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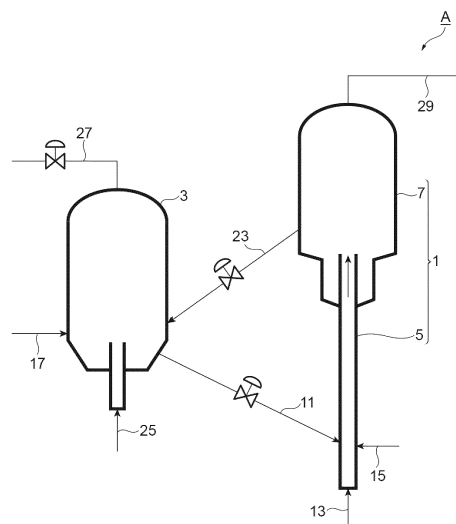
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(54) **METHOD FOR PRODUCING HYDROCARBONS**

Fig.2



Description**Technical Field**

[0001] The present disclosure relates to a method for producing a hydrocarbon.

Background Art

[0002] In domestic refineries in Japan, fluid catalytic cracking (FCC) units play a central role in the production of hydrocarbons (for example,

Patent Literature 1).

[0003] FIG. 1 is a flow chart illustrating an example of a conventional method for producing hydrocarbons from crude oil. In the conventional method for producing hydrocarbons, as shown in FIG. 1, for example, hydrocarbons are produced by using a desulfurized atmospheric residue and a desulfurized vacuum gas oil, which are obtained by treating an atmospheric residue in a residue desulfurization unit, as feedstocks and treating the feedstocks in a fluid catalytic cracking unit.

[0004] Furthermore, as environmental awareness is increasing, attention has been paid to FT synthetic oil having lower sulfur content and nitrogen content as compared with petroleum. FT synthetic oil is produced by Fischer-Tropsch synthesis from synthesis gas, which is a gas mixture of hydrogen gas and carbon monoxide gas. For example, Patent Literature 2 discloses a technology for producing hydrocarbons by treating the FT synthetic oil as a feedstock in a fluid catalytic cracking unit.

Citation List**Patent Literature**

[0005]

Patent Literature 1: Japanese Unexamined Patent Publication No. 2020-186384

Patent Literature 2: Japanese Unexamined Patent Publication No. 2007-503503

Summary of Invention**Technical Problem**

[0006] Coke produced from feedstocks in the course of fluid catalytic cracking adheres to the surface of catalysts. The fluid catalytic cracking unit regenerates catalysts and also utilizes the coke as its own heat source by sending coke-attached catalysts to a regenerator and combusting coke within the regenerator.

[0007] However, as a result of studies conducted by the inventors of the present invention, it was found that when FT synthetic oil is treated in a fluid catalytic cracking unit, the amount of coke produced during fluid catalytic cracking is small, and there is a possibility that the heat source of the fluid catalytic cracking unit may be insufficient as compared to the case of treating oil derived from petroleum. That is, it is difficult to maintain the heat balance of the fluid catalytic cracking unit, and there is room for improvement from the viewpoint of stable operation of the fluid catalytic cracking unit. When a fluid catalytic cracking unit cannot operate stably, the utilization rate of the fluid catalytic cracking unit decreases, which leads to an increase in the production cost for hydrocarbons.

[0008] Thus, an aspect of the present disclosure provides a method for producing a hydrocarbon, which method uses FT synthetic oil as a feedstock and allows stable operation.

Solution to Problem

[0009] An aspect of the present disclosure relates to a method for producing a hydrocarbon, the method including a step of subjecting a feedstock to fluid catalytic cracking by using a fluid catalytic cracking unit including a reactor and a regenerator, in which the feedstock includes FT synthetic oil, and a feed temperature x (unit: $^{\circ}\text{C}$) of the feedstock, a feed rate y_1 (unit: ton/h) of the feedstock, a feed rate y_2 (unit: ton/h) of a fuel oil to be fed into the regenerator, and a circulation rate z_1 (unit: ton/h) of a catalyst circulating through the reactor and the regenerator, satisfy the following Inequality Expression (1).

$$\frac{1}{575}x + \frac{3}{23}y + \frac{9}{184}z - 1 \geq 0 \quad (1)$$

$$y = (y_2/y_1) \times 100$$

$$z = (z_1/y_1)$$

[0010] According to an embodiment, the feedstock may further include a hydrocarbon oil having a higher %C_A than the FT synthetic oil. According to an embodiment, the hydrocarbon oil may include a desulfurized atmospheric residue.

[0011] According to an embodiment, the above-described method for producing a hydrocarbon may further include: a step of mixing FT synthetic oil and a hydrocarbon oil having a higher %C_A than the FT synthetic oil to obtain a feedstock; and a step of feeding the feedstock into the reactor of the fluid catalytic cracking unit. According to an embodiment, the hydrocarbon oil may include clarified oil.

Advantageous Effects of Invention

[0012] According to an aspect of the present disclosure, there is provided a method for producing a hydrocarbon, which method uses FT synthetic oil as a feedstock and enables stable operation.

Brief Description of Drawings

[0013]

[FIG. 1] FIG. 1 is a flowchart illustrating an example of a conventional method for producing a hydrocarbon from crude oil.

[FIG. 2] FIG. 2 is a schematic view illustrating an example of a fluid catalytic cracking unit used for a method for producing a hydrocarbon according to an embodiment.

[FIG. 3] FIG. 3(a) is a graph plotting set values of x and y, while plotting x on the axis of abscissa and y on the axis of ordinate, for Examples and Comparative Examples in which z is 4. FIG. 3(b) is a graph plotting set values of x and y, while plotting x on the axis of abscissa and y on the axis of ordinate, for Examples and Comparative Examples in which z is 8. FIG. 3(c) is a graph plotting set values of x and y, while plotting x on the axis of abscissa and y on the axis of ordinate, for Examples and Comparative Examples in which z is 12.

Description of Embodiments

[0014] Embodiments of the present disclosure will be described below with reference to the drawings. However, the present disclosure is not limited to the following embodiments and is indicated by the scope of claims, and it is intended that all changes in the meaning and the scope equivalent to the scope of claims are included. In each of the drawings, a portion of the configuration may be shown in an exaggerated or simplified manner for the convenience of explanation. In addition, the dimensional ratio of each part may be different in each of the drawings. In the following description of the drawings, the same or similar parts may be assigned with the same or similar reference numerals.

[0015] In the present specification, a synthetic oil produced by Fischer-Tropsch synthesis is referred to as "FT synthetic oil". In the present specification, a wax component included in the FT synthetic oil is referred to as "FT wax". In the present specification, an FT synthetic oil produced by Fischer-Tropsch synthesis and not subjected to distillation is referred to as "FT crude oil". In the present specification, with regard to "ton", not the yard-pound system but the metric system is adopted. That is, 1 ton is 1000 kg.

[0016] In the present specification, the term %C_A means an n-d-m method value (aromatic content). Specifically, %C_A is calculated by the following procedure. That is, the specific gravity (d₄⁷⁰) and the refractive index (n_d⁷⁰) of the feedstock at 70°C are measured. α is calculated by substituting the measured values into the following Formula (a1). With regard to the calculated α, a value determined by substituting α into the following Formula (a2) in a case where α is more than 0, and into the following Formula (a3) in a case where α is less than 0, is the %C_A of the feedstock. The following Formulas (a1) to (a3) are defined with reference to the standard "ASTM D3238". In Formulas (a2) and (a3), M represents the average molecular weight.

$$\alpha = 2.42(n_d^{70} - 1.4600) - (d_4^{70} - 0.8280) \dots (a1)$$

$$\%C_A = 410\alpha + 3660/M \dots (a2)$$

$$\%C_A = 720\alpha + 3660/M \dots (a3)$$

[0017] A method for producing a hydrocarbon according to an embodiment will be described below. The method for producing a hydrocarbon of the present embodiment includes a step of subjecting a feedstock to fluid catalytic cracking by using a fluid catalytic cracking unit including a reactor and a regenerator. The feedstock includes FT synthetic oil. The feed temperature x (unit: °C) of the feedstock, the feed rate y_1 (unit: ton/h) of the feedstock, the feed rate y_2 (unit: ton/h) of the fuel oil to be fed into the regenerator, and the circulation rate z_1 (unit: ton/h) of the catalyst circulating through the reactor and the regenerator, satisfy the following Inequality Expression (1). The following Inequality Expression (1) is derived based on the simulation results of the Examples that will be described below. A specific method for derivation will be described below. It has been revealed by the studies of the present inventors that in the following Inequality Expression (1), factors other than y_1 , y_2 , and z_1 do not affect stable operation of the method for producing a hydrocarbon according to the present embodiment.

$$\frac{1}{575}x + \frac{3}{23}y + \frac{9}{184}z - 1 \geq 0 \quad (1)$$

$$y = (y_2/y_1) \times 100$$

$$z = (z_1/y_1)$$

<Method for producing FT synthetic oil>

[0018] First, an outline of a method for producing FT synthetic oil that is used in the method for producing a hydrocarbon according to the present embodiment will be described. FT synthetic oil is produced by Fischer-Tropsch synthesis, for example, using carbon monoxide and hydrogen gas as feedstocks. The method for producing the FT synthetic oil is not particularly limited, and a known method can be employed. The reaction unit for producing the FT synthetic oil is preferably a fixed bed reaction unit or a slurry fluidized bed reaction unit. In addition, it is preferable to perform the reaction under the conditions in which the conversion rate of carbon monoxide, which is a feedstock, is set to be 50% or more, and even more preferably in the range of 70 to 90%.

[0019] As the slurry fluidized bed reaction unit, for example, a bubbling column type fluidized bed reaction unit can be used. A bubbling column type fluidized bed reaction unit has a reactor that performs Fischer-Tropsch synthesis. Inside the reactor of the bubbling column type fluidized bed reaction unit, liquid hydrocarbons that are liquid at the reaction temperature are accommodated. A catalyst for FT synthesis is dispersed in the liquid hydrocarbons, and the liquid hydrocarbons are in a slurry state. Synthesis gas, which is a gas mixture of carbon monoxide gas and hydrogen gas, is introduced into the liquid hydrocarbons from the lower part of the reactor. The synthesis gas dissolves in the liquid hydrocarbons while rising in the liquid hydrocarbons after becoming bubbles, and comes into contact with the catalyst for FT synthesis. The FT synthetic oil is produced from the synthesis gas by the function of the catalyst for FT synthesis.

[0020] The reaction temperature can be determined depending on the target carbon monoxide conversion rate; however, the reaction temperature is preferably 150 to 300°C, and more preferably 170 to 250°C.

[0021] The reaction pressure is preferably 0.5 to 5.0 MPa, and more preferably 2.0 to 4.0 MPa. When the reaction pressure is 0.5 MPa or more, there is a tendency that the carbon monoxide conversion rate is likely to be 50% or higher, and when the reaction pressure is 5.0 MPa or less, there is a tendency that the occurrence of local heat generation can be suppressed.

[0022] Synthesis gas is obtained by, for example, reforming of hydrocarbons such as natural gas. Synthesis gas only needs to include carbon monoxide gas and hydrogen gas and may be a gas other than a gas obtained by reforming of natural gas or the like.

[0023] The hydrogen/carbon monoxide ratio (molar ratio) in the synthesis gas is preferably 0.5 to 4.0, and more preferably 1.0 to 2.5. When this molar ratio is 0.5 or higher, the reaction temperature does not increase too high while deactivation of the catalyst tends to be suppressed, and when the molar ratio is 4.0 or lower, there is a tendency that production of methane, which is an undesirable byproduct, can be suppressed.

[0024] The gas space velocity of the synthesis gas is preferably 500 to 5000 h⁻¹, and more preferably 1000 to 2500 h⁻¹. When this gas space velocity is 500 h⁻¹ or more, higher productivity is obtained with the same amount of catalyst, and when

the gas space velocity is 5000 h⁻¹ or less, there is a tendency that the conversion rate of carbon monoxide is likely to be 50% or higher.

[0025] As the catalyst for FT synthesis, a catalyst in which an active metal is supported on an inorganic carrier is used. Examples of the inorganic carrier include porous oxides such as silica, alumina, titania, magnesia, and zirconia. Examples of the active metal include cobalt, ruthenium, iron, and nickel. Furthermore, in the catalyst, a compound including a metal element such as zirconium, titanium, hafnium, sodium, lithium, or magnesium may also be supported, in addition to the above-described active metals. These components improve the catalytic activity and contribute to the control of the number of carbon atoms and the distribution thereof in the FT synthetic oil.

[0026] The FT synthetic oil is, for example, a mixture of straight-chained hydrocarbons (normal paraffins) having 5 to 100 carbon atoms. The FT synthetic oil may be a synthetic oil produced by Fischer-Tropsch synthesis and may include straight-chained hydrocarbons having more than 100 carbon atoms. The FT synthetic oil includes almost none of aromatic hydrocarbons, naphthene, and isoparaffin. The FT synthetic oil has, for example, a %C_A of 0. Incidentally, the FT synthetic oil may have a %C_A of more than 0, for example, in a case where aromatic hydrocarbons are included.

[0027] The FT synthetic oil may include an FT wax having a boiling point of higher than 330°C. The FT wax is, for example, a mixture of straight-chained hydrocarbons (normal paraffins) having 17 or more carbon atoms. The percentage content of the FT wax in the FT synthetic oil may be 30% by mass or more, 50% by mass or more, 70% by mass or more, 90% by mass or more, or 95% by mass or more and may be 100% by mass. The percentage content of the FT wax in the FT synthetic oil can be easily controlled by appropriately adjusting the above-described reaction conditions.

<Method for producing hydrocarbon>

[0028] Next, an outline of the method for producing a hydrocarbon according to the present embodiment will be described. Hydrocarbons can be produced by treating a feedstock including FT synthetic oil in a fluid catalytic cracking unit.

[0029] The %C_A of the feedstock may be, for example, 0, may be 1 or more, may be 5 or more, may be 6 or more, or may be 7 or more. The %C_A of the feedstock may be 23 or less, may be 22 or less, or may be 21 or less.

[0030] The FT synthetic oil included in the feedstock may be an oil produced by Fischer-Tropsch synthesis and is not particularly limited. The FT synthetic oil included in the feedstock may be, for example, an FT crude oil, may be an oil obtained by distilling FT crude oil, may be an FT wax, or may be a mixture of these.

[0031] The feedstock may further include a hydrocarbon oil having a higher %C_A than the FT synthetic oil. In this case, in the step of treating the feedstock by using a fluid catalytic cracking unit, the feedstock may be obtained by mixing the FT synthetic oil and a hydrocarbon oil having a higher %C_A than the FT synthetic oil before the feedstock is fed into the reactor of the fluid catalytic cracking unit. As the FT synthetic oil and the hydrocarbon oil are mixed before the feedstock is fed into the reactor of the fluid catalytic cracking unit, the oil constituting the feedstock becomes more uniform as compared to the case where the FT synthetic oil and the hydrocarbon oil are mixed in the reactor. Therefore, the fluid catalytic cracking reaction in the reactor tends to be more stable.

[0032] The above-described hydrocarbon oil is obtained from, for example, refining. Examples of the above-described hydrocarbon oil include RDS-BTM, DS-VGO, and CLO. As shown in FIG. 1, RDS-BTM is a desulfurized atmospheric residue obtained by treating an atmospheric residue in a residue desulfurization unit. The atmospheric residue is obtained by treating crude oil in an atmospheric distillation unit. As shown in FIG. 1, DS-VGO is, for example, a desulfurized vacuum gas oil obtained by treating an atmospheric residue in a vacuum gas oil desulfurization unit. RDS-BTM may or may not include a solvent deasphalted vacuum residual oil as a feedstock thereof. As shown in FIG. 1, CLO (CLarified Oil) is, for example, a product obtained by removing a catalyst from a slurry oil, which is a residual oil obtained by treating RDS-BTM or DS-VGO in a fluid catalytic cracking unit to obtain an oil and further treating the obtained oil in an atmospheric distillation unit. CLO may or may not include FT synthetic oil as a feedstock thereof.

[0033] In a case where the feedstock includes RDS-BTM, the proportion occupied by RDS-BTM in RDS-BTM and FT synthetic oil is 1% by mass or more based on the total mass of RDS-BTM and FT synthetic oil, and the proportion may be 15% by mass or more, may be 30% by mass or more, or may be 45% by mass or more.

[0034] The proportion occupied by RDS-BTM in RDS-BTM and FT synthetic oil is 98% by mass or less based on the total mass of RDS-BTM and FT synthetic oil, and the proportion may be 75% by mass or less, or may be 50% by mass or less.

[0035] The %C_A of RDS-BTM is 5 or more and may be 10 or more, or may be 20 or more. The %C_A of RDS-BTM is 99 or less and may be 80 or less, or may be 60 or less.

[0036] In a case where the feedstock includes DS-VGO, the proportion occupied by DS-VGO in DS-VGO and FT synthetic oil is 1% by mass or more based on the total mass of DS-VGO and FT synthetic oil, and the proportion may be 15% by mass or more, may be 30% by mass or more, or may be 45% by mass or more.

[0037] The proportion occupied by DS-VGO in DS-VGO and FT synthetic oil is 98% by mass or less based on the total mass of DS-VGO and FT synthetic oil, and the proportion may be 75% by mass or less or may be 50% by mass or less.

[0038] The %C_A of DS-VGO is, for example, 1 or more and may be 5 or more, or may be 10 or more. The %C_A of DS-VGO is 99 or less and may be 80 or less, or may be 60 or less.

[0039] In a case where the feedstock includes CLO, the proportion occupied by CLO in CLO and FT synthetic oil is 1% by mass or more based on the total mass of CLO and FT synthetic oil, and the proportion may be 15% by mass or more, may be 30% by mass or more, or may be 45% by mass or more.

[0040] The proportion occupied by CLO in CLO and FT synthetic oil is 98% by mass or less based on the total mass of CLO and FT synthetic oil, and the proportion may be 75% by mass or less or may be 50% by mass or less.

[0041] The %C_A of CLO is, for example, 1 or more and may be 5 or more, may be 10 or more, or may be 20 or more. The %C_A of CLO is 99 or less and may be 80 or less, or may be 60 or less.

[0042] RDS-BTM, DS-VGO, and CLO may be used in combination of two or more kinds such that the %C_A of the feedstock is within the range of the above-mentioned upper limit value and lower limit value.

[0043] The fluid catalytic cracking unit used for fluid catalytic cracking of the feedstock is not particularly limited. Regarding the fluid catalytic cracking unit, a known fluid catalytic cracking unit can be used. FIG. 2 is a schematic view illustrating an example of the fluid catalytic cracking unit used for the method for producing a hydrocarbon according to the present embodiment. A fluid catalytic cracking unit A includes: a reactor 1; a regenerator 3; a line 15 connecting to the reactor 1; a line 17 connecting to the regenerator; a line 11 connecting the reactor 1 and the regenerator 3; a line 23 connecting the reactor 1 and the regenerator 3; a line 27 connecting the regenerator 3 and a boiler (not shown in the drawing); a line 29 connecting the reactor 1 and a recovery unit (not shown in the drawing); and a heating unit (not shown in the drawing) for heating the reactor.

[0044] The reactor 1 is a riser type. The reactor 1 includes a reaction zone 5 and a separation zone 7. The reactor 1 is fed with a feedstock and innumerable catalyst particles (cracking catalyst). The feedstock is fed into the reaction zone 5 through the line 15. In a case where the feedstock further includes a hydrocarbon oil having a higher %C_A than the FT synthetic oil, the feedstock may be obtained by mixing the FT synthetic oil and the hydrocarbon oil in the line 15. In this case, the line 15 may branch off from the middle. By feeding the FT synthetic oil through one branched line of the line 15 and feeding the hydrocarbon oil through the other line, the FT synthetic oil and the hydrocarbon oil are mixed at the confluence of the branched lines, and the feedstock is obtained. Furthermore, in a case where the feedstock further includes a hydrocarbon oil having a higher %C_A than the FT synthetic oil, a mixture obtained by mixing the FT synthetic oil and the hydrocarbon oil in advance may be fed as the feedstock to the reaction zone 5 through the line 15.

[0045] The catalyst particles are fed into the reaction zone 5 through the line 11. In the reaction zone 5, a fluidizing gas 13, which is steam, is blown from the lower part of a layer formed of the catalyst particles. The catalyst particles are fluidized by the fluidizing gas 13. The feedstock and the fluidized catalyst particles move up through the reaction zone 5 together with the fluidizing gas 13. When the feedstock comes into contact with the catalyst particles in the reaction zone 5, catalytic cracking occurs, and hydrocarbons are produced from the feedstock. The hydrocarbons obtained by cracking the feedstock and the catalyst particles used for catalytic cracking are separated in the separation zone 7.

[0046] The separated hydrocarbons are fed into the recovery unit through the line 29. The hydrocarbons are separated into a plurality of components and recovered in the recovery unit. The recovery unit may include, for example, a plurality of distillation columns, absorbers, compressors, strippers, fractionators, splitters, and heat exchangers. The hydrocarbons are fractionated into, for example, gas components and hydrocarbon oil in the distillation column (atmospheric distillation column). The gas components include dry gas and LP gas (LPG). Examples of the hydrocarbon oil include a gasoline fraction (CCG), a gas oil fraction (LCO), a kerosene fraction, clarified oil (CLO), and coke. The recovered clarified oil (CLO) may be fed into the reactor 1 as a feedstock.

[0047] The separated catalyst particles are fed into the regenerator 3 through the line 23. Coke generated during catalytic cracking is attached to the surface of the catalyst particles fed into the regenerator 3, and the catalyst particles have deteriorated catalytic activity. In the regenerator 3, the catalyst particles used for catalytic cracking are regenerated. Air 25 is supplied to the regenerator 3 for the regeneration treatment. In the regenerator 3, by combusting the coke attached to the surface of the catalyst particles, the amount of coke attached to the surface of the catalyst particles is reduced, and at the same time, the temperature of the catalyst particles is increased. The catalyst particles after regeneration are fed into the reaction zone 5 again through the line 11. That is, the catalyst particles circulate between the regenerator 3 and the reactor 1. High-temperature carbon monoxide gas and carbon dioxide gas generated in the course of the regeneration treatment are supplied to, for example, a boiler (not shown in the drawing) or a heat exchanger (not shown in the drawing) through the line 27. In a case where the carbon monoxide gas and carbon dioxide gas generated in the course of the regeneration treatment are supplied to a heat exchanger, for example, the gases are utilized for increasing the temperature of the feedstock.

[0048] A fuel oil is fed into the regenerator 3 through the line 17. As the fuel oil fed into the regenerator 3 is combusted in the regenerator 3, heat is generated. The heat generated by combustion of the fuel oil is utilized for increasing the temperature of the catalyst particles in the regenerator 3. The catalyst particles heated by the fuel oil can suppress, when fed again into the reaction zone 5, a decrease in the temperature of the feedstock as compared to the case where the catalyst particles are not heated by the fuel oil.

[0049] As the fuel oil fed into the regenerator 3 is combusted in the regenerator 3, high-temperature carbon monoxide gas, carbon dioxide gas, and the like are also generated. The high-temperature carbon monoxide gas, carbon dioxide gas,

and the like generated by combustion of the fuel oil are fed into, for example, a boiler (not shown in the drawing) or a heat exchanger (not shown in the diagram) through the line 27 and serves as one of heat sources for the fluid catalytic cracking unit. In a case where the carbon monoxide gas and carbon dioxide gas generated in the course of the regeneration treatment are supplied to a heat exchanger, for example, the gases are utilized for increasing the temperature of the feedstock.

[0050] Therefore, not only the coke attached to the catalyst fed into the regenerator 3 through the line 23 but also the fuel oil fed into the regenerator 3 through the line 17 may be heat sources for the fluid catalytic cracking unit A. Accordingly, by feeding the fuel oil to the regenerator 3, the number of heat sources for the fluid catalytic cracking unit A is increased as compared to the case where only the coke attached to the catalyst fed into the regenerator 3 through the line 23 is combusted inside the regenerator 3. Since the fluid catalytic cracking reaction is an endothermic reaction, it is easier to maintain the heat balance of the fluid catalytic cracking unit A, and stable operation of the fluid catalytic cracking unit A can be more easily realized.

[0051] The feed rate y_1 of the feedstock is the rate of the feedstock to be fed into the reaction zone 5 through the line 15. The feed rate y_1 of the feedstock is, for example, 0.1 [ton/h] or more and may be 1 [ton/h] or more, or may be 10 [ton/h] or more. The feed rate y_1 of the feedstock is, for example, 3000 [ton/h] or less and may be 2000 [ton/h] or less, or may be 1000 [ton/h] or less.

[0052] The feed temperature x of the feedstock is the temperature of the feedstock at the time when the feedstock is fed into the reactor 1. The feed temperature x of the feedstock is, for example, 150°C or higher and may be 200°C or higher, or may be 250°C or higher. The feed temperature x of the feedstock is, for example, 450°C or lower and may be 400°C or lower, or may be 350°C or lower.

[0053] The fuel oil to be fed into the regenerator 3 is not particularly limited as long as it is an oil that can be combusted in the regenerator 3. Examples of the fuel oil to be fed into the regenerator 3 include FT synthetic oil, RDS-BTM, DS-VGO, and CLO.

[0054] The value y obtained by dividing the feed rate y_2 of the fuel oil to be fed into the regenerator 3 by the feed rate y_1 of the feedstock and multiplying the resultant by 100, is, for example, 0.1 or more and may be 1.5 or more, or may be 3 or more. y is, for example, 10 or less and may be 8 or less, or may be 6 or less.

[0055] A value obtained by dividing the circulation rate z_1 of the catalyst circulating between the reactor 1 and the regenerator 3 by the feed rate y_1 of the feedstock is a catalyst/oil ratio (z). The catalyst/oil ratio is 3 [mass/mass] or more and may be 4 [mass/mass] or more, may be 5 [mass/mass] or more, or may be 7.5 [mass/mass] or more. The catalyst/oil ratio is 50 [mass/mass] or less and may be 13 [mass/mass] or less, may be 12 [mass/mass] or less, 11 [mass/mass] or less, or may be 9 [mass/mass] or less.

[0056] The left-hand side of the above-described Inequality Expression (1) may be, for example, 1 or more or may be 2 or more.

[0057] The cracking catalyst used for fluid catalytic cracking may include, for example, an inorganic oxide (matrix component) and zeolite. The inorganic oxide may be, for example, at least one selected from the group consisting of kaolin, montmorillonite, halloysite, bentonite, alumina, silica, boria, chromia, magnesia, zirconia, titania, and silica-alumina. The zeolite may be, for example, at least any of natural zeolite and synthetic zeolite. The natural zeolite may be at least one selected from the group consisting of gmelinite, chabazite, dachiardite, clinoptilolite, faujasite, keyite, heulandite, levynite, erionite, sodalite, cancrinite, ferrierite, brewsterite, offretite, natrolite, and mordenite. The synthetic zeolite may be at least one selected from the group consisting of X-type zeolite, Y-type zeolite, USY-type zeolite, A-type zeolite, L-type zeolite, ZK-4-type zeolite, B-type zeolite, E-type zeolite, F-type zeolite, H-type zeolite, J-type zeolite, M-type zeolite, Q-type zeolite, T-type zeolite, W-type zeolite, Z-type zeolite, α -type zeolite, β -type zeolite, ω -type zeolite, ZSM-5-type zeolite, SAPO-5-type zeolite, SAPO-11-type zeolite, and SAPO-34-type zeolite.

[0058] The reaction temperature for the fluid catalytic cracking of the feedstock may be 500 to 700°C. In a case where the reaction temperature is 500°C or higher, there is a tendency that the cracking ratio is likely to be improved, and the yield of the gasoline fraction is likely to be improved. In a case where the reaction temperature is 700°C or lower, there is a tendency that excessive cracking reaction can be suppressed, and the yield of the gasoline fraction is likely to be improved.

[0059] The reaction time (contact time) of fluid catalytic cracking may be 0.5 to 10 seconds. In a case where the reaction time of fluid catalytic cracking is 0.5 seconds or more, there is a tendency that the cracking ratio is likely to be improved, and the yield of the gasoline fraction is likely to be improved. In a case where the reaction time (contact time) of fluid catalytic cracking is 10 seconds or less, there is a tendency that excessive cracking reaction can be suppressed, and the yield of the gasoline fraction is likely to be improved.

[0060] The mass of steam supplied to the fluid catalytic cracking unit A as a fluidizing gas 13 may be 2 to 50 parts by mass with respect to 100 parts by mass of the feedstock. In a case where the mass of steam is 2 parts by mass or more, the feedstock is sufficiently dispersed, and coking tends to be suppressed. In a case where the mass of steam is 50 parts by mass or less, the contact time can be prevented from becoming too short, and there is a tendency that the yield of the gasoline fraction is likely to be improved.

[0061] The pressure inside the reactor 1 where fluid catalytic cracking is performed may be 101325 to 3×10^5 Pa. In a

case where the pressure is 101325 Pa (standard pressure) or higher, the pressure of gases after cracking does not drop too much, and operation of the recovery unit tends to be stabilized. In a case where the pressure is 3×10^5 Pa or lower, the hydrocarbon partial pressure in the reactor 1 can be prevented from becoming too high, and the cracking ratio can be prevented from becoming too high. Therefore, excessive cracking reaction can be suppressed, and there is a tendency that the yield of the gasoline fraction is likely to be improved.

Examples

[0062] Hereinafter, the present disclosure will be described in more detail by way of Examples; however, the present disclosure is not intended to be limited to these Examples.

<Simulation of hydrocarbon production>

(Examples 1 to 21 and Comparative Examples 1 to 8)

[0063] Whether stable operation of hydrocarbon production by the fluid catalytic cracking unit A is possible was verified by simulation. Specifically, simulation of feeding a feedstock into the reactor 1 and subjecting the feedstock to fluid catalytic cracking to produce hydrocarbons was performed. The simulation was performed using "FCC-SIM™ ver 6.2" (trade name) manufactured by KBC Corporation. In the above-described Inequality Expression (1), x, y, and z were set as shown in Tables 1 to 3. For Examples and Comparative Examples in which z is 4, a graph plotting the set values of x and y, with x being plotted on the axis of abscissa and y being plotted on the axis of ordinate, is shown in FIG. 3(a). Also, for Examples and Comparative Examples in which z is 8, and Examples and Comparative Examples in which z is 12, graphs similar to the case where z is 4 are shown in FIG. 3(b) and FIG. 3(c), respectively.

[0064] Simulation was performed for feedstocks having the compositions shown in Tables 1 to 3. The density at 15°C, the sulfur content, the carbon residue content, the distillation characteristics, the aromatic content, the naphthene content, and the paraffin content for the material of each feedstock were assumed to have the values shown in Table 4. Regarding the distillation characteristics of the material of the feedstock, the 1-volume% distillation temperature (T1), the 10-volume% distillation temperature (T10), the 30-volume% distillation temperature (T30), the 50-volume% distillation temperature (T50), and the 70-volume% distillation temperature (T70) are shown in Table 4.

[0065] The carbon residue content of the material of a feedstock is a value measured by the method of JIS K 2270-2. The sulfur content of the material of the feedstock is a value measured by the method of JIS K 2541-4. The distillation characteristics of the material of the feedstock are values measured by ASTM D2887. The aromatic content, the naphthene content, and the paraffin content of the material of the feedstock are values measured by an n-d-m method.

[0066] A method for measuring the naphthene content and the paraffin content of the material of the feedstock will be described in detail. First, the specific gravity (d_4^{70}), the refractive index (n_d^{70}), and the sulfur content (SC) of the feedstock at 70°C are measured. β is calculated by substituting the measured values of the specific gravity and the refractive index of the feedstock at 70°C into the following Formula (b1). With regard to the calculated β , $\%C_R$ is calculated by substituting β into the following Formula (b2) in a case where β is more than 0, and into the following Formula (b3) in a case where β is less than 0. $\%C_P$ is calculated by substituting the $\%C_R$ into the following Formula (b4). $\%C_N$ is calculated by substituting the $\%C_R$ and the $\%C_A$ for the material of the feedstock measured by an n-d-m method (ASTM D3228-equivalent method) into the following Formula (b5). The following Formulas (b1) to (b5) are defined with reference to the standard "ASTM D3238". In Formula (b2) and Formula (b3), M represents the average molecular weight.

$$\beta = (n_d^{70} - 0.8280) - 1.11 \times (d_4^{70} - 1.460) \dots (b1)$$

$$\%C_R = 775\beta - 3 \times SC + 11500/M \dots (b2)$$

$$\%C_R = 1400\beta - 3 \times SC + 12100/M \dots (b3)$$

$$\%C_P = 100 - \%C_R \dots (b4)$$

$$\%C_N = \%C_R - \%C_A \dots (b5)$$

[0067] The feasibility of the simulation is shown in Tables 1 to 3. The fact that simulation is possible means that ROT is calculated for the set values (a solution is obtained by executing the simulation). The fact that simulation is impossible means that ROT is not calculated for the set values (a solution is not obtained by executing the simulation). ROT (Riser Outlet Temperature) is the temperature of hydrocarbons at the outlet of the reactor 1, through which the hydrocarbons heading from the reactor 1 to the recovery unit pass.

<Evaluation of stable operation>

(Examples 1 to 21 and Comparative Examples 1 to 8)

[0068] The results of the simulation were evaluated on the basis of the following criteria. The results are shown in Tables 1 to 3. When the ROT is 480°C or higher, it is considered that the unit can be stably operated by suppressing solidification of the produced oil or the catalyst (boggling).

(Criteria)

[0069]

A: The simulation is possible, and the ROT is 480°C or higher.

B: The simulation is impossible, or although the simulation is possible, the ROT is lower than 480°C.

[Table 1]

	Example 1	Example 2	Example 3	Example 4	Example 5	Example 6	Example 7	Example 8	Example 9	Example 10
Feedstock composition (% by mass)	100	100	100	100	100	100	100	100	100	100
FCC operation conditions	Z	4	4	4	4	4	4	4	8	8
	x (°C)	200	250	250	300	300	350	350	200	200
	y	3.5	4.5	2.8	4.5	2.2	1.5	3	2	3
Simulation results	Feasibility of simulation	Possible	Possible	Possible	Possible	Possible	Possible	Possible	Possible	Possible
	ROT (°C)	482	508	486	526	490	494	543	495	542
	Evaluation of stable operation	A	A	A	A	A	A	A	A	A

		Example 11	Example 12	Example 13	Example 14	Example 15	Example 16	Example 17	Example 18	Example 19	Example 20
Feedstock composition (% by mass)	FT wax	100	100	100	100	100	100	100	100	100	100
	z	8	8	8	8	8	8	12	12	12	12
	x (°C)	250	250	300	300	350	350	200	200	237.5	250
	y	1.3	3	0.7	1.5	0	1.5	0.5	1.5	0	0
Simulation results	Feasibility of simulation	Possible	Possible	Possible	Possible	Possible	Possible	Possible	Possible	Possible	Possible
	ROT (°C)	524	566	488	532	485	563	490	540	484	492
	Evaluation of stable operation	A	A	A	A	A	A	A	A	A	A

		Example 21	Comparative Example 1	Comparative Example 2	Comparative Example 3	Comparative Example 4	Comparative Example 5	Comparative Example 6	Comparative Example 7	Comparative Example 8
Feedstock composition (% by mass)	FT wax	100	100	100	100	100	100	100	100	100
	z	12	4	4	4	4	8	8	8	12
	x (°C)	250	200	250	300	350	200	250	300	200
	y	1.5	3	1.5	1.5	0	1.5	0	0	0
	FCC operation conditions	Possible	Possible	Impossible	Possible	Impossible	Possible	Impossible	Impossible	Possible
Simulation results	Feasibility of simulation									
	ROT (°C)	540	464	454°C or lower	458	454°C or lower	469	454°C or lower	454°C or lower	460
	Evaluation of stable operation	A	B	B	B	B	B	B	B	B

[Table 4]

		FT wax
Density at 15°C (g/cm ³)		0.82
Sulfur content (% by mass)		0.01
Carbon residue content (% by mass)		0.01
Aromatic content (%C _A)		0
Naphthene content (%C _N)		0
Paraffin content (%C _P)		100
Distillation characteristics (°C)	T1	249
	T10	330
	T30	391
	T50	438
	T70	450

[0070] The above-described Inequality Expression (1) was derived as follows. That is, for Examples and Comparative Examples in which the catalyst/oil ratio was 4, a first straight line was derived as a boundary line that distinguished between Examples 1 to 8, in which the evaluation of stable operation was A, and Comparative Examples 1 to 4, in which the same evaluation was B. The first straight line is a straight line passing through x (feed temperature of feedstock) and y (value obtained by dividing feed rate y₂ by feed rate y₁ and multiplying the resultant by 100) of Examples 1, 3, 5, and 7. The first straight line is represented by the following Formula (A1).

[0071] For Examples and Comparative Examples in which the catalyst/oil ratio was 8, a second straight line was derived as a boundary line that distinguished between Examples 9 to 16, in which the evaluation of stable operation was A, and Comparative Examples 5 to 7, in which the same evaluation was B. The second straight line is a straight line passing through x and y of Examples 9, 11, 13, and 15. The second straight line is represented by the following Formula (A2).

[0072] For Examples and Comparative Examples in which the catalyst/oil ratio was 12, a third straight line was derived as a boundary line that distinguished between Examples 17 to 21, in which the evaluation of stable operation was A, and Comparative Example 8, in which the same evaluation was B. The third straight line is a straight line passing through x and y of Examples 17 and 19. The third straight line is represented by the following Formula (A3). The first to third straight lines are shown in FIGS. 3(a) to 3(c), respectively.

$$Y1 = -\frac{1}{75}X1 + \frac{37}{6} \quad \text{(A1)}$$

[in Formula (A1), X1 represents the feed temperature of the feedstock at a catalyst/oil ratio of 4; and Y1 represents a value obtained by dividing the feed rate of the fuel oil to be fed into the regenerator by the feed rate of the feedstock and multiplying the resultant by 100, at the catalyst/oil ratio of 4.]

$$Y2 = -\frac{1}{75}X2 + \frac{14}{3} \quad \text{(A2)}$$

[in Formula (A2), X2 represents the feed temperature of the feedstock at a catalyst/oil ratio of 8; and Y2 represents a value obtained by dividing the feed rate of the fuel oil to be fed into the regenerator by the feed rate of the feedstock and multiplying the resultant by 100, at the catalyst/oil ratio of 8.]

$$Y3 = -\frac{1}{75}X3 + \frac{19}{6} \quad \text{(A3)}$$

[in Formula (A3), X3 represents the feed temperature of the feedstock at a catalyst/oil ratio of 12; and Y3 represents a value obtained by dividing the feed rate of the fuel oil to be fed into the regenerator by the feed rate of the feedstock and multiplying the resultant by 100, at the catalyst/oil ratio of 12.]

[0073] It can be verified that any four points on the straight lines represented by the above-described Formulas (A1) to (A3) exist on the same plane. The feed temperature of the feedstock at any point on the straight line represented by the

above-described Formula (A1) is designated as X11, and a value obtained by dividing the feed rate of the fuel oil to be fed into the regenerator by the feed rate of the feedstock and multiplying the resultant by 100 is designated as Y11. The feed temperature of the feedstock at any point on the straight line represented by the above-described Formula (A2) is designated as X12, and a value obtained by dividing the feed rate of the fuel oil to be fed into the regenerator by the feed rate of the feedstock and multiplying the resultant by 100 is designated as Y12. The feed temperature of the feedstock at any point on the straight line represented by the above-described Formula (A3) is designated as X13, and a value obtained by dividing the feed rate of the fuel oil to be fed into the regenerator by the feed rate of the feedstock and multiplying the resultant by 100 is designated as Y13. By simultaneously solving the following Formulas (A11) to (A13) represented by X11 to X13 and Y11 to Y13 for a, b, and c, a conditional expression (A21) serving as a boundary line that distinguishes between Examples, in which the evaluation of stable operation is A, and Comparative Examples, in which the same evaluation is B, is derived. Based on the conditional expression (A21), the above-described Inequality Expression (1) is derived as the ranges of the feed temperature of the feedstock allowing stable operation of the fluid catalytic cracking unit, the feed temperature of the fuel oil to be fed into the regenerator, and the catalyst/oil ratio.

$$X11a + Y11b + 4c + d = 0 \quad (A11)$$

$$X12a + Y12b + 8c + d = 0 \quad (A12)$$

$$X13a + Y13b + 12c + d = 0 \quad (A13)$$

$$\frac{1}{575}x + \frac{3}{23}y + \frac{9}{184}z - 1 = 0 \quad (A21)$$

[0074] Examples 1 to 21 satisfy the above-described Inequality Expression (1) (left-hand side is 0 or greater). On the other hand, Comparative Examples 1 to 8 do not satisfy the above-described Inequality Expression (1) (left-hand side is less than 0). From this, it could be verified that when the above-described Inequality Expression (1) is satisfied, the unit can be stably operated.

Reference Signs List

[0075] 1: reactor, 3: regenerator, A: fluid catalytic cracking unit.

Claims

1. A method for producing a hydrocarbon, the method comprising:

a step of subjecting a feedstock to fluid catalytic cracking by using a fluid catalytic cracking unit including a reactor and a regenerator,
wherein the feedstock to be fed into the reactor includes FT synthetic oil,
a feed temperature x (unit: °C) of the feedstock, a feed rate y1 (unit: ton/h) of the feedstock, a feed rate y2 (unit: ton/h) of a fuel oil to be fed into the regenerator, and a circulation rate z1 (unit: ton/h) of a catalyst circulating through the reactor and the regenerator satisfy the following Inequality Expression (1).

$$\frac{1}{575}x + \frac{3}{23}y + \frac{9}{184}z - 1 \geq 0 \quad (1)$$

$$y = (y2/y1) \times 100$$

$$z = (z1/y1)$$

2. The method for producing a hydrocarbon according to claim 1, wherein the feedstock further includes a hydrocarbon

oil having a higher %C_A than the FT synthetic oil.

3. The method for producing a hydrocarbon according to claim 2, wherein the hydrocarbon oil includes a desulfurized atmospheric residue.

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4. The method for producing a hydrocarbon according to claim 1, wherein in the step, the feedstock is obtained by mixing the FT synthetic oil and a hydrocarbon oil having a higher %C_A than the FT synthetic oil before the feedstock is fed into the reactor of the fluid catalytic cracking unit.

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5. The method for producing a hydrocarbon according to claim 4, wherein the hydrocarbon oil includes clarified oil.

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Fig.1

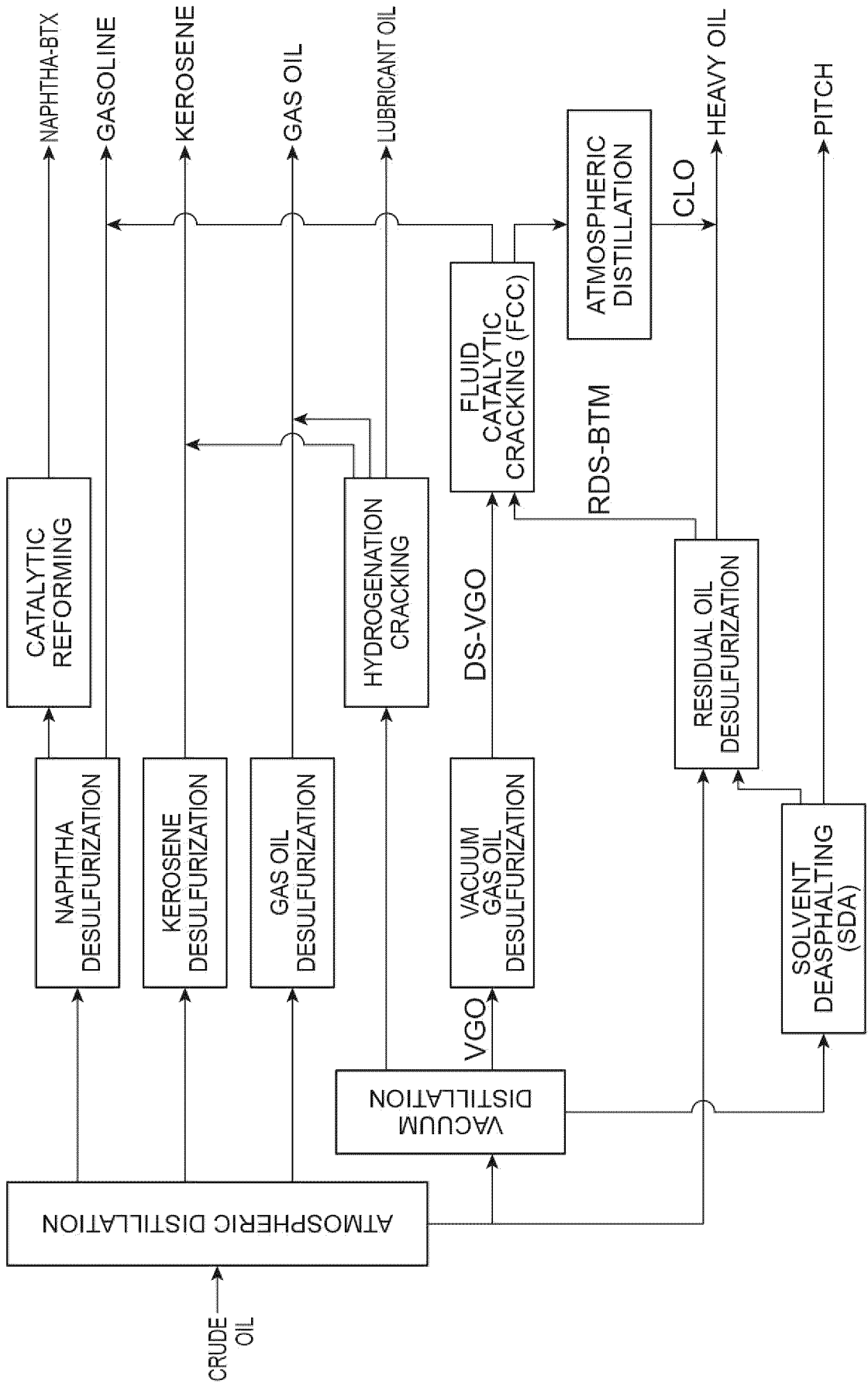


Fig.2

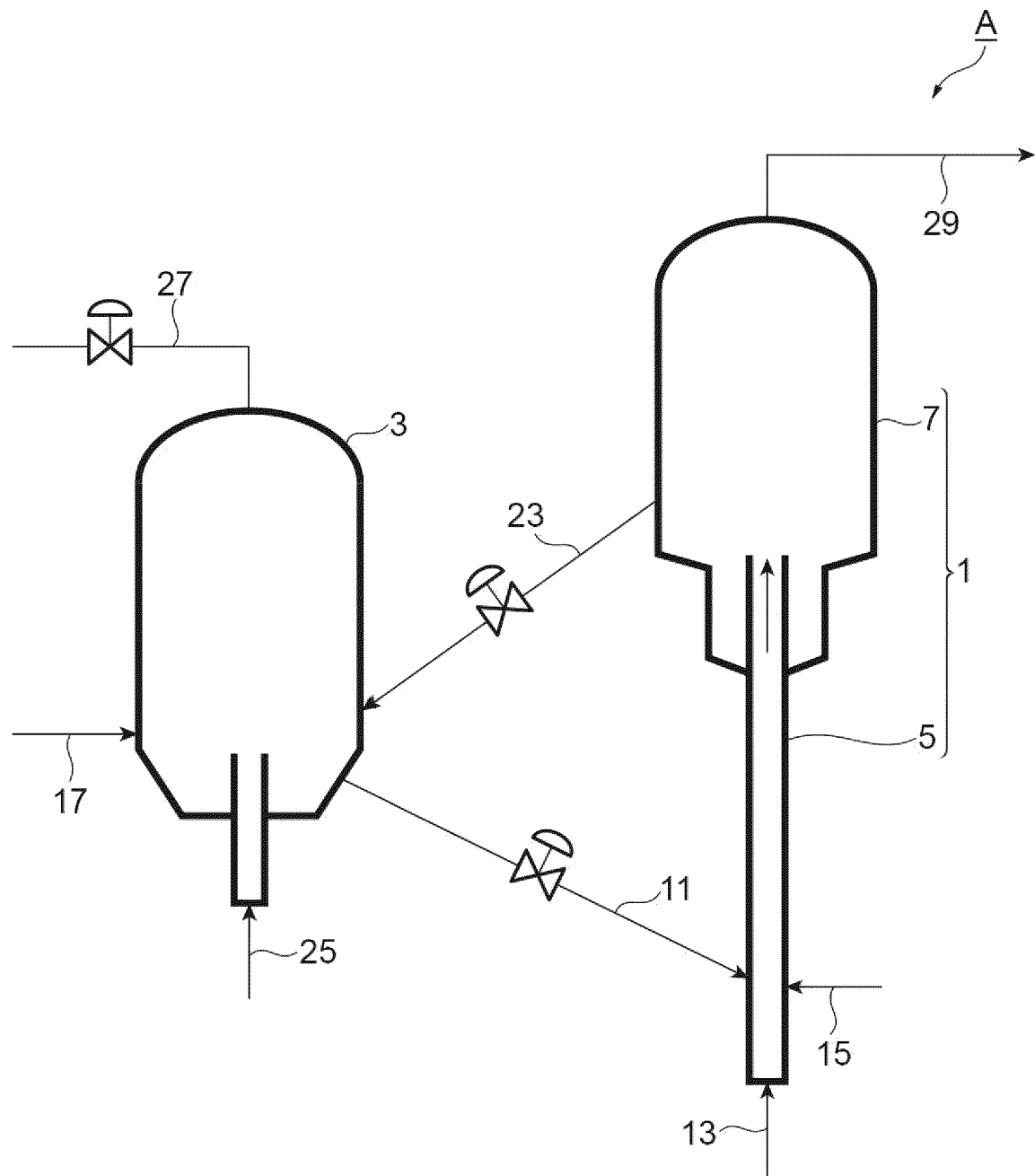
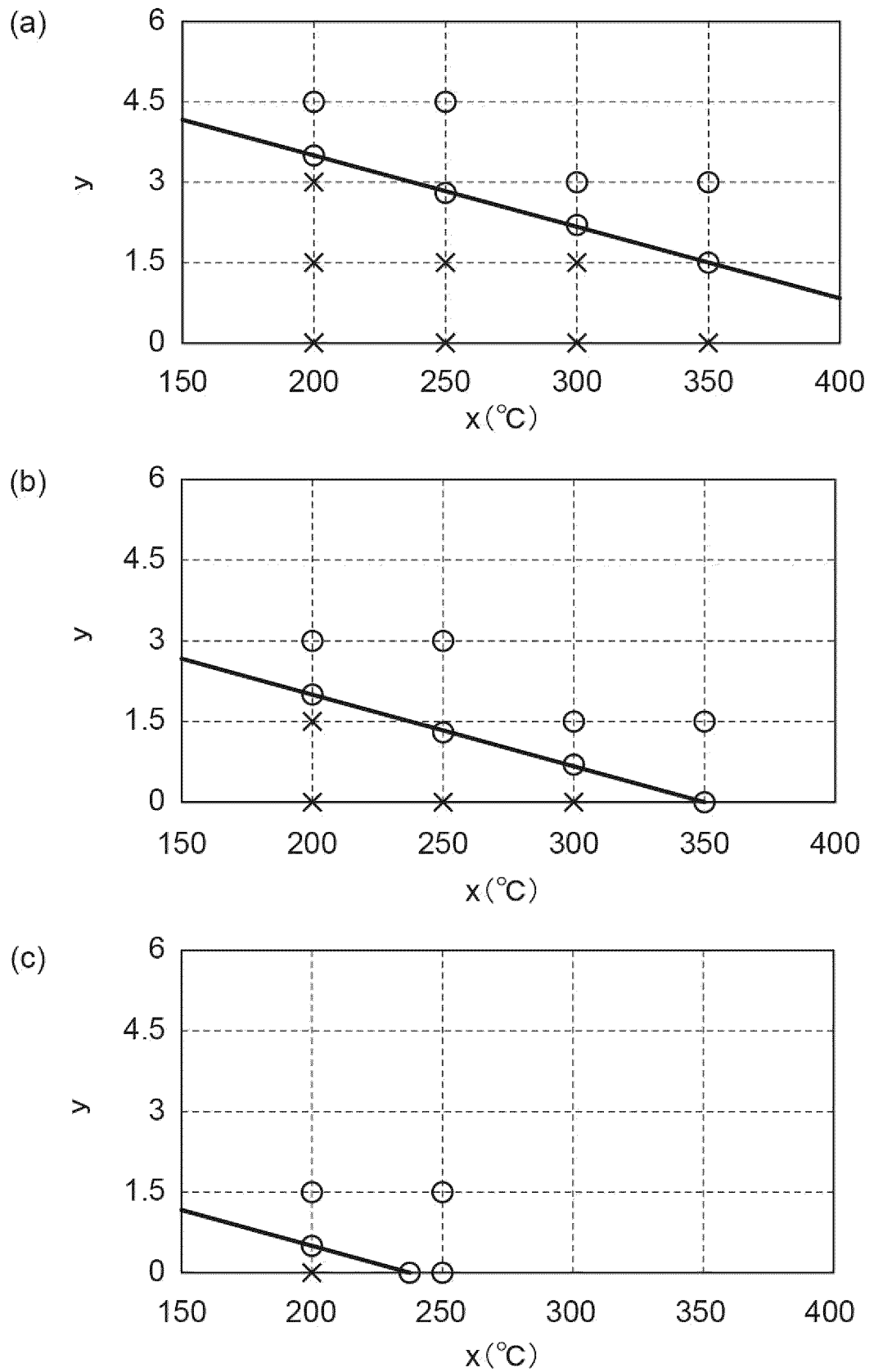


Fig.3

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2023/019726

A. CLASSIFICATION OF SUBJECT MATTER*C10G 11/18*(2006.01)i

FI: C10G11/18

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C10G11/18

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

Published examined utility model applications of Japan 1922-1996
 Published unexamined utility model applications of Japan 1971-2023
 Registered utility model specifications of Japan 1996-2023
 Published registered utility model applications of Japan 1994-2023

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	WO 2008/026635 A1 (NIPPON OIL CORPORATION) 06 March 2008 (2008-03-06)	1-5
A	JP 2008-500418 A (SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V.) 10 January 2008 (2008-01-10)	1-5
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A	US 4684756 A (MOBIL OIL CORPORATION) 04 August 1987 (1987-08-04)	1-5

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

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Date of the actual completion of the international search

15 June 2023

Date of mailing of the international search report

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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/JP2023/019726

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REFERENCES CITED IN THE DESCRIPTION

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