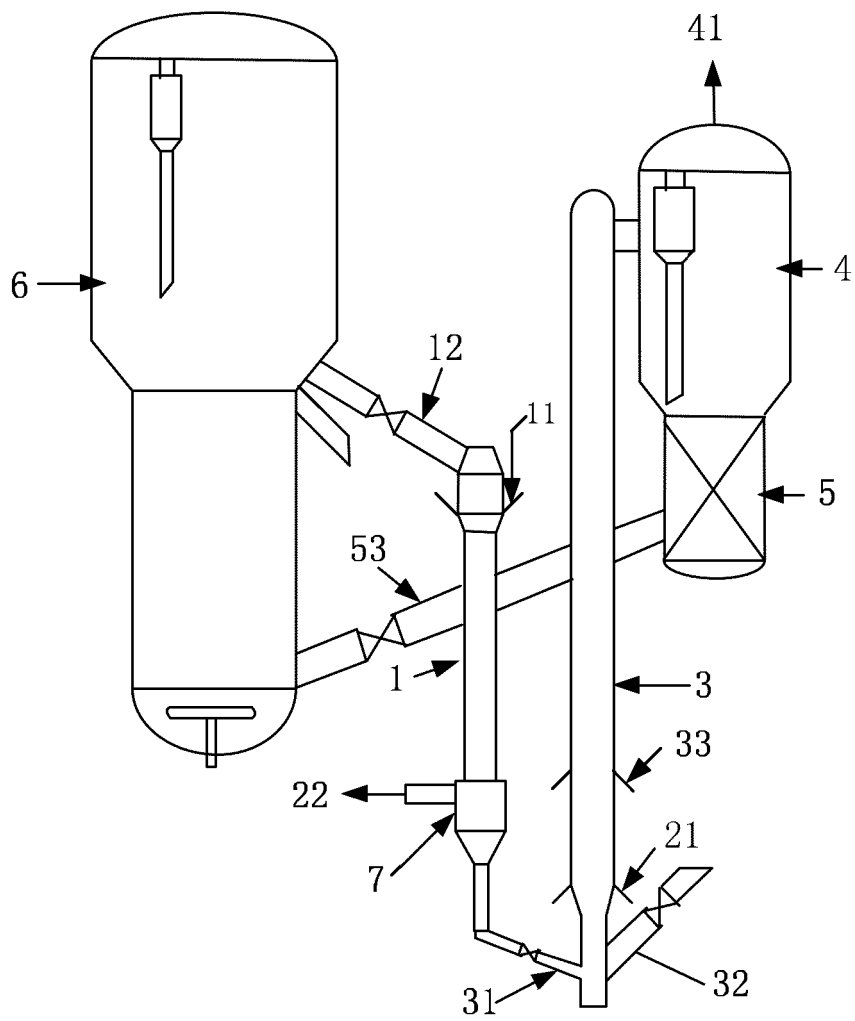


Figure 1

Description**Technical Field**

5 **[0001]** The present application relates to the petroleum refining and petrochemical processing processes, specifically to the process and the apparatus for producing lower carbon olefins and BTX by the catalytic pyrolysis of the full distillate hydrocarbon-containing feedstock oil.

Background Technology

10 **[0002]** As the growth rate of refined oil consumption continues to slow down and the demand for basic organic raw materials represented by lower carbon olefins and aromatics grows rapidly, the chemical material-based refineries will become the future development trend. At present, the chemical industry-based refineries mainly include the following three configurations: (1) crude oil is subjected to the pretreatment such as solvent deasphalting or hydrofining, and then
 15 directly sent to the steam pyrolysis unit to produce chemical materials, but this method is generally limited to light crude oil; (2) the fractions of crude oil are hydrocracked to maximize the production of heavy naphtha, which are treated with the reforming unit to maximize the production of aromatics; (3) the light fraction of crude oil is sent to steam pyrolysis unit, and the heavy fraction is sent to the catalytic pyrolysis unit to maximize the production of lower carbon olefins. The above three configurations have been industrialized, and the yield of chemical materials is between 35% and 55%. It
 20 can be seen that the configuration of the existing chemical industry-based refineries mainly relies on the combination of a plurality of key units including steam pyrolysis, reforming, hydrofining, hydrocracking, catalytic pyrolysis and the others. Among them, the catalytic pyrolysis process has its unique advantages in the production of chemical materials and the adaptability of raw materials, and can simultaneously produce propylene, ethylene and BTX.

25 **[0003]** Chinese patent CN1978411B discloses a combined process for preparing small molecule olefins. In this process, the catalytic pyrolysis catalyst and the pyrolysis raw material are mixed and contacted in a single reactor, and the spent catalyst and the reaction hydrocarbon product are separated. The spent catalyst is sent to a regenerator to perform the coke-burning and regeneration. The regenerated hot catalyst is divided into two parts, wherein one part of the regenerated hot catalyst is returned to the above-mentioned reactor; and the other part of the regenerated hot catalyst is firstly mixed and contacted with heavy petroleum hydrocarbons in another reactor to perform the pre-coking, then a C4-C8 olefin-rich raw material is mixed and contacted with the coked catalyst to perform the catalytic pyrolysis reaction, the spent catalyst and the reaction hydrocarbon product are separated, the resulting spent catalyst is sent together with the spent catalyst obtained in the previous step to the regenerator to perform the coke-burning and regeneration; the reaction hydrocarbon product is separated to produce the small molecular olefins such as propylene as the target product. The process can convert olefin-rich light raw materials into small molecular olefin products such as propylene with high
 30 selectivity, while maintaining the heat balance of the apparatus itself.

35 **[0004]** Chinese patent CN102899078A discloses a catalytic pyrolysis process for producing propylene. This process is based on a combined reactor composed of two risers and one fluidized bed. First, the heavy feedstock oil and the first catalyst are introduced into the first riser reactor to perform the reaction. The catalyst and the hydrocarbon product are separated, and the latter is introduced into the separation system. The pyrolysis heavy oil is introduced into the
 40 second riser reactor, and contacted with the catalyst introduced into the second riser reactor to perform the reaction. The light hydrocarbon is introduced into the second riser reactor, and contacted with the mixture formed from the reaction by contacting the pyrolysis heavy oil with the second pyrolysis catalyst. The light hydrocarbon includes the C4 hydrocarbon or the gasoline fraction obtained from the product separation system. Then the hydrocarbon product from the reaction in the second riser reactor and the catalyst are introduced into the fluidized bed reactor to perform the reaction. Through
 45 the optimization of the process, different feedstocks can be selectively converted with suitable catalysts in higher yields of propylene and butene.

50 **[0005]** Chinese patent CN101045667B discloses a combined catalytic conversion process for producing lower carbon olefins. In this process, a heavy oil feedstock is contacted with a regenerated catalyst and an optional coke-deposited catalyst in a down-flow tubular reactor, and at least a part of the other products except for lower carbon olefins is introduced into a riser reactor and contacted with the regenerated catalyst to perform the reaction. After the reaction in the riser, the catalyst is introduced into the catalyst pre-lifting section of the down-flow tubular reactor, mixed with the regenerated catalyst entering the down-flow tubular reactor, and then contacted with the heavy oil feedstock. The process uses a combined reactor form of the down-flow reactor for the reaction of the heavy oil feedstock and the riser reactor for the reaction of the intermediate olefin product so as to increase the yield of lower carbon olefins.

55 **[0006]** Chinese patent CN109370644A discloses a process for producing lower carbon olefins and aromatics by catalytic pyrolysis of crude oil. This process divides the crude oil into light and heavy fractions, and the cut point is between 150°C and 300°C. The light fraction and the heavy fraction are reacted in different reaction zones of the same reactor. The used catalyst contains an aluminosilicate salt composed of silicon dioxide and dialuminum trioxide as the

main component, and alkali metal oxides, alkaline earth metal oxides, titanium, iron oxides, vanadium and nickel oxides. The process is based on a dense-phase deliver bed reactor for processing lower carbon olefins by catalytic pyrolysis of heavy oil, and a technical solution is proposed aiming at the production of lower carbon olefins by catalytic pyrolysis of crude oil.

[0007] In the above processes, the studies have been made from the aspects of exploiting the new reactor structure, developing the novel catalytic materials, controlling the reaction depth to improve propylene selectivity, and the like, and the processes for producing lower carbon olefins and aromatics by catalytic pyrolysis have been proposed, but there is still no preparation process and reactor structure aimed at maximizing the production of chemical materials from crude oil.

Summary of the Invention

[0008] Aiming at the characteristics of different hydrocarbon compositions and different cutting temperatures of various hydrocarbon-containing feedstock oils, the purpose of this disclosure is to propose an apparatus and process suitable for processing a hydrocarbon-containing feedstock oil to perform the catalytic pyrolysis, in order to maximize the utilization of the hydrocarbon-containing feedstock oil to produce lower carbon olefins and BTX.

[0009] In order to achieve the above objects, the disclosure provides a process for producing lower carbon olefins and light aromatics by catalytic pyrolysis of hydrocarbon-containing feedstock oil, wherein the process comprises the steps of:

S1, cutting the hydrocarbon-containing feedstock oil into a light distillate oil and a heavy distillate oil, wherein the weight ratio of the light distillate oil to the heavy distillate oil (light distillate oil/heavy distillate oil) is X;

S2, introducing the light distillate oil and a first catalyst into a first down-flow reactor to perform a first catalytic pyrolysis to produce a stream after the first catalytic pyrolysis; optionally S2', introducing the stream after the first catalytic pyrolysis into a fluidized bed reactor to perform a second catalytic pyrolysis to produce a stream after the second catalytic pyrolysis;

S3, subjecting the stream after the first catalytic pyrolysis to a gas-solid separation to produce a first reaction hydrocarbon product and a first spent catalyst, or subjecting the stream after the second catalytic pyrolysis to a gas-solid separation to produce a second reaction hydrocarbon product and a second spent catalyst;

S4, introducing a continuous catalyst, the heavy distillate oil and a second catalyst into a second up-flow reactor to perform a third catalytic pyrolysis, and then subjecting to a gas-solid separation to produce a third reaction hydrocarbon product and a third spent catalyst; the continuous catalyst is at least a part of the first spent catalyst or at least a part of the second spent catalyst; the weight ratio of the second catalyst to the continuous catalyst (second catalyst/continuous catalyst) is R;

S5, separating out lower carbon olefins and light aromatics from any of the first reaction hydrocarbon product, the second reaction hydrocarbon product and the third reaction hydrocarbon product or a mixture of the first reaction hydrocarbon product and the third reaction hydrocarbon product or a mixture of the second reaction hydrocarbon product and the third reaction hydrocarbon product, and separating out a light olefin fraction, and returning the light olefin fraction to the second up-flow reactor of step S4 or the fluidized bed reactor of step S2', wherein R and X satisfy the following relation:

$$(4.84 \times T_0 - 3340) / (780 + 5 \times T_0 - 6 \times T_3) < R/X < (0.968 \times T_0 - 630) / (668 + 0.2 \times T_0 - 1.2 \times T_3)$$

T₀ is the temperature (unit: °C) when the second catalyst enters step S4, and T₃ is the outlet temperature (unit: °C) of the second up-flow reactor.

[0010] Optionally, according to the process of the disclosure, the outlet temperature T₃ of the second up-flow reactor is 530-650°C, preferably 560-640°C, further preferably 580-630°C, further more preferably 600-630°C; and/or, the temperature T₀ when the second catalyst enters step S4 is 690-750°C, preferably 700-740°C, further preferably 705-730°C, further more preferably 710-725°C.

[0011] Optionally, according to the process of the disclosure, in step S1, the hydrocarbon-containing feedstock oil is cut into the light distillate oil and the heavy distillate oil at the cut point of any temperature between 100-400°C, so that the weight ratio of the light distillate oil to the heavy distillate oil (light distillate oil/heavy distillate oil) is X.

[0012] Optionally, according to the process of the disclosure, in the first down-flow reactor, the conditions of the first catalytic pyrolysis comprise: the outlet temperature of the first down-flow reactor is 610-720°C, the gas-solid residence time is 0.1-3.0 seconds, the catalyst-oil ratio is 15-80; and/or, in the fluidized bed reactor, the conditions of the second catalytic pyrolysis comprise: the reaction temperature in the fluidized bed reactor is 600-690°C, the weight hourly space velocity is 2-20 h⁻¹; and/or, in the second up-flow reactor, the conditions of the third catalytic pyrolysis comprise: the

gas-solid residence time is 0.5-8 seconds, the catalyst-oil ratio is 8-40.

[0013] Optionally, according to the process of the disclosure, in the first down-flow reactor, the conditions of the first catalytic pyrolysis comprise: the outlet temperature of the first down-flow reactor is 650-690°C, the gas-solid residence time is 0.5-1.5 seconds, the catalyst-oil ratio is 25-65; and/or, in the fluidized bed reactor, the conditions of the second catalytic pyrolysis comprise: the reaction temperature in the fluidized bed reactor is 640-670°C, the weight hourly space velocity is 4-12 h⁻¹; and/or, in the second up-flow reactor, the conditions of the third catalytic pyrolysis comprise: the gas-solid residence time is 1.5-5 seconds, the catalyst-oil ratio is 10-30.

[0014] Optionally, according to the process of the disclosure, in step S4, the continuous catalyst and the second catalyst are firstly mixed, and then the subsequent catalytic pyrolysis reaction is performed, and/or, in presence of step S2', in step S3 of the gas solid separation, the separated catalyst is stripped to produce the second spent catalyst; and/or, in step S4, the light olefin fraction obtained from step S5 contacts a mixture of the second catalyst and the continuous catalyst earlier than the heavy distillate oil to perform the catalytic pyrolysis; preferably the light olefin (fraction) contacts a mixture of the second catalyst and the continuous catalyst 0.3-1.0 seconds earlier than the heavy distillate oil to perform the catalytic pyrolysis, more preferably the light olefin fraction contacts a mixture of the second catalyst and the continuous catalyst 0.4-0.8 seconds earlier than the heavy distillate oil to perform the catalytic pyrolysis; and/or, the process includes step S0 before step S1, wherein the hydrocarbon-containing feedstock oil is subjected to the desalination and dehydration treatment, and the resulting dehydrated and desalinized hydrocarbon-containing feedstock oil is introduced into step S1 for cutting.

[0015] Optionally, according to the process of the disclosure, the process further comprises: in step S4 of the gas solid separation, the separated catalyst is stripped to produce the third spent catalyst; and/or the third spent catalyst and optionally the first spent catalyst or the second spent catalyst not entering the second up-flow reactor are subjected to coke-burning and regeneration at a temperature of 690-750°C, preferably 700-740°C, further preferably 705-730°C, further more preferably 710-725°C to produce a regenerated catalyst; and/or, any of the first reaction hydrocarbon product, the second reaction hydrocarbon product and the third reaction hydrocarbon product or a mixture of the first reaction hydrocarbon product and the third reaction hydrocarbon product or a mixture of the second reaction hydrocarbon product and the third reaction hydrocarbon product is separated to produce dry gas, C3 fraction, C4 fraction, light gasoline, heavy gasoline, diesel and slurry oil, from which lower carbon olefins and light aromatics are produced by separation, and a light olefin fraction is separated out; and/or in absence of step S2', in step S5, the light olefin fraction is separated out from any of the first reaction hydrocarbon product and the third reaction hydrocarbon product or a mixture of two, and the light olefin fraction is returned to the second up-flow reactor of step S4; in presence of step S2', in step S5, the light olefin fraction is separated out from any of the second reaction hydrocarbon product and the third reaction hydrocarbon product or a mixture of two, and the light olefin fraction is returned to the fluidized bed reactor of step S2'.

[0016] Optionally, according to the process of the disclosure, the hydrocarbon-containing feedstock oil is one of or a mixture of two or more of crude oil, coal liquefaction oil, synthetic oil, tar sand oil, shale oil, tight oil and animal and vegetable oil and fat, or their respective partial fractions, or hydro-upgraded oils of their respective heavy fractions.

[0017] Optionally, according to the process of the disclosure, the first catalyst and the second catalyst each independently comprise an active component and a support, the active component is at least one of ultra-stabilized Y zeolite optionally containing rare earth, ZSM-5 zeolite, pentasil silica-rich zeolite and beta zeolite, said support is at least one of alumina, silica, amorphous silica alumina, zirconia, titania, boron oxide and alkali-earth oxide.

[0018] Optionally, according to the process of the disclosure, the first catalyst and the second catalyst each independently comprise a regenerated catalyst, preferably the first catalyst and the second catalyst are the regenerated catalyst, and/or, the whole of the first spent catalyst or the whole of the second spent catalyst is used as the continuous catalyst.

[0019] The present disclosure also provides an apparatus for producing lower carbon olefins and light aromatics by the catalytic pyrolysis of a hydrocarbon-containing feedstock oil, wherein the apparatus comprises the following units:

a hydrocarbon-containing feedstock oil-cutting unit, wherein the hydrocarbon-containing feedstock oil is cut into a light distillate oil and a heavy distillate oil, so that the weight ratio of the light distillate oil to the heavy distillate oil (light distillate oil/heavy distillate oil) is X,

a first down-flow reaction unit, wherein the light distillate oil and a first catalyst are introduced to the upper part of the reaction unit to perform the first catalytic pyrolysis, and a stream after the first catalytic pyrolysis is obtained from the lower part of the reaction unit;

an optional fluidized-bed reaction unit, wherein the stream after the first catalytic pyrolysis is introduced to perform the second catalytic pyrolysis to produce a stream after the second catalytic pyrolysis;

a first gas solid separation unit, wherein the stream after the first catalytic pyrolysis is introduced to perform the gas solid separation to produce a first reaction hydrocarbon product and a first spent catalyst, or wherein the stream after the second catalytic pyrolysis is introduced to perform the gas solid separation to produce a second reaction

hydrocarbon product and a second spent catalyst;

a second up-flow reaction unit, wherein a continuous catalyst, a second catalyst and the heavy distillate oil are introduced from the lower part of the reaction unit to perform the third catalytic pyrolysis, and a stream after the third catalytic pyrolysis is obtained from the upper part of the reaction unit, the continuous catalyst is at least a part of the first spent catalyst or at least a part of the second spent catalyst, the weight ratio of the second catalyst to the continuous catalyst (second catalyst/continuous catalyst) is R,

a second gas solid separation unit, wherein the stream after the third catalytic pyrolysis is introduced to perform the gas solid separation to produce a third reaction hydrocarbon product and a third spent catalyst;

a separation unit, wherein any of the first reaction hydrocarbon product, the second reaction hydrocarbon product and the third reaction hydrocarbon product or a mixture of the first reaction hydrocarbon product and the third reaction hydrocarbon product or a mixture of the second reaction hydrocarbon product and the third reaction hydrocarbon product is introduced, and lower carbon olefins and light aromatics are separated out, and a light olefin fraction is separated out, and the light olefin fraction is returned to the second up-flow reaction unit or the fluidized-bed reaction unit;

wherein R and X satisfy the following relation:

$$(4.84 \times T_0 - 3340) / (780 + 5 \times T_0 - 6 \times T_3) < R/X < (0.968 \times T_0 - 630) / (668 + 0.2 \times T_0 - 1.2 \times T_3)$$

T₀ is the temperature (unit: °C) when the second catalyst enters the second up-flow reaction unit, and T₃ is the outlet temperature (unit: °C) of the second up-flow reaction unit.

[0020] Optionally, the apparatus of the present disclosure further comprises a regeneration unit, wherein the third spent catalyst and optionally the first spent catalyst or the second spent catalyst not entering the second up-flow reactor are introduced to perform the coke-burning and regeneration at a temperature of 690-750°C, preferably 700-740°C, further preferably 705-730°C, further more preferably 710-725°C to produce a regenerated catalyst.

[0021] Optionally, for the apparatus according to the present disclosure, if the apparatus comprises the fluidized-bed reaction unit, the first gas solid separation unit further comprises a stripping unit, wherein the catalyst obtained from the gas solid separation is subjected to stripping to produce a second spent catalyst.

[0022] The second gas solid separation unit further comprises a stripping unit, wherein the catalyst obtained from the gas solid separation is subjected to stripping to produce a third spent catalyst.

[0023] Optionally, for the apparatus according to the present disclosure, the apparatus further comprises a dehydration and desalination unit, wherein the hydrocarbon-containing feedstock oil is subjected to the desalination and dehydration treatment, and the resulting dehydrated and desalinized hydrocarbon-containing feedstock oil is introduced to the hydrocarbon-containing feedstock oil-cutting unit to be cut.

[0024] Optionally, for the apparatus according to the present disclosure, the position where the continuous catalyst and the second catalyst are introduced into the second up-flow reaction unit is upstream the feed inlet of the light olefin fraction.

[0025] Optionally, for the apparatus according to the present disclosure, in the second up-flow reaction unit, the feed inlet of the light olefin fraction from the separation unit is upstream the feed inlet of the heavy distillate oil.

Technical effect

[0026] In the present disclosure, through the above-mentioned specific process, according to the hydrocarbon composition characteristics and the pyrolysis reaction characteristics of different fractions of the hydrocarbon-containing feedstock oil, the hydrocarbon-containing feedstock oil is cut into two parts, light distillate oil and heavy distillate oil, and the light distillate oil is subjected to pyrolysis in the down-flow reactor at a high temperature for a short residence time so that lower carbon olefins and BTX can be produced with high selectivity, and at the same time the production of methane can be significantly reduced. At the same time, for the heavy distillate oil, by using an up-flow reactor, the production of lower carbon olefins and BTX can be maximized.

[0027] In addition, in the present disclosure, by arranging a fluidized bed reactor at the downstream of the first down-flow reactor, the light olefins in the stream after the catalytic pyrolysis can be further converted, and the production of lower carbon olefins can be maximized.

[0028] In the present disclosure, in the first down-flow reactor, the residence time of the light distillate oil is short, the coke formation of the reaction is low, and the yields of lower carbon olefins and BTX are high; in addition, in the fluidized bed reactor, the light olefin fraction is further converted. Thus, the first spent catalyst leaving the first down-flow reactor or the second spent catalyst leaving the fluidized bed reactor still has a higher activity, and coke deposits are loaded on the catalyst. When the catalyst is used in the catalytic pyrolysis of the heavy distillate oil in the second up-flow reactor,

the yield of lower carbon olefins can be increased, and the generation of dry gas and coke can be inhibited.

[0029] More importantly, in the present disclosure, by allowing the weight ratio (X) of the light distillate oil to the heavy distillate oil, both of which are obtained by cutting, and the weight ratio (R) of the second catalyst to the continuous catalyst to satisfy a specific relation, depending on the type of the hydrocarbon-containing feedstock oil, the cutting ratio can be flexibly adjusted. Correspondingly, the weight ratio of the second catalyst to the continuous catalyst can be adjusted so that in the second up-flow reactor, the catalyst activity is more closely matched to the composition of the heavy distillate oil, the yield of by-products such as dry gas and coke can be significantly reduced while maximizing the production of light olefins and BTX.

[0030] In addition, through the above-mentioned technical solutions, the process for producing lower carbon olefins and BTX by catalytic pyrolysis of the hydrocarbon-containing feedstock oil provided by the present disclosure can significantly improve the yield of lower carbon olefins and light aromatics and the economy of the apparatus.

[0031] Other features and merits of the present disclosure will be described in detail in the following detailed description.

Brief description of the drawings

[0032] The accompanying drawing is intended to provide a further understanding of the present disclosure and constitutes a part of the description and together with the following detailed description, serves to explain the present disclosure, but does not constitute a limitation of the present disclosure. In the accompanying drawings:

Figure 1 is a schematic diagram of one embodiment of the apparatus of the present disclosure.

Figure 2 is a schematic diagram of another embodiment of the apparatus of the present disclosure.

Description of the reference numerals

[0033]

- | | | | |
|-----|--|-----|--|
| 1. | Down-flow reactor | 32. | Second catalyst (regenerated catalyst) delivery pipe |
| 11. | Feed nozzle of light distillate oil | 33. | Feed nozzle of heavy distillate oil |
| 12. | First catalyst (regenerated catalyst) delivery pipe | 4. | Settler |
| 13. | Mushroom head distributor | 41. | Hydrocarbon product outlet of the third reactor |
| 2. | Fluidized bed reactor | 5. | Stripper |
| 21. | Feed nozzle of light olefin fraction | 51. | First stripper |
| 22. | Hydrocarbon product outlet of first reaction/hydrocarbon product outlet of second reaction | 52. | Second stripper |
| 3. | Up-flow reactor | 53. | Third spent catalyst delivery pipe |
| 31. | Continuous catalyst delivery pipe | 6. | Regenerator |
| | | 7. | Gas solid separator |

Detailed description

[0034] Specific embodiments of the present disclosure will be described in detail below. It should be understood that the specific embodiments described herein are only used to illustrate and explain the present disclosure and are not intended to limit the present disclosure.

[0035] Any specific numerical value disclosed herein (including the endpoints of the numerical range) is/are not limited to the exact value of the numerical value, but should be understood to further cover the values close to the exact value, for example all possible values within the range between $\pm 5\%$ of the exact value. Moreover, for the disclosed numerical ranges, one or more new numerical ranges, that are obtained by arbitrarily combining the endpoint values of the disclosed numerical ranges, or arbitrarily combining the endpoint values of the disclosed numerical ranges with the specific point values in the disclosed numerical ranges, or arbitrarily combining the specific point values in the disclosed numerical ranges, should also be deemed to be specifically disclosed herein.

[0036] Unless otherwise indicated, the terms used herein have the same meaning as commonly understood by those skilled in the art. If a term is defined herein and its definition is different from the common understanding in the art, the definition herein shall prevail.

[0037] In the present application, except for what is explicitly indicated, any item or matter not mentioned is directly

applicable to those known in the art without any changes. Moreover, any of the embodiments described herein can be freely combined with one or more other embodiments described herein, and the resulting technical solutions or technical ideas are regarded as part of the original disclosure or the original record of the present disclosure, and should not be regarded as new content that has not been disclosed or anticipated in this specification, unless those skilled in the art believe that the combination is obviously unreasonable.

[0038] The disclosure provides a process for producing lower carbon olefins and light aromatics by catalytic pyrolysis of a hydrocarbon-containing feedstock oil, wherein the process comprises the steps of:

51, cutting the hydrocarbon-containing feedstock oil into a light distillate oil and a heavy distillate oil, wherein the weight ratio of the light distillate oil to the heavy distillate oil (light distillate oil/heavy distillate oil) is X;

S2, introducing the light distillate oil and a first catalyst into a first down-flow reactor to perform a first catalytic pyrolysis to produce a stream after the first catalytic pyrolysis; optionally S2', introducing the stream after the first catalytic pyrolysis into a fluidized bed reactor to perform a second catalytic pyrolysis to produce a stream after the second catalytic pyrolysis;

S3, subjecting the stream after the first catalytic pyrolysis to a gas-solid separation to produce a first reaction hydrocarbon product and a first spent catalyst, or subjecting the stream after the second catalytic pyrolysis to a gas-solid separation to produce a second reaction hydrocarbon product and a second spent catalyst;

S4, introducing a continuous catalyst, the heavy distillate oil and a second catalyst into a second up-flow reactor to perform a third catalytic pyrolysis, and then subjecting to a gas-solid separation to produce a third reaction hydrocarbon product and a third spent catalyst; the continuous catalyst is at least a part of the first spent catalyst or at least a part of the second spent catalyst; the weight ratio of the second catalyst to the continuous catalyst (second catalyst/continuous catalyst) is R;

S5, separating out lower carbon olefins and light aromatics from any of the first reaction hydrocarbon product, the second reaction hydrocarbon product and the third reaction hydrocarbon product or a mixture of the first reaction hydrocarbon product and the third reaction hydrocarbon product or a mixture of the second reaction hydrocarbon product and the third reaction hydrocarbon product, and separating out a light olefin fraction, and returning the light olefin fraction to the second up-flow reactor of step S4 or the fluidized bed reactor of step S2',

wherein R and X satisfy the following relation:

$$(4.84 \times T_0 - 3340) / (780 + 5 \times T_0 - 6 \times T_3) < R/X < (0.968 \times T_0 - 630) / (668 + 0.2 \times T_0 - 1.2 \times T_3)$$

T₀ is the temperature (unit: °C) when the second catalyst enters step S4, and T₃ is the outlet temperature (unit: °C) of the second up-flow reactor.

[0039] In the present disclosure, sometimes any of the first reaction hydrocarbon product, the second reaction hydrocarbon product and the third reaction hydrocarbon product or a mixture of two or more thereof is simply referred to as the reaction hydrocarbon product.

[0040] In the present disclosure, lower carbon olefins refer to ethylene, propylene, butene and isomers thereof. Light aromatics refer to BTX, i.e., benzene, toluene and xylene. In the present disclosure, lower carbon olefins can be obtained from the separation of dry gas, C₃ fraction and C₄ fraction; light aromatics can be obtained from the separation of the light gasoline and the heavy gasoline.

[0041] In this disclosure, the C₃ fraction refers to the hydrocarbons having 3 carbon atoms in the reaction hydrocarbon product, including propane and propylene; the C₄ fraction refers to the hydrocarbons having 4 carbon atoms in the reaction hydrocarbon product, including butane, butene and isomers thereof; light gasoline refers to all fractions or partial fractions having a distillation range within the range of 30-90°C, wherein the "partial fractions" refers to those fractions having a distillation range within a part of the range of 30-90°C (for example, the fractions having a distillation range within the range of 30-60°C or 40-60°C or 60-90°C or the like); heavy gasoline refers to the fractions having a distillation range within the range of 30-200°C except for light gasoline.

[0042] In the present disclosure, the light distillate oil and the heavy distillate oil are defined as follows: the hydrocarbon-containing feedstock oil is cut at a certain cutting temperature, and the obtained light fraction is referred to as the light distillate oil, and the rest is referred to as the heavy distillate oil. Those skilled in the art can cut the hydrocarbon-containing feedstock oil according to methods known in the art (including but not limited to fractionation, distillation, etc.) as required, as long as the weight ratio of the light distillate oil to the heavy distillate oil (light distillate oil/heavy distillate oil) is X, and the X value can satisfy the following relation of the present disclosure. In an embodiment of the present disclosure, X is in the range between any two numerical values selected from 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 2.0, 3.0, 4.0, 5.0, 6.0, 7.0, 8.0, 9.0, and 10.0. In an embodiment of the present disclosure, X is 0.1-2.0, preferably 0.12-1.0, further preferably 0.15-0.6.

[0043] In an embodiment of the present disclosure, in step S1, the hydrocarbon-containing feedstock oil is cut into the light distillate oil and the heavy distillate oil at the cut point of any temperature between 100-400°C, so that the weight ratio of the light distillate oil to the heavy distillate oil (light distillate oil/heavy distillate oil) is X. In an embodiment of the present disclosure, the cut point is for example 150°C, 160°C, 170°C, 180°C, 190°C, 200°C, 210°C, 220°C, 230°C, 240°C, 250°C, 260°C, 270°C, 280°C, 290°C, 300°C, 310°C, 320°C, 330°C, 340°C, 350°C, 360°C, 370°C, 380°C, 390°C, 400°C.

[0044] In the present disclosure, the hydrocarbon-containing feedstock oil may be various feedstock oils known in the art (in the present invention, the hydrocarbon-containing feedstock oil is sometimes simply referred to as feedstock oil), for example, it may be one of or a mixture of two or more of crude oil, coal liquefaction oil, synthetic oil, tar sand oil, shale oil, tight oil and animal and vegetable oil and fat, or their respective partial fractions, or hydro-upgraded oils of their respective heavy fractions. In an embodiment of the present disclosure, the hydrocarbon-containing feedstock oil is preferably crude oil, a partial fraction of crude oil, or a hydro-upgraded oil of heavy oil derived from crude oil. Those skilled in the art know that "partial fractions" can be obtained by subjecting the feedstock oil to conventional treatments in the art, including but not limited to atmospheric distillation, vacuum distillation, and the like. Those skilled in the art can determine the manner of this conventional treatment as required. In an embodiment of the present disclosure, crude oil can be used as the hydrocarbon-containing feedstock oil of the present disclosure, or crude oil can also be subjected to atmospheric distillation or vacuum distillation as required, and the residual fraction (the partial fraction of crude oil) after extracting a part of fractions can be used as the hydrocarbon-containing feedstock oil of the present disclosure, or a product obtained by hydro-upgrading heavy oil derived from crude oil (hydro-upgraded oil of heavy oil) as required is used as the hydrocarbon-containing feedstock oil of the present disclosure. It is known in the art that hydro-upgrading includes but is not limited to hydrodesulfurization, hydrodenitrogenation, hydrodemetallization, hydrosaturation and other treatments.

[0045] In an embodiment of the present disclosure, the process includes step S0 before step S1 wherein the hydrocarbon-containing feedstock oil is subjected to the desalination and dehydration treatment, the resulting dehydrated and desalinized hydrocarbon-containing feedstock oil is introduced into step S1 for cutting.

[0046] According to the present disclosure, in step S2, in the first down-flow reactor, the conditions of the first catalytic pyrolysis comprise: the outlet temperature of the first down-flow reactor is 610-720°C, preferably 650-690°C. The conditions for the first catalytic pyrolysis further comprise: the gas-solid residence time is 0.1-3.0 seconds, preferably 0.5-1.5 seconds. In the first down-flow reactor, the catalyst-oil ratio of the catalyst to the light distillate oil can be a catalyst-oil ratio commonly used in the catalytic pyrolysis (based on the weight ratio of catalyst/light distillate oil), for example, it can be 15-80, preferably 25-65.

[0047] In the present disclosure, there is no limitation on the manner in which the light distillate oil and the first catalyst are introduced into the first down-flow reactor, as long as the light distillate oil and the first catalyst are introduced at the upper end of the first down-flow reactor. Preferably, the light distillate oil and the first catalyst are respectively introduced from different feed inlets of the first down-flow reactor.

[0048] In the present disclosure, there is no limitation on the first catalyst, and it may be a catalyst that is known in the art and can be used for the catalytic pyrolysis of crude oil. For example, the first catalyst can comprise an active component and a support, and the active component is at least one of ultra-stabilized Y zeolite optionally containing rare earth, ZSM-5 zeolite, pentasil silica-rich zeolite and beta zeolite. Said support is at least one of alumina, silica, amorphous silica alumina, zirconia, titania, boron oxide and alkali-earth oxide.

[0049] In an embodiment of the present disclosure, there is no particular limitation on the structure of the first down-flow reactor, as long as it can realize feeding from the upper part and discharging from the lower part, for example, it can be an iso-diameter or diameter-changing down-flow tubular reactor.

[0050] In the present disclosure, since no additional heat source is used in the first down-flow reactor, the outlet temperature of the first down-flow reactor reflects the reaction temperature in the reactor. In the present disclosure, the degree of the catalytic pyrolysis of the light distillate oil in the first down-flow reactor can be adjusted by changing the temperature of the first catalyst, the gas-solid residence time in the reactor, the outlet temperature of the first down-flow reactor, and the like.

[0051] In an embodiment of the present disclosure, the first catalyst is a fresh catalyst. In an embodiment of the present disclosure, the first catalyst comprises a regenerated catalyst from the regenerator. Preferably, the first catalyst is a regenerated catalyst from the regenerator.

[0052] In the present disclosure, there is no particular limitation on the temperature of the first catalyst entering the down-flow reactor, as long as when the first catalyst contacts the light distillate oil, the catalytic pyrolysis can occur, and the temperature satisfies the conditions of the above-mentioned first catalytic pyrolysis of the present disclosure. When the regenerated catalyst is used as the first catalyst, the first catalyst is directly fed from the regenerator through first catalyst (regenerated catalyst) delivery pipe. Since the delivery pipe between the regenerator and the first down-flow reactor is short, therefore, the temperature of the first catalyst can be regarded as the temperature of the regenerator, or the temperature when the regenerated catalyst leaves the regenerator (the outlet temperature of the regenerator). In

an embodiment of the present disclosure, the temperature of the first catalyst entering the down-flow reactor is the temperature of the regenerator, or the temperature when the regenerated catalyst leaves the regenerator (the outlet temperature of the regenerator), usually 690-750°C, preferably 700-740°C, further preferably 705-730°C, further more preferably 710-725°C. In addition, at this time, as required, the catalyst from the regenerator may be fed into the first down-flow reactor after being further heated or cooled. In the process of the present disclosure, at the start-up, the fresh catalyst can be heated to the desired temperature, and then introduced into the first down-flow reactor; thereafter, the regenerated catalyst from the regenerator can be used directly. In an embodiment of the present disclosure, it is preferred that the first catalyst directly comes from the regenerator without further heating or cooling it.

[0053] In the present disclosure, in case that the light distillate oil is introduced into the first down-flow reactor, the light fraction oil may also be preheated at first as required. The temperature of the preheated light distillate oil is, for example, 30-100°C. In addition, the light distillate oil can also be atomized with water vapor at first, and then the light distillate oil is introduced into the first down-flow reactor by using water vapor as carrier. In the present disclosure, the stream after the first catalytic pyrolysis includes the first reaction hydrocarbon product obtained by catalytic pyrolysis of the light distillate oil and the first spent catalyst after the coking (carbonization) of the first catalyst. The first spent catalyst still has a relatively high activity, and coke deposits are loaded on the catalyst. When it is introduced as the continuous catalyst into the subsequent second up-flow reactor, it helps the catalytic pyrolysis of the heavy distillate oil, improves the yield of lower carbon olefins and inhibits the generation of dry gas and coke.

[0054] In the present disclosure, in step S3, the stream after the first catalytic pyrolysis is subjected to a gas-solid separation to produce a first reaction hydrocarbon product and a first spent catalyst. There is no particular limitation on the manner of the gas solid separation, and the manners well known in the art can be used, for example using a settler or a cyclone separator to realize the separation of the catalyst from the first reaction hydrocarbon product.

[0055] In an embodiment of the present disclosure, the first reaction hydrocarbon product is separated to produce dry gas, C3 fraction, C4 fraction, light gasoline, heavy gasoline, diesel and slurry oil, from which lower carbon olefins and light aromatics are produced by separation, and the light olefin fraction is separated out. Among others, the C4 fraction and/or the light gasoline is the light olefin fraction. In an embodiment of the present disclosure, the first reaction hydrocarbon product is introduced into a fractionation device or a gas separation device for fractionation, so as to realize the above-mentioned separation. In an embodiment of the present disclosure, the light olefin fraction is introduced into the second up-flow reactor in the under-mentioned step S4.

[0056] In an embodiment of the present disclosure, at least a portion of the first spent catalyst is introduced as the continuous catalyst into the under-mentioned second up-flow reactor. In an embodiment of the present disclosure, the first spent catalyst that does not enter the under-mentioned second up-flow reactor is introduced into the regeneration step, in which the regeneration of the catalyst is performed. Preferably, all of the first spent catalyst is introduced as the continuous catalyst into the under-mentioned second up-flow reactor, where the amount of the first spent catalyst as the continuous catalyst substantially corresponds to the amount of the first catalyst.

[0057] In an embodiment of the present disclosure, the stream after the first catalytic pyrolysis is subjected to a gas-solid separation, and the separated catalyst is further stripped to remove the hydrocarbon products adsorbed therein to obtain the first spent catalyst.

[0058] In an embodiment of the present disclosure, step S2' may also be included after step S2 and before step S3, wherein the stream after the first catalytic pyrolysis is introduced into a fluidized bed reactor to perform the second catalytic pyrolysis to produce the stream after the second catalytic pyrolysis, thus, the light olefin fraction can be further converted, and the production of lower carbon olefins can be maximized.

[0059] In this disclosure, the "fluidized bed reactor" is also referred to as the "fluidizing reactor", and has a catalyst density of 150-450 kg/m³.

[0060] According to the present disclosure, in step S2', in the fluidized bed reactor, the conditions of the second catalytic pyrolysis comprise: the reaction temperature in the fluidized bed reactor is 600-690°C, preferably 640-670°C. The conditions of the second catalytic pyrolysis further comprise: the weight hourly space velocity is 2-20 h⁻¹, preferably 4-12 h⁻¹.

[0061] According to an embodiment of the present disclosure, instead of introducing a new catalyst into the fluidized bed, the stream after the first catalytic pyrolysis can be directly introduced to perform the catalytic pyrolysis. According to an embodiment of the present disclosure, no additional heat source is applied to the fluidized bed, but the heat of the stream after the first catalytic pyrolysis can be used directly. The introduced stream after the first catalytic pyrolysis includes the first reaction hydrocarbon product obtained by catalytic pyrolysis of the light distillate oil and the first spent catalyst after the coking (carbonization) of the first catalyst. The first spent catalyst still has a relatively high activity, and can continue to deepen the degree of the catalytic pyrolysis in the fluidized bed reactor to further convert the light olefin fraction into lower carbon olefins.

[0062] According to an embodiment of the present disclosure, the light olefin fraction is separated out from the reaction hydrocarbon product of the present disclosure, and the light olefin fraction is returned to the fluidized bed reactor to further convert it into lower carbon olefins. More specifically, the reaction hydrocarbon product is separated to produce

dry gas, C3 fraction, C4 fraction, light gasoline, heavy gasoline, diesel and slurry oil, from which lower carbon olefins and light aromatics are produced by separation, and the light olefin fraction is separated out. Among others, the C4 fraction and/or the light gasoline is the light olefin fraction. In an embodiment of the present disclosure, the reaction hydrocarbon product is introduced into a fractionation device or a gas separation device, so as to realize the above-mentioned separation.

[0063] In the present disclosure, the stream after the second catalytic pyrolysis contains a second reaction hydrocarbon product and a second spent catalyst. The second spent catalyst still has a relatively high activity, and coke deposits are loaded on the catalyst. When it is introduced as the continuous catalyst into the subsequent second up-flow reactor, it helps the catalytic pyrolysis of the heavy distillate oil, improves the yield of lower carbon olefins and inhibits the generation of dry gas and coke.

[0064] In the present disclosure, in step S3, the stream after the second catalytic pyrolysis is subjected to the gas-solid separation to produce a second reaction hydrocarbon product and a second spent catalyst. There is no particular limitation on the manner of the gas solid separation, and the manners well known in the art can be used, for example using a settler or a cyclone separator to realize the separation of the catalyst from the second reaction hydrocarbon product.

[0065] In an embodiment of the present disclosure, the second reaction hydrocarbon product is separated to produce dry gas, C3 fraction, C4 fraction, light gasoline, heavy gasoline, diesel and slurry oil, from which lower carbon olefins and light aromatics are produced by separation, and the light olefin fraction is separated out. Among others, the C4 fraction and/or the light gasoline is the light olefin fraction. In an embodiment of the present disclosure, the second reaction hydrocarbon product is introduced into a fractionation device or a gas separation device, so as to realize the above-mentioned separation.

[0066] In an embodiment of the present disclosure, the stream after the second catalytic pyrolysis is subjected to a gas-solid separation, and the separated catalyst is further stripped to remove the hydrocarbon products adsorbed therein to obtain the second spent catalyst. In the present disclosure, at least a part of the second spent catalyst is introduced as the continuous catalyst into the under-mentioned second up-flow reactor.

[0067] In an embodiment of the present disclosure, the second spent catalyst that does not enter the under-mentioned second up-flow reactor is introduced into the regeneration step, in which the regeneration of the catalyst is performed. Preferably, all of the second spent catalyst is introduced as the continuous catalyst into the under-mentioned second up-flow reactor, where the amount of the second spent catalyst as the continuous catalyst substantially corresponds to the amount of the first catalyst.

[0068] In the present disclosure, in step S4, a continuous catalyst, the heavy distillate oil and a second catalyst are introduced into a second up-flow reactor to perform a third catalytic pyrolysis, and then subjected to a gas-solid separation to produce a third reaction hydrocarbon product and a third spent catalyst; the continuous catalyst is at least a part of the first spent catalyst or at least a part of the second spent catalyst.

[0069] In an embodiment of the present disclosure, in the second up-flow reactor, the conditions of the third catalytic pyrolysis comprise: the outlet temperature T3 of the second up-flow reactor is 530-650°C, preferably 560-640°C, further preferably 580-630°C, further more preferably 600-630°C. The conditions for the third catalytic pyrolysis further comprise: the gas-solid residence time is 0.5-8 seconds, preferably 1.5-5 seconds. In the second up-flow reactor, the catalyst-oil ratio of the catalyst to the heavy distillate oil can be a catalyst-oil ratio commonly used in the catalytic pyrolysis (based on the weight ratio of catalyst/heavy distillate oil), for example, it can be 8-40, preferably 10-30.

[0070] In an embodiment of the present disclosure, in step S4, the continuous catalyst and the second catalyst are firstly mixed, and then the subsequent catalytic pyrolysis reaction is performed. More specifically, in an embodiment of the present disclosure, the continuous catalyst and the second catalyst are each independently fed to the bottom of the second up-flow reactor and mixed, and the mixed catalyst (hereinafter, sometimes also referred to as the catalyst mixture or the mixed catalyst) is used for the catalytic pyrolysis reaction in the second up-flow reactor. In an embodiment of the present disclosure, the continuous catalyst and the second catalyst are mixed in the bottom area of the second up-flow reactor, and the mixed catalyst is lifted in the second up-flow reactor with a pre-lift medium to perform the downstream catalytic pyrolysis reaction. In an embodiment of the present disclosure, the pre-lift medium may be dry gas, water vapor, or a mixture thereof. In an embodiment of the present disclosure, in step S4, the second catalyst is not limited, and it can be a catalyst that is known in the art and can be used for the catalytic pyrolysis of crude oil. For example, the second catalyst comprises an active component and a support, and the active component is at least one of ultrastabilized Y zeolite optionally containing rare earth, ZSM-5 zeolite, pentasil silica-rich zeolite and beta zeolite. Said support is at least one of alumina, silica, amorphous silica alumina, zirconia, titania, boron oxide and alkali-earth oxide.

[0071] In an embodiment of the present disclosure, there is no particular limitation on the structure of the second up-flow reactor, as long as it can realize feeding from the bottom and discharging from the upper part, for example, it can be an iso-diameter or diameter-changing riser reactor, or a composite reactor of the iso-diameter or diameter-changing riser reactor and the fluidized bed.

[0072] In an embodiment of the present disclosure, the second catalyst is a fresh catalyst. In an embodiment of the

present disclosure, the second catalyst comprises a regenerated catalyst from the regenerator. In an embodiment of the present disclosure, the second catalyst is a regenerated catalyst from the regenerator. When a fresh catalyst is used as the second catalyst, the catalyst needs to be preheated so that when the fresh catalyst enters step S4, its temperature satisfies the relation of the present disclosure. Preferably, the second catalyst is a regenerated catalyst from the regenerator.

[0073] In the present disclosure, the weight ratio of the second catalyst to the continuous catalyst is R, and said R and X satisfy the following relation:

$$(4.84 \times T_0 - 3340) / (780 + 5 \times T_0 - 6 \times T_3) < R/X < (0.968 \times T_0 - 630) / (668 + 0.2 \times T_0 - 1.2 \times T_3)$$

T₀ is the temperature (unit: °C) when the second catalyst enters step S4, and T₃ is the outlet temperature (unit: °C) of the second up-flow reactor.

[0074] The inventors of the present disclosure surprisingly found that by allowing the cutting proportion of the light distillate oil and the heavy distillate oil of the hydrocarbon-containing feedstock oil in step S1 (the weight ratio of the light distillate oil/the heavy distillate oil) and the weight ratio of the second catalyst to the continuous catalyst to satisfy the above-mentioned relation, the components of the hydrocarbon-containing feedstock oil, the cutting proportion, and the activity of the catalysts (especially the activity of the catalyst in the second up-flow reactor) can be better matched, so that the yields of dry gas and coke can be significantly reduced while maximizing the production of light olefins and BTX. Without wishing to be bound by any theory, the inventors of the present disclosure speculate that the catalyst as the continuous catalyst is from either the first spent catalyst or the second spent catalyst; due to the low coke formation in the first down-flow reactor and in the fluidized bed reactor, the first spent catalyst and the second spent catalyst have relatively high catalytic activities and meanwhile are loaded with a certain amount of coke deposits; this kind of the catalyst is mixed at a certain proportion with a second catalyst (a fresh catalyst or a regenerated catalyst from the regenerator), and the mixing proportion and the cutting proportion of the hydrocarbon-containing feedstock oil are matched to satisfy the above-mentioned relation of the present disclosure; the resulting catalyst mixture can maintain an excellent catalytic activity, and meanwhile the excessive coking caused by the too high catalyst activity will neither be incurred, nor the insufficient catalytic cracking of the heavy distillate oil caused by the too low catalyst activity will be incurred. In the present disclosure, the proportion for cutting the hydrocarbon-containing feedstock oil into the light distillate oil and the heavy distillate oil and the mixing proportion of the continuous catalyst and the second catalyst satisfy a specific relation, and the activity of the mixed catalyst in the second up-flow reactor can be adjusted according to the composition of the hydrocarbon-containing feedstock oil, the cutting proportion and the like so as to maximize the yields of lower carbon olefins and BTX from the heavy distillate oil.

[0075] In an embodiment of the present disclosure, $(4.84 \times T_0 - 3340) / (780 + 5 \times T_0 - 6 \times T_3)$ is greater than 0. In the present disclosure, T₀ is greater than T₃.

[0076] In the present disclosure, T₀ is the temperature when the second catalyst enters step S4. Specifically, it refers to the temperature when the second catalyst (the fresh catalyst or the regenerated catalyst) enters the second up-flow reactor, i.e., the temperature when it reaches the bottom of the second up-flow reactor before it is mixed with the continuous catalyst. When the regenerated catalyst is used as the second catalyst, since the delivery pipe between the regenerator and the second up-flow reactor is short, therefore, the temperature of the regenerator or the catalyst temperature when the regenerated catalyst leaves the regenerator (the outlet temperature of the regenerator) can be regarded as the temperature when the second catalyst enters step S4.

[0077] In an embodiment of the present disclosure, the outlet temperature T₃ of the second up-flow reactor is 530-650°C, preferably 560-640°C, further preferably 580-630°C, further more preferably 600-630°C; and/or, the temperature T₀ when the second catalyst enters step S4 is 690-750°C, preferably 700-740°C, further preferably 705-730°C, further more preferably 710-725°C.

[0078] In an embodiment of the present disclosure, the third reaction hydrocarbon product is separated to produce dry gas, C3 fraction, C4 fraction, light gasoline, heavy gasoline, diesel and slurry oil, from which lower carbon olefins and light aromatics are produced by separation, and the light olefin fraction is separated out. Among others, the C4 fraction and/or the light gasoline is the light olefin fraction. In an embodiment of the present disclosure, the third reaction hydrocarbon product is introduced into a fractionation device or a gas separation device, so as to realize the above-mentioned separation.

[0079] In the present disclosure, in absence of step S2', in step S5, lower carbon olefins and light aromatics are separated from any of the first reaction hydrocarbon product and the third reaction hydrocarbon product or a mixture of two, and the separated light olefin fraction is returned to the second up-flow reactor.

[0080] In the present disclosure, in presence of step S2', in step S5, lower carbon olefins and light aromatics are separated from any of the second reaction hydrocarbon product and the third reaction hydrocarbon product or a mixture of two, and the separated light olefin fraction is returned to the fluidized bed reactor.

[0081] In an embodiment of the present disclosure, in step S4, the light olefin fraction obtained from the under-mentioned step S5 contacts the catalyst mixture earlier than the heavy distillate oil to perform the catalytic pyrolysis reaction, and then the heavy distillate oil contacts the catalyst mixture to perform the catalytic pyrolysis reaction. Preferably, the light olefin fraction contacts the catalyst mixture 0.3-1.0 seconds earlier than the heavy distillate oil. More preferably, the light olefin fraction contacts the catalyst mixture 0.4-0.8 seconds earlier than the heavy distillate oil.

[0082] In an embodiment of the present disclosure, the product of the third catalytic pyrolysis is subjected to a gas-solid separation to produce a third reaction hydrocarbon product and a third spent catalyst. There is no particular limitation on the manner of the gas solid separation, and the manners well known in the art can be used, for example using a settler or a cyclone separator to realize the separation of the catalyst from the third reaction hydrocarbon product.

[0083] In an embodiment of the present disclosure, the stream after the third catalytic pyrolysis is subjected to a gas-solid separation, and the separated catalyst is further stripped to remove the hydrocarbon products adsorbed therein to obtain the third spent catalyst. In an embodiment of the present disclosure, the third spent catalyst is sent to the regenerator to perform the regeneration of the catalyst.

[0084] In an embodiment of the present disclosure, the temperature of the regenerator is a temperature commonly used in the art, and it may be 690-750°C, preferably 700-740°C, further preferably 705-730°C, and further more preferably 710-725°C. In an embodiment of the present disclosure, the temperature of the regenerator or the catalyst temperature when the regenerated catalyst leaves the regenerator (the outlet temperature of the regenerator) can be regarded as the temperature when the second catalyst enters step S4. Therefore, in an embodiment of the present disclosure, the temperature T0 when the second catalyst come to step S4 can be 690-750°C, preferably 700-740°C, further preferably 705-730°C, further more preferably 710-725°C.

[0085] In an embodiment of the present disclosure, the regenerated catalyst is used as the first catalyst and the second catalyst.

[0086] In the present disclosure, in step S5, lower carbon olefins and light aromatics are separated from any of the first reaction hydrocarbon product, the second reaction hydrocarbon product and the third reaction hydrocarbon product or a mixture of the first reaction hydrocarbon product and the third reaction hydrocarbon product or a mixture of the second reaction hydrocarbon product and the third reaction hydrocarbon product, and the light olefin fraction is separated out, and the light olefin fraction is returned to the second up-flow reactor of step S4 or the fluidized bed reactor of step S2'. More specifically, the reaction hydrocarbon product is separated to produce dry gas, C3 fraction, C4 fraction, light gasoline, heavy gasoline, diesel and slurry oil, from which lower carbon olefins and light aromatics are produced by separation, and the light olefin fraction is separated out. Among others, the C4 fraction and/or the light gasoline is the light olefin fraction. Preferably, the reaction hydrocarbon product is introduced into a fractionation device or a gas separation device, so as to realize the above-mentioned separation. In step S5, the first reaction hydrocarbon product and the third reaction hydrocarbon product can be separated separately, or both can be combined and then separated together; or the second reaction hydrocarbon product and the third reaction hydrocarbon product can be separated separately, or both can be combined and then separated together.

[0087] In an embodiment of the present disclosure, the process for separating the light olefin fraction from the reaction hydrocarbon product is not limited, and the separation can be carried out in a manner known in the art, including but not limited to the following method, the reaction hydrocarbon product is sent to the fractionation, absorption and stabilization units to separate out the liquefied gas and the stabilized gasoline, the liquefied gas is sent to the subsequent gas separation device to separate out the C3 fraction and the C4 fraction, and the stabilized gasoline is sent to the light and heavy gasoline splitting column to separate out the light gasoline and the heavy gasoline. The C4 fraction and/or the light gasoline is the light olefin fraction. Lower carbon olefins and light aromatics can be separated therefrom.

[0088] In more detail, in an embodiment of the present disclosure, it provides a process for producing lower carbon olefins and light aromatics by catalytic pyrolysis of hydrocarbon-containing feedstock oil, wherein the process comprises the steps of:

S1, cutting the hydrocarbon-containing feedstock oil into a light distillate oil and a heavy distillate oil, wherein the weight ratio of the light distillate oil to the heavy distillate oil (light distillate oil/heavy distillate oil) is X;

S2, introducing the light distillate oil and a first catalyst into a first down-flow reactor to perform a first catalytic pyrolysis to produce a stream after the first catalytic pyrolysis; S3, subjecting the stream after the first catalytic pyrolysis to a gas-solid separation to produce a first reaction hydrocarbon product and a first spent catalyst;

S4, introducing a continuous catalyst, the heavy distillate oil and a second catalyst into a second up-flow reactor to perform a third catalytic pyrolysis, and then subjecting to a gas-solid separation to produce a third reaction hydrocarbon product and a third spent catalyst; the continuous catalyst is at least a part of the first spent catalyst; the weight ratio of the second catalyst to the continuous catalyst (second catalyst/continuous catalyst) is R;

S5, separating out lower carbon olefins and light aromatics from any of the first reaction hydrocarbon product and the third reaction hydrocarbon product or a mixture of two, and separating out a light olefin fraction, and returning the light olefin fraction to the second up-flow reactor of step S4,

wherein R and X satisfy the following relation:

$$(4.84 \times T_0 - 3340) / (780 + 5 \times T_0 - 6 \times T_3) < R/X < (0.968 \times T_0 - 630) / (668 + 0.2 \times T_0 - 1.2 \times T_3)$$

T₀ is the temperature (unit: °C) when the second catalyst enters step S4, and T₃ is the outlet temperature (unit: °C) of the second up-flow reactor.

[0089] In more detail, in an embodiment of the present disclosure, it provides a process for producing lower carbon olefins and light aromatics by catalytic pyrolysis of hydrocarbon-containing feedstock oil, wherein the process comprises the steps of:

S1, cutting the hydrocarbon-containing feedstock oil into a light distillate oil and a heavy distillate oil, wherein the weight ratio of the light distillate oil to the heavy distillate oil (light distillate oil/heavy distillate oil) is X;
 S2, introducing the light distillate oil and a first catalyst into a first down-flow reactor to perform a first catalytic pyrolysis to produce a stream after the first catalytic pyrolysis;
 S2', introducing the stream after the first catalytic pyrolysis into a fluidized bed reactor to perform a second catalytic pyrolysis to produce a stream after the second catalytic pyrolysis;
 S3, subjecting the stream after the second catalytic pyrolysis to a gas-solid separation to produce a second reaction hydrocarbon product and a second spent catalyst;
 S4, introducing a continuous catalyst, the heavy distillate oil and a second catalyst into a second up-flow reactor to perform a third catalytic pyrolysis, and then subjecting to a gas-solid separation to produce a third reaction hydrocarbon product and a third spent catalyst; the continuous catalyst is at least a part of the second spent catalyst; the weight ratio of the second catalyst to the continuous catalyst (second catalyst/continuous catalyst) is R;
 S5, separating out lower carbon olefins and light aromatics from any of the second reaction hydrocarbon product and the third reaction hydrocarbon product or a mixture of two, and separating out a light olefin fraction, and returning the light olefin fraction to the fluidized bed reactor of step S2',
 wherein R and X satisfy the following relation:

$$(4.84 \times T_0 - 3340) / (780 + 5 \times T_0 - 6 \times T_3) < R/X < (0.968 \times T_0 - 630) / (668 + 0.2 \times T_0 - 1.2 \times T_3)$$

T₀ is the temperature (unit: °C) when the second catalyst enters step S4, and T₃ is the outlet temperature (unit: °C) of the second up-flow reactor.

[0090] In an embodiment of the present disclosure, the light olefin fraction is the C₄ fraction and/or the light gasoline in the reaction hydrocarbon product.

[0091] The present disclosure further provides the following technical solutions:

A1. A process for producing lower carbon olefins and light aromatics by catalytic cracking of a hydrocarbon-containing feedstock oil, wherein the process comprises the steps of:

S1, cutting a desalinized and dehydrated hydrocarbon-containing feedstock oil into a light distillate oil and a heavy distillate oil; wherein the cut point for said cutting is any temperature between 100-400 °C;
 S2, introducing the light distillate oil and a first catalyst into a first down-flow reactor to perform a first catalytic pyrolysis to produce a stream after the first catalytic pyrolysis; Optionally S2', introducing the stream after the first catalytic pyrolysis into a fluidized bed reactor to perform a second catalytic pyrolysis to produce a stream after the second catalytic pyrolysis;
 S3, subjecting the stream after the first catalytic pyrolysis to a gas-solid separation to produce a first reaction hydrocarbon product and a first spent catalyst, or subjecting the stream after the second catalytic pyrolysis to a gas-solid separation to produce a second reaction hydrocarbon product and a second spent catalyst;
 S4, introducing a continuous catalyst, the heavy distillate oil and a second catalyst into a second up-flow reactor to perform a third catalytic pyrolysis, and then subjecting to a gas-solid separation to produce a third reaction hydrocarbon product and a third spent catalyst; the continuous catalyst is the first spent catalyst or the second spent catalyst; the weight ratio of the second catalyst to the continuous catalyst is 0.2-5: 1;
 S5, separating out a light olefin fraction from the first reaction hydrocarbon product and the second reaction hydrocarbon product, and returning the light olefin fraction to the fluidized bed reactor or the second up-flow reactor.

A2, The process according to A1, wherein in step S1, the cut point for said cutting is any temperature between 200-380°C.

A3, The process according to A1, wherein in step S4, the weight ratio of the second catalyst to the continuous catalyst is 0.5-3:1.

A4, The process according to A1, wherein

in the first down-flow reactor, the conditions of said first catalytic cracking comprise: the outlet temperature of the first down-flow reactor is 610-720°C, the gas-solid residence time is 0.1-3.0 seconds;

in the fluidized bed reactor, the conditions of said second catalytic cracking comprise: the reaction temperature in the fluidized bed reactor is 600-670°C, the weight hourly space velocity is 2-20 h⁻¹;

in the second up-flow reactor, the conditions of said third catalytic cracking comprise: the outlet temperature of the second up-flow reactor is 530-650°C, the gas-solid residence time is 0.5-8 seconds.

A5, The process according to A4, wherein

in the first down-flow reactor, the conditions of said first catalytic cracking comprise: the outlet temperature of the first down-flow reactor is 650-690°C, the gas-solid residence time is 0.5-1.5 seconds;

In the fluidized bed reactor, the conditions of said second catalytic cracking comprise: the reaction temperature in the fluidized bed reactor is 620-640°C, the weight hourly space velocity is 4-12 h⁻¹;

In the second up-flow reactor, the conditions of said third catalytic cracking comprise: the outlet temperature of the second up-flow reactor is 560-640°C, the gas-solid residence time is 1.5-5 seconds.

A6, The process according to A1, wherein

the light olefin fraction contacts the second catalyst 0.3-1.0 seconds earlier than the heavy distillate oil to perform the catalytic pyrolysis; preferably the light olefin fraction contacts the second catalyst 0.4-0.8 seconds earlier than the heavy distillate oil to perform the catalytic pyrolysis.

A7, The process according to A1, wherein the process further comprises:

the third spent catalyst is subjected to coke-burning and regeneration to produce a regenerated catalyst;

said first hydrocarbon product and said second hydrocarbon product are separated to produce dry gas, C3 fraction, C4 fraction, light gasoline, heavy gasoline, diesel and slurry oil;

the light olefin fraction is the C4 fraction in said first hydrocarbon product and said second hydrocarbon product and/or the fraction in the range of 30-90°C in said first hydrocarbon product and said second hydrocarbon product.

A8, The process according to A1, wherein the hydrocarbon-containing feedstock oil is one of or a mixture of two or more of conventional mineral oil, coal liquefaction oil, synthetic oil, tar sand oil, shale oil, tight oil and animal and vegetable oil and fat.

A9, The process according to A1, wherein the first catalyst and the second catalyst each independently comprise an active component and a support, the active component is at least one of ultra-stabilized Y zeolite optionally containing rare earth, ZSP zeolite, pentasil silica-rich zeolite and beta zeolite.

A10, The process according to A1, wherein the first catalyst and the second catalyst each independently comprise a regenerated catalyst.

[0092] The present disclosure also provides an apparatus for producing lower carbon olefins and light aromatics by the catalytic pyrolysis of a hydrocarbon-containing feedstock oil, wherein the apparatus comprises the following units:

a hydrocarbon-containing feedstock oil-cutting unit, wherein the hydrocarbon-containing feedstock oil is cut into a light distillate oil and a heavy distillate oil, so that the weight ratio of the light distillate oil to the heavy distillate oil (light distillate oil/heavy distillate oil) is X,

a first down-flow reaction unit, wherein the light distillate oil and a first catalyst are introduced to the upper part of the reaction unit to perform the first catalytic pyrolysis, and a stream after the first catalytic pyrolysis is obtained from the lower part of the reaction unit;

an optional fluidized-bed reaction unit, wherein the stream after the first catalytic pyrolysis is introduced to perform the second catalytic pyrolysis to produce a stream after the second catalytic pyrolysis;

a first gas solid separation unit, wherein the stream after the first catalytic pyrolysis is introduced to perform the gas solid separation to produce a first reaction hydrocarbon product and a first spent catalyst, or wherein the stream after the second catalytic pyrolysis is introduced to perform the gas solid separation to produce a second reaction hydrocarbon product and a second spent catalyst;

a second up-flow reaction unit, wherein a continuous catalyst, a second catalyst and the heavy distillate oil are introduced from the lower part of the reaction unit to perform the third catalytic pyrolysis, and a stream after the third catalytic pyrolysis is obtained from the upper part of the reaction unit, the continuous catalyst is at least a part of the first spent catalyst or at least a part of the second spent catalyst, the weight ratio of the second catalyst to the continuous catalyst (second catalyst/continuous catalyst) is R,

a second gas solid separation unit, wherein the stream after the third catalytic pyrolysis is introduced to perform the gas solid separation to produce a third reaction hydrocarbon product and a third spent catalyst;

a separation unit, wherein any of the first reaction hydrocarbon product, the second reaction hydrocarbon product and the third reaction hydrocarbon product or a mixture of the first reaction hydrocarbon product and the third reaction hydrocarbon product or a mixture of the second reaction hydrocarbon product and the third reaction hydrocarbon product is introduced, and lower carbon olefins and light aromatics are separated out, and a light olefin fraction is separated out, and the light olefin fraction is returned to the second up-flow reaction unit or the fluidized-bed reaction unit;

wherein R and X satisfy the following relation:

$$(4.84 \times T_0 - 3340) / (780 + 5 \times T_0 - 6 \times T_3) < R/X < (0.968 \times T_0 - 630) / (668 + 0.2 \times T_0 - 1.2 \times T_3)$$

T₀ is the temperature (unit: °C) when the second catalyst enters the second up-flow reaction unit, and T₃ is the outlet temperature (unit: °C) of the second up-flow reaction unit.

[0093] In the present disclosure, T₀ is the temperature (unit: °C) when the second catalyst enters the second up-flow reaction unit. Specifically, it refers to the temperature when it reaches the bottom of the second up-flow reactor before it is mixed with the continuous catalyst.

[0094] In an embodiment of the present disclosure, the apparatus further comprises a regeneration unit, wherein the third spent catalyst and optionally the first spent catalyst or the second spent catalyst not entering the second up-flow reactor are introduced to perform the coke-burning and regeneration to produce a regenerated catalyst. Preferably, only the third spent catalyst is introduced into the regeneration unit. In an embodiment of the present disclosure, the temperature of the regeneration unit is a temperature commonly used in the art, and it may be 690-750°C, preferably 700-740°C, further preferably 705-730°C, further more preferably 710-725°C.

[0095] In an embodiment of the present disclosure, the outlet temperature T₃ of said second up-flow reaction unit is 530-650°C, preferably 560-640°C, further preferably 580-630°C, further more preferably 600-630°C.

[0096] In an embodiment of the present disclosure, the temperature T₀ when the second catalyst enters the second up-flow reaction unit is 690-750°C, preferably 700-740°C, further preferably 705-730°C, further more preferably 710-725°C.

[0097] In an embodiment of the present disclosure, the apparatus further comprises a dehydration and desalination unit, wherein the hydrocarbon-containing feedstock oil is subjected to the desalination and dehydration treatment, and the resulting dehydrated and desalinized hydrocarbon-containing feedstock oil is introduced to the hydrocarbon-containing feedstock oil-cutting unit to be cut.

[0098] In an embodiment of the present disclosure, there is no particular limitation on the structure of the first down-flow reaction unit, as long as it can realize feeding from the upper part and discharging from the lower part, for example, it can be an iso-diameter or diameter-changing down-flow tubular reactor.

[0099] In an embodiment of the present disclosure, in absence of the fluidized-bed reaction unit, in the separation unit, lower carbon olefins and light aromatics are separated from any of the first reaction hydrocarbon product and the third reaction hydrocarbon product or a mixture of two, and the separated light olefin fraction is returned to said second up-flow reaction unit.

[0100] In the present disclosure, in presence of the fluidized-bed reaction unit, in the separation unit, lower carbon olefins and light aromatics are separated from any of the second reaction hydrocarbon product and the third reaction hydrocarbon product or a mixture of two, and the separated light olefin fraction is returned to the fluidized bed reactor.

[0101] In an embodiment of the present disclosure, the first gas solid separation unit and the second gas solid separation unit include devices well known in the art that can realize the gas-solid separation, for example a settler or a cyclone separator.

[0102] In an embodiment of the present disclosure, the apparatus further comprises at least one stripping unit, which can be arranged in the gas-solid separation unit, wherein the catalyst obtained by the gas-solid separation is stripped to remove the hydrocarbon products adsorbed therein.

[0103] More specifically, in an embodiment of the present disclosure, if the apparatus comprises the fluidized-bed reaction unit, the first gas solid separation unit further comprises a stripping unit, wherein the catalyst obtained from the gas solid separation is subjected to stripping to remove the hydrocarbon products adsorbed therein and produce a

second spent catalyst. In an embodiment of the present disclosure, the second gas solid separation unit further comprises a stripping unit, wherein the catalyst obtained from the gas solid separation is subjected to stripping to remove the hydrocarbon products adsorbed therein and produce a third spent catalyst.

[0104] In an embodiment of the present disclosure, the continuous catalyst and the second catalyst are introduced into the bottom of the second up-flow reaction unit and mixed; and the mixed catalyst is used for the subsequent catalytic pyrolysis reaction.

[0105] In an embodiment of the present disclosure, the position where the continuous catalyst and the second catalyst are introduced into the second up-flow reaction unit is upstream the feed inlet of the light olefin fraction.

[0106] In an embodiment of the present disclosure, in the second up-flow reaction unit, the feed inlet of the light olefin fraction is upstream the feed inlet of the heavy distillate oil.

[0107] In an embodiment of the present disclosure, there is no particular limitation on the structure of the second up-flow reactor, as long as it can realize feeding from the bottom and discharging from the upper part, for example, it can be an iso-diameter or diameter-changing riser reactor, or a composite reactor of the iso-diameter or diameter-changing riser reactor and the fluidized bed.

[0108] In more detail, the present disclosure provides an apparatus for producing lower carbon olefins and light aromatics by catalytic pyrolysis of hydrocarbon-containing feedstock oil, wherein the apparatus comprises the following units:

a hydrocarbon-containing feedstock oil-cutting unit, wherein the hydrocarbon-containing feedstock oil is cut into a light distillate oil and a heavy distillate oil, so that the weight ratio of the light distillate oil to the heavy distillate oil (light distillate oil/heavy distillate oil) is X,

a first down-flow reaction unit, wherein the light distillate oil and a first catalyst are introduced to the upper part of the reaction unit to perform the first catalytic pyrolysis, and a stream after the first catalytic pyrolysis is obtained from the lower part of the reaction unit;

a first gas solid separation unit, wherein the stream after the first catalytic pyrolysis is introduced to perform the gas solid separation to produce a first reaction hydrocarbon product and a first spent catalyst;

a second up-flow reaction unit, wherein a continuous catalyst, a second catalyst and the heavy distillate oil are introduced from the lower part of the reaction unit to perform the third catalytic pyrolysis, and a stream after the third catalytic pyrolysis is obtained from the upper part of the reaction unit, the continuous catalyst is at least a part of the first spent catalyst, the weight ratio of the second catalyst to the continuous catalyst (second catalyst/continuous catalyst) is R,

a second gas solid separation unit, wherein the stream after the third catalytic pyrolysis is introduced to perform the gas solid separation to produce a third reaction hydrocarbon product and a third spent catalyst;

a separation unit, wherein any of the first reaction hydrocarbon product and the third reaction hydrocarbon product or a mixture of two is introduced, and lower carbon olefins and light aromatics are separated out, and a light olefin fraction is separated out, and the light olefin fraction is returned to the second up-flow reaction unit;

wherein R and X satisfy the following relation:

$$(4.84 \times T_0 - 3340) / (780 + 5 \times T_0 - 6 \times T_3) < R/X < (0.968 \times T_0 - 630) / (668 + 0.2 \times T_0 - 1.2 \times T_3)$$

T₀ is the temperature (unit: °C) when the second catalyst enters the second up-flow reaction unit, and T₃ is the outlet temperature (unit: °C) of the second up-flow reaction unit.

[0109] In more detail, the present disclosure provides an apparatus for producing lower carbon olefins and light aromatics by catalytic pyrolysis of hydrocarbon-containing feedstock oil, wherein the apparatus comprises the following units:

a hydrocarbon-containing feedstock oil-cutting unit, wherein the hydrocarbon-containing feedstock oil is cut into a light distillate oil and a heavy distillate oil, so that the weight ratio of the light distillate oil to the heavy distillate oil (light distillate oil/heavy distillate oil) is X,

a first down-flow reaction unit, wherein the light distillate oil and a first catalyst are introduced to the upper part of the reaction unit to perform the first catalytic pyrolysis, and a stream after the first catalytic pyrolysis is obtained from the lower part of the reaction unit;

an fluidized-bed reaction unit, wherein the stream after the first catalytic pyrolysis is introduced to perform the second catalytic pyrolysis to produce a stream after the second catalytic pyrolysis;

a first gas solid separation unit, wherein the stream after the second catalytic pyrolysis is introduced to perform the gas solid separation to produce a second reaction hydrocarbon product and a second spent catalyst;

a second up-flow reaction unit, wherein a continuous catalyst, a second catalyst and the heavy distillate oil are introduced from the lower part of the reaction unit to perform the third catalytic pyrolysis, and a stream after the third

catalytic pyrolysis is obtained from the upper part of the reaction unit, the continuous catalyst is at least a part of the second spent catalyst, the weight ratio of the second catalyst to the continuous catalyst (second catalyst/continuous catalyst) is R,

a second gas solid separation unit, wherein the stream after the third catalytic pyrolysis is introduced to perform the gas solid separation to produce a third reaction hydrocarbon product and a third spent catalyst;

a separation unit, wherein any of the second reaction hydrocarbon product and the third reaction hydrocarbon product or a mixture of two is introduced, and lower carbon olefins and light aromatics are separated out, and a light olefin fraction is separated out, and the light olefin fraction is returned to the fluidized-bed reaction unit;

wherein R and X satisfy the following relation:

$$(4.84 \times T_0 - 3340) / (780 + 5 \times T_0 - 6 \times T_3) < R/X < (0.968 \times T_0 - 630) / (668 + 0.2 \times T_0 - 1.2 \times T_3)$$

T₀ is the temperature (unit: °C) when the second catalyst enters the second up-flow reaction unit, and T₃ is the outlet temperature (unit: °C) of the second up-flow reaction unit.

[0110] The apparatus for producing lower carbon olefins and light aromatics by catalytic pyrolysis of hydrocarbon-containing feedstock oil of the present disclosure is used to implement the process for producing lower carbon olefins and light aromatics by catalytic pyrolysis of hydrocarbon-containing feedstock oil of the present disclosure.

[0111] Hereinafter, with reference to Figure 1 and Figure 2, two embodiments of the present disclosure will be described in detail respectively, but the present disclosure is not limited thereto.

[0112] One specific embodiment of the present disclosure is shown in Figure 1, the hot first catalyst (regenerated catalyst) is transported to the first down-flow reactor 1 through the first catalyst delivery pipe (regenerated catalyst delivery pipe) 12. The light distillate oil is sprayed into the first down-flow reactor 1 through the feed nozzle 11, contacts the first catalyst to perform the catalytic pyrolysis reaction. After the reaction, the stream after the first catalytic pyrolysis is subjected to the separation of the catalyst and the reaction hydrocarbon product in the gas solid separator 7. The resulting first reaction hydrocarbon product is introduced into a separation device (not shown in the figure) through the hydrocarbon product outlet 22 of the down-flow reactor. The first spent catalyst is introduced as the continuous catalyst into the bottom of the second up-flow reactor 3 through the continuous catalyst delivery pipe 31. The second catalyst (regenerated catalyst) is introduced into the bottom of the second up-flow reactor 3 through the second catalyst delivery pipe (the regenerated catalyst delivery pipe) 32. The first spent catalyst (continuous catalyst) and the second catalyst are mixed, and the mixed catalyst is lifted upwards with the pre-lift medium. The light olefin fraction is sprayed into the second up-flow reactor 3 through the feed nozzle 21 of the light olefin fraction, and contacts the catalyst to perform the reaction. The heavy distillate oil is sprayed into the second up-flow reactor 3 through the feed nozzle 33 of the heavy distillate oil and contacts the oil/catalyst mixture from the bottom to perform the reaction. After the reaction, the obtained stream after the third catalytic pyrolysis is sent to the settler 4, in which the third spent catalyst and the third reaction hydrocarbon product are separated. The third reaction hydrocarbon product is introduced into a separation device (not shown in the figure) through the hydrocarbon product outlet 41 of the third reactor. The third spent catalyst is introduced into the stripper 5 to remove the hydrocarbon product adsorbed therein, and then sent to the regenerator 6 through the delivery pipe 53 for regeneration. The regenerated catalyst is returned to the first down-flow reactor and the second up-flow reactor for reuse. The reaction hydrocarbon product (the first reaction hydrocarbon product and the third reaction hydrocarbon product) are separated by a separation device (preferably a fractionation device and a gas separation device) to produce dry gas, C₃ fraction, C₄ fraction, light gasoline, heavy gasoline, diesel, slurry oil, from which lower carbon olefins and light aromatics are produced by separation. In addition, a light olefin fraction is separated from the reaction hydrocarbon product, and the light olefin fraction is introduced through the feed nozzle 21 of the light olefin fraction to the second up-flow reactor 3.

[0113] Another specific embodiment of the present disclosure is shown in Figure 2, the hot first catalyst (regenerated catalyst) is transported to the first down-flow reactor 1 through the first catalyst delivery pipe (regenerated catalyst delivery pipe) 12. The light distillate oil is sprayed into the first down-flow reactor 1 through the feed nozzle 11, and contacts the first catalyst to perform the catalytic pyrolysis reaction. After the reaction, the stream after the first catalytic pyrolysis is introduced into the fluidized bed reactor 2 through the outlet mushroom head distributor 13 of the first down-flow reactor. The pyrolysis reaction continues to occur in the fluidized bed reactor. After the reaction, the stream after the second catalytic pyrolysis is obtained and separated in a cyclone separator to produce a second reaction hydrocarbon product and a second spent catalyst. The second reaction hydrocarbon product is introduced into a separation device (not shown in the figure) through the hydrocarbon product outlet 22 of the second reaction. The second spent catalyst is introduced into the first stripper 5 to remove the hydrocarbon product adsorbed therein, and then introduced as the continuous catalyst into the bottom of the second up-flow reactor 3 through the continuous catalyst delivery pipe 31. The second catalyst (regenerated catalyst) is introduced into the bottom of the second up-flow reactor 3 through the

second catalyst delivery pipe (the regenerated catalyst delivery pipe) 32. The second spent catalyst (continuous catalyst) and the second catalyst are mixed, and the mixed catalyst is lifted upwards with the pre-lift medium. The heavy distillate oil is sprayed into the second up-flow reactor 3 through the feed nozzle 33 of the heavy distillate oil and contacts the catalyst to perform the reaction. After the reaction, the obtained stream after the third catalytic pyrolysis is sent to the settler 4, in which the third spent catalyst and the third reaction hydrocarbon product are separated. The third reaction hydrocarbon product is introduced into a separation device (not shown in the figure) through the hydrocarbon product outlet 41 of the third reactor. The third spent catalyst is introduced into the second stripper 52 to remove the hydrocarbon product adsorbed therein, and then sent to the regenerator 6 through the third spent catalyst delivery pipe 53 for regeneration. The regenerated catalyst is returned to the first down-flow reactor and the second up-flow reactor for reuse. The reaction hydrocarbon product (the second reaction hydrocarbon product and the third reaction hydrocarbon product) are separated by a separation device (preferably a fractionation device and a gas separation device) to produce dry gas, C3 fraction, C4 fraction, light gasoline, heavy gasoline, diesel, slurry oil, from which lower carbon olefins and light aromatics are produced by separation. In addition, a light olefin fraction is separated from the reaction hydrocarbon product, and the light olefin fraction is returned to the fluidized bed reactor through the feed nozzle 21 of the light olefin fraction.

Examples

[0114] The present disclosure is further described in detail through the examples hereinafter. The raw materials used in the examples can all be obtained commercially. The catalytic pyrolysis catalyst used in the examples and comparative examples of the present disclosure was industrially produced by Catalyst Qilu Branch of China Petroleum & Chemical Corporation, and the brand name was DMMC-2. The catalyst contained ZSM-5 zeolite with an average pore size of less than 0.7 nanometers and ultra-stabilized Y zeolite. The catalyst was hydrothermally aged at 800°C for 17 hours with saturated steam before use. The main physical and chemical properties of the catalyst were shown in Table 1. The hydrocarbon-containing feedstock oil used in the examples and the comparative examples was a crude oil from Jiangsu Oilfield, and its properties were listed in Table 2.

Table 1

Catalyst	Catalyst
Physical properties	
Specific surface/m ² ·g ⁻¹	125
Pore volume/cm ³ ·g ⁻¹	0.197
Apparent density/g·cm ⁻³	0.86
Chemical composition	
Al ₂ O ₃ /%	56.8
SiO ₂ /%	42.9
Micro-activity/%	68

Table 2

Item	Crude oil A
Density (20°C)/(g·cm ⁻³)	0.849
Freezing point/°C	35
Kinematic viscosity (80°C)/(mm ² /s)	6.8
Carbon residue/%	3.5
Resin content/%	8.4
Asphaltene content/%	0.2
Mass percent of less than 250°C fraction/%	16.3
Mass percent of less than 320°C fraction/%	28.6

(continued)

Item	Crude oil A
Mass percent of less than 350°C fraction/%	34.6

Example 1

[0115] The light/heavy distillate oil cut point of crude oil A processed in this example was 320°C, and the cut ratio (the weight ratio of light distillate oil/heavy distillate oil) was 0.4.

[0116] A modified medium-size apparatus operated in a continuous reaction-regeneration mode was used to perform the test, and its flow process was shown in Figure 1. A high temperature regeneration catalyst having a temperature of 720°C was introduced from a regenerator to the top of a down-flow tubular reactor 1 through a regeneration chute, a light distillate oil preheated to 45°C was atomized by water vapor and then sent to the down-flow tubular reactor 1 through a feed nozzle to contact a first catalyst to perform the catalytic pyrolysis reaction, wherein the catalyst-oil ratio was 40, the outlet temperature of the reactor was 665°C, and the gas-solid residence time was 0.8 seconds, a stream after the first catalytic pyrolysis was separated by cyclone to produce a first reaction hydrocarbon product and a first spent catalyst, the first reaction hydrocarbon product was sent to a separation system, the whole of the first spent catalyst was introduced into the bottom of a riser reactor 3. At the same time, a regenerated catalyst having a temperature of 720°C (a second catalyst) was introduced from the regenerator through a regenerated catalyst delivery pipe 32 into the bottom of the riser reactor 3. The weight ratio of the second catalyst to the first spent catalyst (the second catalyst/the first spent catalyst) was 0.25. The first spent catalyst and the second catalyst were mixed at the bottom of the riser reactor 3, and the mixed catalyst flowed upward under the action of the pre-lifting steam. At the same time, the light olefin fraction was sent to the lower part of the riser reactor 3 through the feed nozzle of the light olefin fraction under the atomization medium of water vapour to contact the mixed catalyst and react. The nozzle of the heavy distillate oil was 800 mm above the feed nozzle of the light olefin fraction. The heavy distillate oil was atomized by water vapor, and then injected into the riser reactor through the feed nozzle of the heavy distillate oil to perform the catalytic pyrolysis reaction, wherein the catalyst-oil ratio was 20, the outlet temperature T3 of the reactor was 610°C, and the gas-solid residence time in the reactor was 1.5 seconds. The stream after the catalytic pyrolysis was sent to a settler to perform the oil and catalyst separation to produce a third reaction hydrocarbon product and a third spent catalyst. The third reaction hydrocarbon product was introduced into the separation system. The first reaction hydrocarbon product and the third reaction hydrocarbon product were separated into cracked gas, light gasoline, heavy gasoline, diesel and slurry oil in the separation system. Partial fraction of light gasoline (distillation range of 30-60°C) was returned to the riser reactor 3 as the light olefin fraction through the feed nozzle of the light olefin fraction. The third spent catalyst was sent to a stripper to remove the hydrocarbon products adsorbed on the third spent catalyst, and then it was sent to the regenerator through the spent catalyst chute, and contacted the air to perform the coke-burning and regeneration at 720°C. The regenerated catalyst was returned through the regeneration chute to the reactor for the recycle use. The medium-size apparatus was electrically heated to maintain the temperature of the reaction-regeneration system. After the apparatus run stably (the composition of the product remained basically unchanged), the compositions of the cracked gas and gasoline obtained from the reaction hydrocarbon product were analyzed to obtain the yields of low-carbon olefins (hereinafter referred to as triple-olefins) and light aromatics (hereinafter referred to as BTX) in the product.

[0117] The main operation conditions and results were listed in Table 3.

Example 2

[0118] The same apparatus and the reaction steps identical to those of Example 1 were used, except that the light/heavy distillate oil cut point of the processed crude oil A was 250°C, the cut ratio (the weight ratio of light distillate oil/heavy distillate oil) was 0.195, in addition, the weight ratio of the second catalyst to the first spent catalyst (the second catalyst/the first spent catalyst) was 0.03, the temperature of the regenerator was 700°C (namely, the temperature T0 when the second catalyst come to step S4 was 700°C), the outlet temperature T3 of the riser reactor was 570°C.

[0119] The other main operation conditions and results were listed in Table 3.

Example 3

[0120] The same apparatus and the reaction steps identical to those of Example 1 were used, except that the light/heavy distillate oil cut point of the processed crude oil A was 350°C, the cut ratio (the weight ratio of light distillate oil/heavy distillate oil) was 0.529, in addition, the weight ratio of the second catalyst to the first spent catalyst (the second catalyst/the first spent catalyst) was 0.6, the temperature of the regenerator was 740°C (namely, the temperature T0 when the second

catalyst come to step S4 was 740°C), the outlet temperature T3 of the riser reactor was 630°C.

[0121] The other main operation conditions and results were listed in Table 3.

Example 4

[0122] The same apparatus and the reaction steps identical to those of Example 1 were used.

[0123] The light/heavy distillate oil cut point of crude oil A processed in this example was 250°C, and the cut ratio (the weight ratio of light distillate oil/heavy distillate oil) was 0.195.

[0124] Except for the conditions listed in Table 3, the same conditions as those in Example 1 were used.

[0125] The results were listed in Table 3.

Example 5

[0126] The same apparatus and the reaction steps identical to those of Example 1 were used.

[0127] The light/heavy distillate oil cut point of crude oil A processed in this example was 350°C, and the cut ratio (the weight ratio of light distillate oil/heavy distillate oil) was 0.529.

[0128] Except for the conditions listed in Table 3, the same conditions as those in Example 1 were used.

[0129] The results were listed in Table 3.

Example 6

[0130] The light/heavy distillate oil cut point of crude oil A processed in this example was 320°C, and the cut ratio (the weight ratio of light distillate oil/heavy distillate oil) was 0.4.

[0131] A modified medium-size apparatus operated in a continuous reaction-regeneration mode was used to perform the test, and its flow process was shown in Figure 2. A high temperature regeneration catalyst having a temperature of 720°C was introduced from a regenerator to the top of a down-flow tubular reactor 1 through a regeneration chute, a light distillate oil preheated to 45°C was atomized by water vapor and then sent to the down-flow tubular reactor 1 through a feed nozzle to contact a first catalyst to perform the catalytic pyrolysis reaction, wherein the catalyst-oil ratio was 40, the outlet temperature of the reactor was 670°C, and the gas-solid residence time was 0.6 seconds, a stream after the first catalytic pyrolysis was sent to a fluidized bed reactor 2 through an outlet distributor to further perform the catalytic pyrolysis reaction, wherein the reaction temperature was 655°C, the weight hourly space velocity was 4 h⁻¹; in addition, the light olefin fraction was atomized by water vapor, then sent to the bottom of the fluidized bed reactor 2 through a feed nozzle 21 to contact a hot catalyst and react, a stream after the second catalytic pyrolysis was separated by cyclone to produce a second reaction hydrocarbon product and a second spent catalyst. The second reaction hydrocarbon product was introduced into a subsequent separation system, and the separated second spent catalyst was stripped and wholly introduced into the bottom of the riser reactor 3. At the same time, a regenerated catalyst having a temperature of 720°C (a second catalyst) was introduced from the regenerator through a regenerated catalyst delivery pipe 32 into the bottom of the second riser reactor 3. The weight ratio of the second catalyst to the second spent catalyst (second catalyst/second spent catalyst) was 0.25. The second spent catalyst and the second catalyst were mixed at the bottom of the reactor 3, and the mixed catalyst flowed upward under the action of the pre-lifting steam. The heavy distillate oil was atomized by water vapor, then inject into the riser reactor 3 through the nozzle of the heavy distillate oil to contact the catalyst and perform the catalytic pyrolysis reaction, wherein the catalyst-oil ratio was 20, the outlet temperature T3 of the reactor was 610°C, and the gas-solid residence time in the reactor was 1.5 seconds. The stream after the catalytic pyrolysis was sent to a settler to perform the oil and catalyst separation to produce a third reaction hydrocarbon product and a third spent catalyst. The reaction hydrocarbon product was introduced into the separation system. The second reaction hydrocarbon product and the third reaction hydrocarbon product were separated into cracked gas, light gasoline, heavy gasoline, diesel and slurry oil in the separation system. Partial fraction of light gasoline (distillation range of 30-60°C) was returned to the fluidized bed reactor 2 as the light olefin fraction. The third spent catalyst was sent to a stripper to remove the hydrocarbon products adsorbed on the third spent catalyst, and then it was sent to the regenerator through the spent catalyst chute, and contacted the air to perform the coke-burning and regeneration at 720°C. The regenerated catalyst was returned through the regeneration chute to the reactor for the recycle use. The medium-size apparatus was electrically heated to maintain the temperature of the reaction-regeneration system. After the apparatus run stably (the composition of the product remained basically unchanged), the compositions of the cracked gas and gasoline obtained from the reaction hydrocarbon product were analyzed to obtain the yields of triple-olefins and BTX in the product.

[0132] The main operation conditions and results were listed in Table 3.

Example 7

[0133] The same apparatus and the reaction steps identical to those of Example 6 were used, except that the light/heavy distillate oil cut point of the processed crude oil A was 250°C, the cut ratio (the weight ratio of the light distillate oil/the heavy distillate oil) was 0.195, in addition, the weight ratio of the second catalyst to the second spent catalyst (second catalyst/second spent catalyst) was 0.03, the temperature of the regenerator was 700°C (namely, the temperature T0 when the second catalyst come to step S4 was 700°C), the outlet temperature T3 of the riser reactor was 570°C.

[0134] The other main operation conditions and results were listed in Table 3.

Example 8

[0135] The same apparatus and the reaction steps identical to those of Example 6 were used, except that the light/heavy distillate oil cut point of the processed crude oil A was 350°C, the cut ratio (the weight ratio of the light distillate oil/the heavy distillate oil) was 0.529, in addition, the weight ratio of the second catalyst to the second spent catalyst (second catalyst/second spent catalyst) was 0.6, the temperature of the regenerator was 740°C (namely, the temperature T0 when the second catalyst come to step S4 was 740°C), the outlet temperature T3 of the riser reactor was 630°C.

[0136] The other main operation conditions and results were listed in Table 3.

Comparative Example 1

[0137] The same apparatus and the reaction steps and the reaction conditions identical to those of Example 1 were used, except that the light olefin fraction obtained from the separation of the reaction hydrocarbon product was not refluxed to the riser reactor 3.

[0138] The other main operation conditions and results were listed in Table 3.

Comparative Example 2

[0139] The same apparatus and the reaction steps identical to those of Example 1 were used, except that the weight ratio of the second catalyst to the first spent catalyst (the second catalyst/the first spent catalyst) was 0.1, the temperature of the regenerator was 740°C (namely, the temperature T0 when the second catalyst come to step S4 was 740°C), the outlet temperature T3 of the riser reactor was 610°C.

[0140] The other main operation conditions and results were listed in Table 3.

Comparative Example 3

[0141] The same apparatus and the reaction steps identical to those of Example 1 were used, except that the weight ratio of the second catalyst to the first spent catalyst (the second catalyst/the first spent catalyst) was 0.5, the temperature of the regenerator was 700°C (namely, the temperature T0 when the second catalyst come to step S4 was 700°C), the outlet temperature T3 of the riser reactor was 610°C.

[0142] The other main operation conditions and results were listed in Table 3.

Comparative Example 4

[0143] The same apparatus and the reaction steps and the reaction conditions identical to those of Example 1 were used, except that the second catalyst was not introduced into the lower part of the riser reactor 3, but only the first spent catalyst was used.

[0144] The other main operation conditions and results were listed in Table 3.

Comparative Example 5

[0145] The same apparatus and the reaction steps and the reaction conditions identical to those of Example 1 were used, except that the first spent catalyst was not introduced into the lower part of the riser reactor 3, but only the second catalyst was used.

[0146] The other main operation conditions and results were listed in Table 3.

Comparative Example 6

[0147] The same apparatus, the same reaction steps and the same reaction conditions identical to those of Example

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1 were used, except that the light distillate oil was sent to the riser reactor, namely, the first down-flow tubular reactor 1 was changed to the riser reactor (in Comparative Example 6, various parameters of the down-flow tubular reactor in Table 3 represented various parameters of the up-flow tubular reactor).

[0148] The other main operation conditions and results were listed in Table 3.

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Table 3

Item	Examples								Comparative Examples							
	1	2	3	4	5	6	7	8	1	2	3	4	5	6*		
Cut ratio X of light distillate oil/heavy distillate oil	0.4	0.195	0.529	0.195	0.529	0.4	0.195	0.529	0.4	0.4	0.4	0.4	0.4	0.4		
Processing capacity for crude oil A/(kg/h)	1	1	1	1	1	1	1	1	1	1	1	1	1	1		
Outlet temperature of down-flow tubular reactor/°C	665	660	670	665	665	670	665	675	665	665	665	665	665	665		
Gas-solid residence time of light distillate oil/s	0.8	0.8	0.8	0.8	1.8	0.6	0.6	0.6	0.8	0.8	0.8	0.8	0.8	0.8		
Catalyst circulation rate of down-flow tubular reactor/(kg/h)	11.4	9.0	11.1	9.8	13.8	11.4	9.0	11.1	11.4	8.3	18.0	11.4	11.4	11.4		
Reaction temperature of fluidized bed/°C						655	650	660								
Weight hourly space velocity of fluidized bed/h ⁻¹						4	4	4								
Temperature T0 of the second catalyst sent to the riser reactor/°C	720	700	740	700	720	720	700	740	720	740	700	-	720	720		
Outlet temperature T3 of the riser reactor/°C	610	570	630	600	630	610	570	630	610	610	610	610	610	610		
Gas-solid residence time of heavy distillate oil/s	1.5	2	1.2	1.5	1.5	1.5	2	1.2	1.5	1.5	1.5	1.5	1.5	1.5		
Weight ratio (R) of second catalyst/continuous catalyst	0.25	0.03	0.6	0.1	0.4	0.25	0.03	0.6	0.25	0.1	0.5	-	-	0.25		
Catalyst circulation rate of riser reactor/(kg/h)	14.3	9.2	17.7	10.8	19.4	14.3	9.2	17.7	14.3	9.1	27.0	11.4	14.3	14.3		
Recycled rate of light olefins/(kg/h)	0.12	0.2	0.1	0.15	0.15	0.12	0.2	0.1	0	0.12	0.12	0.12	0.12	0.12		
Gas-solid residence time of light olefins/s	0.5	0.5	0.5	0.5	0.5				-	0.5	0.5	0.5	0.5	0.5		
R/X	0.63	0.15	1.13	0.51	0.76	0.63	0.15	1.13	0.63	0.25	1.25	-	-	0.63		
(4.84×T0-3340)/(780+5×T0-6×T3)	0.20	0.06	0.35	0.07	0.24	0.20	0.06	0.35	0.20	0.29	0.08	-	-	0.20		
(0.968×T0-630)/(668+0.2×T0-1.2×T3)	0.84	0.38	1.44	0.54	1.20	0.84	0.38	1.44	0.84	1.03	0.63	-	-	0.84		
Product distribution/%																
Dry gas	15.7	12.5	24.3	14.4	19.6	16.5	13.1	25.3	13.4	17.8	16.9	15.2	18.2	17.6		
Liquefied gas	47.1	46.6	41.6	46.9	45.2	47	46.7	41.3	45.8	45.5	45.8	46.7	46.1	46.5		
Gasoline	21.3	24.1	18.9	22.3	20.3	20.7	23.7	18.2	25.2	20.7	21.3	21.9	19.7	19.5		
Diesel	5.1	5.8	4.2	5.4	4.3	4.9	5.6	4.1	4.9	4.8	4.7	5.3	4.6	5		
Slurry oil	1.9	2.3	1.5	2.1	1.5	1.8	2.1	1.3	1.9	1.8	1.6	2.1	1.6	1.8		
Coke	8.9	8.7	9.5	8.9	9.1	9.1	8.8	9.8	8.8	9.4	9.7	8.8	9.8	9.6		

(continued)

Item	Examples								Comparative Examples					
	1	2	3	4	5	6	7	8	1	2	3	4	5	6*
Total	100	100.0	100	100	100	100	100	100	100	100	100	100	100	100
Triple-olefins+BTX yield/%	62.8	61.4	64.7	62.2	64.9	63.4	61.7	65.0	59.1	59.7	60.6	60.9	60.5	61.0
Methane+coke yield/%	11.9	10.8	13.6	11.3	12.8	12.2	11.3	14.1	11.3	13.0	13.1	11.8	13.4	13.3
Ratio of (triple-olefins+BTX) yield/(methane+coke) yield	5.28	5.69	4.76	5.50	5.07	5.20	5.46	4.61	5.23	4.59	4.63	5.16	4.51	4.59
*(the down-flow tubular reactor was replaced by an up-flow tubular reactor)														

[0149] It can be seen from the data in Table 3 that the process for producing lower carbon olefins and BTX by catalytic pyrolysis of a hydrocarbon-containing feedstock oil provided by the present disclosure can significantly increase the yields of lower carbon olefins and light aromatics, and at the same time, inhibit the yields of by-products such as dry gas and coke.

[0150] The preferred embodiments of the present disclosure have been described in detail above, but the present disclosure is not limited to the specific details in the above embodiments. Within the scope of the technical concept of the present disclosure, various simple modifications can be made to the technical solutions of the present disclosure, and these simple modifications all belong to the protection scope of the present disclosure.

[0151] In addition, it should be noted that each specific technical feature described in the above-mentioned embodiments may be combined in any suitable manner under the circumstance that there is no contradiction. In order to avoid the unnecessary repetition, various possible combinations are not described in the present disclosure.

[0152] In addition, any combination of the various embodiments of the present disclosure can be made, and the same should be considered as the disclosure of the present invention as long as the idea of the present invention is not violated.

Claims

1. A process for producing lower carbon olefins and light aromatics by catalytic pyrolysis of hydrocarbon-containing feedstock oil, wherein the process comprises the steps of:

S1, cutting the hydrocarbon-containing feedstock oil into a light distillate oil and a heavy distillate oil, wherein the weight ratio of the light distillate oil to the heavy distillate oil (light distillate oil/heavy distillate oil) is X;
 S2, introducing the light distillate oil and a first catalyst into a first down-flow reactor to perform a first catalytic pyrolysis to produce a stream after the first catalytic pyrolysis; Optionally S2', introducing the stream after the first catalytic pyrolysis into a fluidized bed reactor to perform a second catalytic pyrolysis to produce a stream after the second catalytic pyrolysis;
 S3, subjecting the stream after the first catalytic pyrolysis to a gas-solid separation to produce a first reaction hydrocarbon product and a first spent catalyst, or subjecting the stream after the second catalytic pyrolysis to a gas-solid separation to produce a second reaction hydrocarbon product and a second spent catalyst;
 S4, introducing a continuous catalyst, the heavy distillate oil and a second catalyst into a second up-flow reactor to perform a third catalytic pyrolysis, and then subjecting to a gas-solid separation to produce a third reaction hydrocarbon product and a third spent catalyst; the continuous catalyst is at least a part of the first spent catalyst or at least a part of the second spent catalyst; the weight ratio of the second catalyst to the continuous catalyst (second catalyst/continuous catalyst) is R;
 S5, separating out lower carbon olefins and light aromatics from any of the first reaction hydrocarbon product, the second reaction hydrocarbon product and the third reaction hydrocarbon product or a mixture of the first reaction hydrocarbon product and the third reaction hydrocarbon product or a mixture of the second reaction hydrocarbon product and the third reaction hydrocarbon product, and separating out a light olefin fraction, and returning the light olefin fraction to the second up-flow reactor of step S4 or the fluidized bed reactor of step S2', wherein R and X satisfy the following relation:

$$(4.84 \times T_0 - 3340) / (780 + 5 \times T_0 - 6 \times T_3) < R/X < (0.968 \times T_0 - 630) / (668 + 0.2 \times T_0 - 1.2 \times T_3)$$

T₀ is the temperature (unit: °C) when the second catalyst enters step S4, and T₃ is the outlet temperature (unit: °C) of the second up-flow reactor.

2. The process according to claim 1, wherein the outlet temperature T₃ of the second up-flow reactor is 530-650°C, preferably 560-640°C, further preferably 580-630°C, further more preferably 600-630°C; and/or the temperature T₀ when the second catalyst enters step S4 is 690-750°C, preferably 700-740°C, further preferably 705-730°C, further more preferably 710-725°C.
3. The process according to claim 1 or 2, wherein, in step S1, the hydrocarbon-containing feedstock oil is cut into the light distillate oil and the heavy distillate oil at the cut point of any temperature between 100-400°C, so that the weight ratio of the light distillate oil to the heavy distillate oil (light distillate oil/heavy distillate oil) is X.
4. The process according to any of claims 1-3, wherein,

in the first down-flow reactor, the conditions of the first catalytic pyrolysis comprise: the outlet temperature of the first down-flow reactor is 610-720°C, the gas-solid residence time is 0.1-3.0 seconds, the catalyst-oil ratio is 15-80; and/or

in the fluidized bed reactor, the conditions of the second catalytic pyrolysis comprise: the reaction temperature in the fluidized bed reactor is 600-690°C, the weight hourly space velocity is 2-20 h⁻¹; and/or

in the second up-flow reactor, the conditions of the third catalytic pyrolysis comprise: the gas-solid residence time is 0.5-8 seconds, the catalyst-oil ratio is 8-40.

5. The process according to any of claims 1-4, wherein,

in the first down-flow reactor, the conditions of the first catalytic pyrolysis comprise: the outlet temperature of the first down-flow reactor is 650-690°C, the gas-solid residence time is 0.5-1.5 seconds, the catalyst-oil ratio is 25-65; and/or

in the fluidized bed reactor, the conditions of the second catalytic pyrolysis comprise: the reaction temperature in the fluidized bed reactor is 640-670°C, the weight hourly space velocity is 4-12 h⁻¹; and/or

in the second up-flow reactor, the conditions of the third catalytic pyrolysis comprise: the gas-solid residence time is 1.5-5 seconds, the catalyst-oil ratio is 10-30.

6. The process according to any of claims 1-5, wherein,

in presence of step S2', in step S3 of the gas solid separation, the separated catalyst is stripped to produce the second spent catalyst; and/or

in step S4, the continuous catalyst and the second catalyst are firstly mixed, and then the subsequent catalytic pyrolysis reaction is performed; and/or

in step S4, the light olefin fraction obtained from step S5 contacts a mixture of the second catalyst and the continuous catalyst earlier than the heavy distillate oil; preferably the light olefin fraction contacts a mixture of the second catalyst and the continuous catalyst 0.3-1.0 seconds earlier than the heavy distillate oil, more preferably the light olefin fraction contacts a mixture of the second catalyst and the continuous catalyst 0.4-0.8 seconds earlier than the heavy distillate oil; and/or

the process includes step S0 before step S1, wherein the hydrocarbon-containing feedstock oil is subjected to the desalination and dehydration treatment, and the resulting dehydrated and desalinized hydrocarbon-containing feedstock oil is introduced into step S1 for cutting.

7. The process according to any of claims 1-6, wherein the process further comprises:

in step S4 of the gas solid separation, the separated catalyst is stripped to produce the third spent catalyst; and/or the third spent catalyst and optionally the first spent catalyst or the second spent catalyst not entering the second up-flow reactor are subjected to coke-burning and regeneration at a temperature of 690-750°C, preferably 700-740°C, further preferably 705-730°C, further more preferably 710-725°C to produce a regenerated catalyst; and/or

any of the first reaction hydrocarbon product, the second reaction hydrocarbon product and the third reaction hydrocarbon product or a mixture of the first reaction hydrocarbon product and the third reaction hydrocarbon product or a mixture of the second reaction hydrocarbon product and the third reaction hydrocarbon product is separated to produce dry gas, C3 fraction, C4 fraction, light gasoline, heavy gasoline, diesel and slurry oil, from which lower carbon olefins and light aromatics are produced by separation, and a light olefin fraction is separated out; and/or

in absence of step S2', in step S5, the light olefin fraction is separated out from any of the first reaction hydrocarbon product and the third reaction hydrocarbon product or a mixture of two, and the light olefin fraction is returned to the second up-flow reactor of step S4; in presence of step S2', in step S5, the light olefin fraction is separated out from any of the second reaction hydrocarbon product and the third reaction hydrocarbon product or a mixture of two, and the light olefin fraction is returned to the fluidized bed reactor of step S2'.

8. The process according to any of claims 1-7, wherein the hydrocarbon-containing feedstock oil is one of or a mixture of two or more of crude oil, coal liquefaction oil, synthetic oil, tar sand oil, shale oil, tight oil and animal and vegetable oil and fat, or their respective partial fractions, or hydro-upgraded oils of their respective heavy fractions.

9. The process according to any of claims 1-8, wherein the first catalyst and the second catalyst each independently comprise an active component and a support, the active component is at least one of ultra-stabilized Y zeolite

optionally containing rare earth, ZSM-5 zeolite, pentasil silica-rich zeolite and beta zeolite, said support is at least one of alumina, silica, amorphous silica alumina, zirconia, titania, boron oxide and alkali-earth oxide.

10. The process according to any of claims 1-9, wherein the first catalyst and the second catalyst each independently comprise a regenerated catalyst, preferably the first catalyst and the second catalyst are the regenerated catalyst, and/or the whole of the first spent catalyst or the whole of the second spent catalyst is used as the continuous catalyst.

11. An apparatus for producing lower carbon olefins and light aromatics by the catalytic pyrolysis of a hydrocarbon-containing feedstock oil, wherein the apparatus comprises the following units:

a hydrocarbon-containing feedstock oil-cutting unit, wherein the hydrocarbon-containing feedstock oil is cut into a light distillate oil and a heavy distillate oil, so that the weight ratio of the light distillate oil to the heavy distillate oil (light distillate oil/heavy distillate oil) is X,

a first down-flow reaction unit, wherein the light distillate oil and a first catalyst are introduced to the upper part of the reaction unit to perform the first catalytic pyrolysis, and a stream after the first catalytic pyrolysis is obtained from the lower part of the reaction unit;

an optional fluidized-bed reaction unit, wherein the stream after the first catalytic pyrolysis is introduced to perform the second catalytic pyrolysis to produce a stream after the second catalytic pyrolysis;

a first gas solid separation unit, wherein the stream after the first catalytic pyrolysis is introduced to perform the gas solid separation to produce a first reaction hydrocarbon product and a first spent catalyst, or wherein the stream after the second catalytic pyrolysis is introduced to perform the gas solid separation to produce a second reaction hydrocarbon product and a second spent catalyst;

a second up-flow reaction unit, wherein a continuous catalyst, a second catalyst and the heavy distillate oil are introduced from the lower part of the reaction unit to perform the third catalytic pyrolysis, and a stream after the third catalytic pyrolysis is obtained from the upper part of the reaction unit, the continuous catalyst is at least a part of the first spent catalyst or at least a part of the second spent catalyst, the weight ratio of the second catalyst to the continuous catalyst (second catalyst/continuous catalyst) is R,

a second gas solid separation unit, wherein the stream after the third catalytic pyrolysis is introduced to perform the gas solid separation to produce a third reaction hydrocarbon product and a third spent catalyst;

a separation unit, wherein any of the first reaction hydrocarbon product, the second reaction hydrocarbon product and the third reaction hydrocarbon product or a mixture of the first reaction hydrocarbon product and the third reaction hydrocarbon product or a mixture of the second reaction hydrocarbon product and the third reaction hydrocarbon product is introduced, and lower carbon olefins and light aromatics are separated out, and a light olefin fraction is separated out, and the light olefin fraction is returned to the second up-flow reaction unit or the fluidized-bed reaction unit;

wherein R and X satisfy the following relation:

$$(4.84 \times T_0 - 3340) / (780 + 5 \times T_0 - 6 \times T_3) < R/X < (0.968 \times T_0 - 630) / (668 + 0.2 \times T_0 - 1.2 \times T_3)$$

T₀ is the temperature (unit: °C) when the second catalyst enters the second up-flow reaction unit, and T₃ is the outlet temperature (unit: °C) of the second up-flow reaction unit.

12. The apparatus according to claim 11, which further comprises a regeneration unit, wherein the third spent catalyst and optionally the first spent catalyst or the second spent catalyst not entering the second up-flow reactor are introduced to perform the coke-burning and regeneration at a temperature of 690-750°C, preferably 700-740°C, further preferably 705-730°C, further more preferably 710-725°C to produce a regenerated catalyst.

13. The apparatus according to claim 11 or 12, wherein if the apparatus comprises the fluidized-bed reaction unit, the first gas solid separation unit further comprises a stripping unit, wherein the catalyst obtained from the gas solid separation is subjected to stripping to produce a second spent catalyst.

14. The apparatus according to any of claims 11-13, wherein the second gas solid separation unit further comprises a stripping unit, wherein the catalyst obtained from the gas solid separation is subjected to stripping to produce a third spent catalyst.

15. The apparatus according to any of claims 11-14, wherein the apparatus further comprises a dehydration and de-

salination unit, wherein the hydrocarbon-containing feedstock oil is subjected to the desalination and dehydration treatment, and the resulting dehydrated and desalinized hydrocarbon-containing feedstock oil is introduced to the hydrocarbon-containing feedstock oil-cutting unit to be cut.

- 5 **16.** The apparatus according to any of claims 11-15, wherein the position where the continuous catalyst and the second catalyst are introduced into the second up-flow reaction unit is upstream the feed inlet of the light olefin fraction.
- 10 **17.** The apparatus according to any of claims 11-15, wherein in the second up-flow reaction unit, the feed inlet of the light olefin fraction from the separation unit is upstream the feed inlet of the heavy distillate oil.

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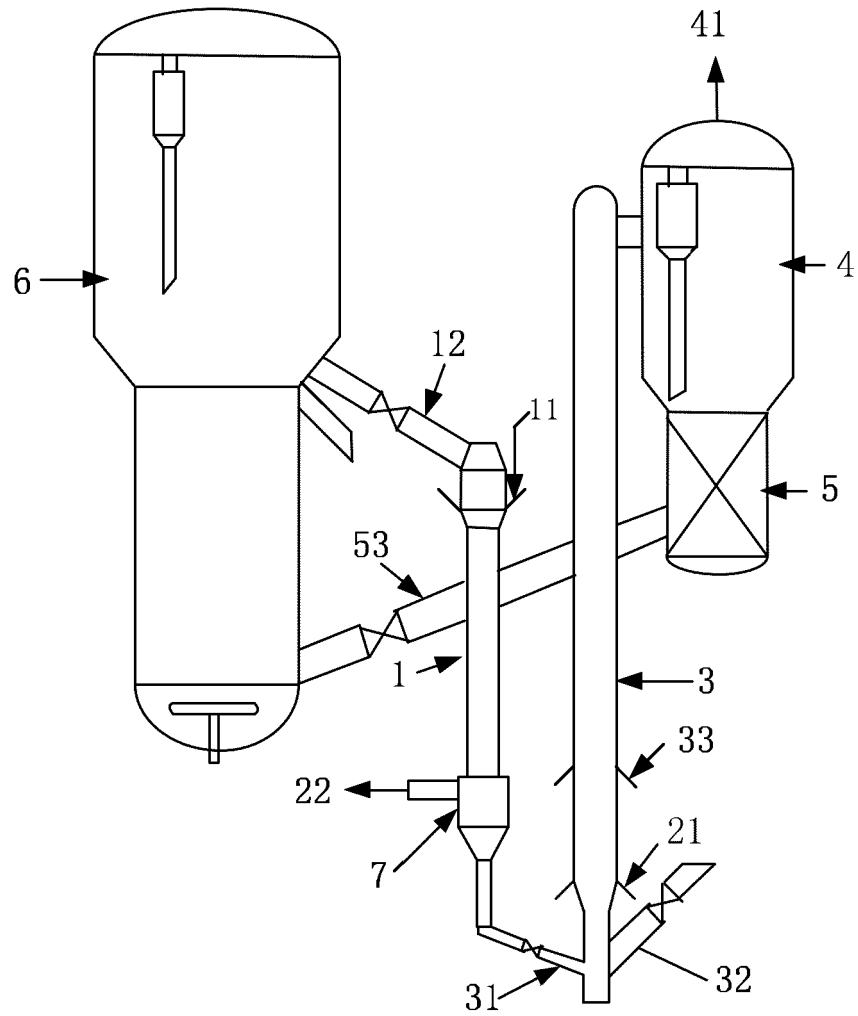


Figure 1

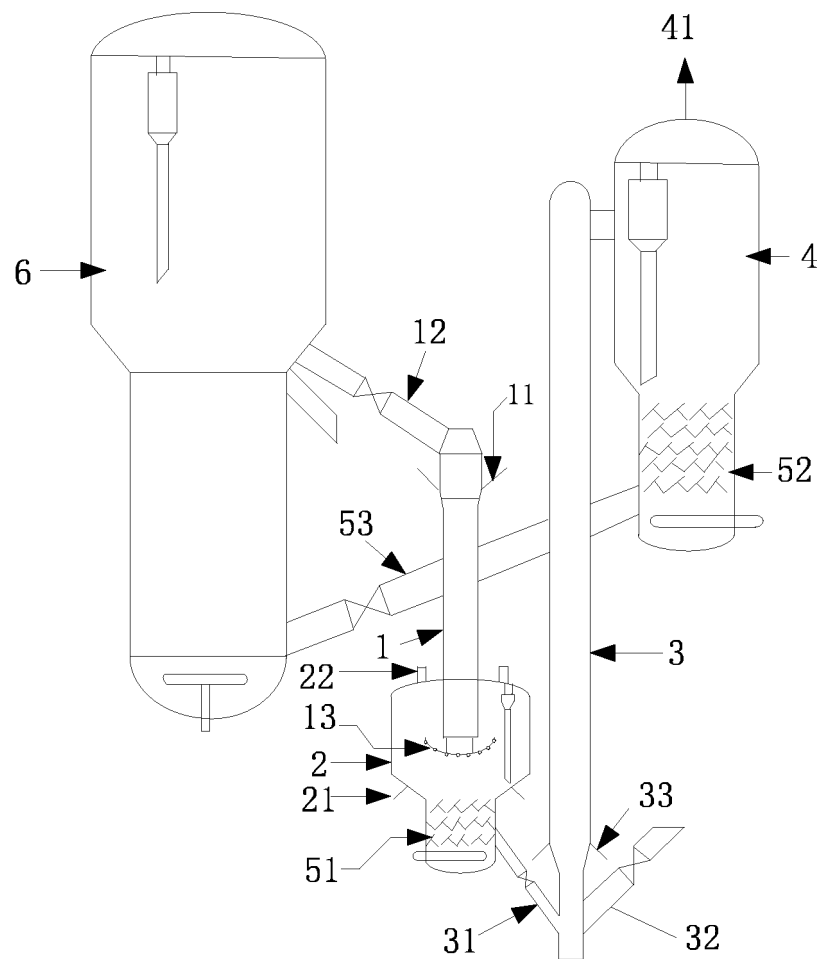


Figure 2

INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2021/127339

5	A. CLASSIFICATION OF SUBJECT MATTER		
	C10G 51/06(2006.01)i; C10G 11/04(2006.01)i; C10G 55/06(2006.01)i; C10G 69/00(2006.01)i		
	According to International Patent Classification (IPC) or to both national classification and IPC		
	B. FIELDS SEARCHED		
10	Minimum documentation searched (classification system followed by classification symbols) C10G		
	Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
15	Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) CNTXT; DWPI; ENTXTC; CNKI; Web of Science: 催化裂化, 催化裂解, 低碳烯烃, 乙烯, 丙烯, 轻芳烃, 苯, 甲苯, 二甲苯, BTX, 下流, 下行, 轻, 重, 闪蒸, 切割, FCC, catalytic cracking, pyrolyzing, pyrolysis, low carbon olefins, light olefins, ethylene, propylene, light aromatics, benzene, toluene, xylene, downer, down flowing, light, heavy, flash, cut+		
	C. DOCUMENTS CONSIDERED TO BE RELEVANT		
20	Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
	Y	CN 111630137 A (SAUDI ARABIAN OIL CO. et al.) 04 September 2020 (2020-09-04) figures 2-3, comparative example 1, paragraphs 35-59, 81, 112	11-17,
25	Y	US 2004211704 A1 (TOTAL RAFFINAGE DISTRIBUTION S.A.) 28 October 2004 (2004-10-28) figure 1, paragraphs 20, 87	11-17
	Y	CN 101045667 A (CHINA PETROLEUM & CHEMICAL CORPORATION et al.) 03 October 2007 (2007-10-03) figure 1, description page 7 paragraph 1	11-17,
30	Y	US 4966681 A (MOBIL OIL CORP.) 30 October 1990 (1990-10-30) figures 1-2, description column 10 lines 25-68	11-17,
	A	US 2013172173 A1 (MUKTHIYAR S et al.) 04 July 2013 (2013-07-04) entire document	1-17
35			
	<input type="checkbox"/> Further documents are listed in the continuation of Box C. <input checked="" type="checkbox"/> See patent family annex.		
40	* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "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) "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 "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 "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 "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 "&" document member of the same patent family		
45			
50	Date of the actual completion of the international search 14 January 2022		Date of mailing of the international search report 25 January 2022
55	Name and mailing address of the ISA/CN China National Intellectual Property Administration (ISA/CN) No. 6, Xitucheng Road, Jimenqiao, Haidian District, Beijing 100088, China		Authorized officer
	Facsimile No. (86-10)62019451		Telephone No.

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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.

PCT/CN2021/127339

Patent document cited in search report	Publication date (day/month/year)	Patent family member(s)	Publication date (day/month/year)
CN 111630137 A	04 September 2020	JP 2021511422 A	06 May 2021
		US 2021047573 A1	18 February 2021
		SG 11202006892 Q A	28 August 2020
		KR 20200111757 A	29 September 2020
		US 2019225894 A1	25 July 2019
		US 10889768 B2	12 January 2021
		EP 3743485 A1	02 December 2020
		WO 2019147465 A1	01 August 2019
US 2004211704 A1	28 October 2004	AT 286107 T	15 January 2005
		US 7544333 B2	09 June 2009
		FR 2811327 A1	11 January 2002
		FR 2811327 B1	25 October 2002
		US 2002096452 A1	25 July 2002
		US 6767451 B2	27 July 2004
		DE 60108007 D1	03 February 2005
		DE 60108007 T2	08 December 2005
		EP 1170355 A1	09 January 2002
		EP 1170355 B1	29 December 2004
		CA 2352018 A1	05 January 2002
		CA 2352018 C	02 February 2010
		ES 2236159 T3	16 July 2005
CN 101045667 A	03 October 2007	CN 101045667 B	12 May 2010
US 4966681 A	30 October 1990	EP 0259156 A1	09 March 1988
		AU 7780087 A	10 March 1988
		AU 607435 B2	07 March 1991
		JP S6384632 A	15 April 1988
		EP 0416041 A1	13 March 1991
		EP 0416041 A4	11 September 1991
		WO 9011340 A1	04 October 1990
		CA 1302936 C	09 June 1992
		AU 4033989 A	22 October 1990
		AU 620134 B2	13 February 1992
		EP 0489723 A2	10 June 1992
US 2013172173 A1	04 July 2013	EP 2591071 A1	15 May 2013
		EP 2591071 B1	12 December 2018
		TR 201903230 T4	21 March 2019
		WO 2012004805 A1	12 January 2012

Form PCT/ISA/210 (patent family annex) (January 2015)

REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- CN 1978411 B [0003]
- CN 102899078 A [0004]
- CN 101045667 B [0005]
- CN 109370644 A [0006]