

SPECIFICATION

PROCESS FOR REMOVING TRACE METALS IN LIQUID HYDROCARBONS BY ADSORPTION AND APPARATUS THEREFOR

FIELD OF THE INVENTION

The present invention relates to a process for removing trace metals occurring in liquid hydrocarbons by adsorption and an apparatus therefor. More particularly, it relates to a process suitable for removing, by adsorption, trace metals, in particular mercury, occurring in natural gas condensates containing asphaltene which is a kind of crude oil, and to an apparatus therefor.

PRIOR ART

Mercury occurring in naphthas, natural gas condensates and like liquid hydrocarbons as feedstocks for petroleum products causes poisoning, hence activity deterioration, of catalysts, in particular noble metal catalysts (e.g. Pt, Pd), used in petroleum refining processes. In cases where hydrocarbon gases such as ethylene and propylene or liquid hydrocarbons such as naphthas are used as raw chemical materials, too, mercury acts as a catalyst poison and inhibits the activity of catalysts. Furthermore, mercury can form amalgams with a number of metals and therefore, particularly when aluminum-based alloys are used as equipment construction materials, amalgam corrosion becomes a matter of concern.

Therefore, various methods of removing mercury contained in liquid hydrocarbons have so far been investigated, and methods of removing mercury in which various adsorbents for mercury are used have been proposed. For example, the sulfide of a heavy metal such as

molybdenum, tungsten or vanadium as supported on a support of alumina or the like has been proposed as a mercury adsorbent (see e.g. Japanese Patent Publication No. 24623/1994). Further, a mercury adsorbent comprising sulfur supported on a porous support has been proposed. For example, sulfur-supporting active carbon prepared by admixing activated carbon with sulfur particle and heating the mixture at a specific temperature (see Japanese Patent Laid-Open No. 7891/1984) and activated carbon containing an organosulfur compound (see Japanese Patent Laid-Open No. 114632/1987) have been disclosed. When such mercury adsorbent is used, mercury reacts with the above metal sulfide or sulfur component and removed, in the form of mercury sulfide, from liquid hydrocarbons.

However, the above-mentioned methods of removing mercury by adsorption are generally intended for the treatment of naphthas. In the case of asphaltene-containing hydrocarbons, such as natural gas condensates, which contain asphaltene in larger amounts as compared with mercury, a large amount of asphaltene is adsorbed on the adsorbents for mercury and therefore the adsorbents soon become incapable of adsorbing mercury. A conceivable means for avoiding this is to remove asphaltene in natural gas condensates beforehand by adsorption. However, this means requires constant monitoring of the state of asphaltene adsorption, resulting in complicated operations therefor. If the timing of monitoring is wrong, the mercury-adsorbing activity will be immediately impaired.

SUMMARY OF THE INVENTION

Accordingly it is an object of the present invention to solve such problems as mentioned above and provide a process capable of removing trace metals in asphaltene-containing liquid hydrocarbons

by adsorption over a long period of time with high efficiency as well as an apparatus therefor.

The present inventors made intensive investigations in an attempt to solve the above problems and, as a result, found that the above problems can be solved when at least two first adsorption treatment zones are disposed in parallel for the adsorption of asphaltene in natural gas condensates and connected to each other in series such that either one is on the upstream side and the other is on the downstream side, for continuous operation and for changeover/exchange operation. Such and other findings have now led to completion of the present invention.

Thus, in a first aspect thereof, the present invention provides a process for removing trace metals in liquid hydrocarbons by adsorption using a first adsorption treatment zone comprising a bed packed with a porous inorganic adsorbent and a second adsorption treatment zone comprising a bed packed with a porous carbonaceous material, which process comprises the steps of:

- (1) using at least two such first adsorption zones disposed in parallel, connecting the same to each other in series such that either one is on the upstream side and the other is on the downstream side, and feeding a trace metal-containing liquid hydrocarbon to the upstream side first adsorption treatment zone,
- (2) contacting said liquid hydrocarbon with said porous inorganic adsorbent in said upstream side first adsorption treatment zone,
- (3) passing the adsorption-treated liquid hydrocarbon from said upstream side first adsorption treatment zone through the downstream side first adsorption treatment zone,
- (4) exchanging the adsorbent in said upstream side first adsorption treatment zone while continuing the adsorption treatment in said

downstream side first adsorption treatment zone,

(5) then changing the connection so that the first adsorption treatment zone in which the adsorbent exchange has been finished can now serve as the downstream side one,

(6) feeding said liquid hydrocarbon treated in said first adsorption treatment zone(s) to said second adsorption treatment zone, and

(7) contacting said liquid hydrocarbon with the porous carbonaceous material in said second adsorption treatment zone.

In a second aspect thereof, the invention provides an apparatus for removing trace metals in liquid hydrocarbons by adsorption using a first adsorption treatment zone comprising a bed packed with a porous inorganic adsorbent and a second adsorption treatment zone comprising a bed packed with a porous carbonaceous material, which apparatus comprises:

(1) at least two such first adsorption treatment zones disposed in parallel and connected via a piping to each other in series such that either one is on the upstream side and the other is on the downstream side,

(2) a piping for feeding liquid hydrocarbons to either of said at least two first adsorption treatment zones disposed in parallel such that the adsorbent in said upstream side first adsorption treatment zone can be exchanged while continuing the adsorption treatment in said downstream side first adsorption treatment zone, and a piping between said at least two first adsorption treatment zones disposed in parallel which piping has directional control valves,

(3) a piping connecting the downstream end of either of said first adsorption treatment zones to said second adsorption treatment zone or to one of a plurality of such second adsorption treatment zones, and

(4) a directional control valve disposed in said piping for feeding liquid

hydrocarbons from the downstream end of either of said first adsorption treatment zones to said second adsorption treatment zone or zones.

DETAILED DESCRIPTION OF THE INVENTION

The present invention will be hereinafter described in detail.

The liquid hydrocarbon to be subjected to treatment for removing trace metals by adsorption according to the invention is not limited to any particular species provided that it occurs as a liquid in its ordinary state. It may contain sulfur compounds, nitrogen compounds and like compounds in addition to trace metals. More specifically, there may be mentioned natural gas condensates, naphthas as raw materials for petrochemicals, blending stocks for various petroleum products such as naphthas, and the like. The process and apparatus of the invention are particularly effective in treating asphaltene-containing natural gas condensates.

The trace metals in said liquid hydrocarbons include mercury, arsenic, vanadium, nickel, etc. Among such trace metals, mercury the content of which is highest can be most effectively removed by the process and apparatus of the invention. While mercury may occur as elementary mercury, inorganic mercury or organic mercury, every form of mercury can be removed by adsorption according to the invention. In the practice of the invention, the metal contents in liquid hydrocarbons are not critical. Metals contained in large amounts can be removed almost completely. Natural gas condensates produced in Southeast Asia, for instance, generally may contain 10 to 5,000 ppb of mercury depending on producing areas, which can be removed by adsorption according to the invention. The content of asphaltene generally may be 1-100ppm, which can be efficiently removed by the process of the present invention.

As the porous inorganic adsorbent to be packed in the first adsorption treatment zones in the practice of the invention, there may be mentioned activated clay, silica gel, zeolites, alumina, silica alumina and the like, and mixtures of two or more of these. Among them, activated clay is preferred particularly in treating asphaltene-containing natural gas condensates owing to its adsorptivity and economical feature.

Activated clay is a product derived from acid clay, which is a kind of clay, by treatment with sulfuric acid or the like for further activity improvement. From the chemical composition viewpoint, it is composed of SiO_2 , Al_2O_3 , Fe_2O_3 , CaO , MgO and K_2O . It has a porous structure and has various catalytic activities and high adsorptivity. It is used as an adsorbent support in the practice of the invention.

The packed bed volume in the first adsorption treatment zones is preferably 5 to 30 times the packed bed volume in the second adsorption treatment zone or zones. By employing such packing volume ratio in treating asphaltene-containing liquid hydrocarbons such as natural gas condensates, the frequency of changeover in the first adsorption treatment zones due to asphaltene adsorption can be reduced.

The first adsorption zones each comprising a bed packed with said porous inorganic adsorbent are not limited in form and shape but include columns, drums and boxes, for instance.

The porous carbonaceous material to be packed in the second adsorption treatment zone or zones includes activated carbon, adsorbents produced by carbonization of synthetic resins, and the like. From the adsorptivity and economy viewpoint, activated carbon is preferred, however.

The active carbon to be used here may be any of wide varieties of

carbon material provided that it has a large specific surface area not less than $100 \text{ m}^2/\text{g}$ and high adsorptivity. The raw material for active carbon is not limited to any particular species. Thus, coal, coke, charcoal, boneblack and carbonization products derived from coconut husks, wood, resins and so forth can be used. The activation can be performed by treating with steam or carbon dioxide at a high temperature of 1,000 to 1,200 °C or by treating with zinc chloride, phosphoric acid, concentrated sulfuric acid or the like. Generally, an activating gas containing 15 to 60 % by volume of steam is used. However, for attaining further improvements in trace metal-adsorbing capacity, it is particularly desirable that the carbonaceous material be activated in an atmosphere containing not more than 15 % by volume of steam. As a specific feature of activated carbon, a specific surface area of 100 to 2,500 m^2/g is preferred and a specific surface area of 500 to 1,500 m^2/g is more preferred. The residue on ignition is preferably not more than 10 % by weight. By using an activated carbon species having these physical properties, the trace metal elimination efficiency can be further increased.

The form and shape of activated carbon are not critical. Thus, powdery, cylindrical, spherical, fiber and honeycomb forms may be used. Granulated or molded carbon can be prepared in the conventional manner by adding 30 to 60 parts of petroleum pitch or coal tar or the like as a binder to 100 parts of a carbonaceous material, followed by kneading, molding and activation.

In the practice of the invention, such activated carbon as mentioned above may be used singly or in the form of an adsorbent supporting thereon an alkali metal sulfide and/or an alkaline earth metal sulfide.

The amount of the alkali metal sulfide and alkaline earth metal

sulfide to be supported is not critical but preferably within the range of 0.1 to 30 % by weight relative to the support. An amount below 0.1 % by weight tends to lead to a decreased trace metal-adsorbing capacity. When supported in an amount exceeding 30 % by weight, such metal sulfides tend to inhibit adsorption by the support to thereby slow down the improvement in adsorptivity for trace metals.

Now, the process and apparatus of the invention are described step by step.

At least two first adsorption treatment zones having respective packed beds packed with the same porous inorganic adsorbent are disposed in parallel and connected in series via a piping such that either one is on the upstream side and the other is on the downstream side. A raw material liquid hydrocarbon, which contains the trace metals, is fed in the form of an ascending or descending stream to the upstream side first adsorption treatment zone, where said liquid hydrocarbon comes into contact with the porous inorganic adsorbent. The liquid hydrocarbon is then fed to the downstream side first adsorption treatment zone connected in series via a piping, for contacting in the same manner.

When the adsorptivity of the adsorbent in the upstream side first adsorption treatment zone is found decreased, adsorbent exchange is carried out, during which the downstream side first adsorption treatment zone alone or a plurality of remaining first adsorption treatment zones (when three or more first adsorption treatment zones are used) are operated consecutively for adsorption treatment by adequately operating the directional control valves and feeding the raw material liquid hydrocarbon thereto in the form of an ascending or descending stream. After completion of the adsorbent exchange, the upstream side first adsorption treatment zone is connected to the

downstream side of the downstream side first adsorption treatment zone in series and the two (or more) first zones are operated for adsorption treatment.

The liquid hydrocarbon treated by adsorption in the first adsorption treatment zones is then fed, through a connecting pipe, to the second adsorption treatment zone or zones as an ascending or descending stream. One second adsorption treatment zone may suffice but, from the longrun continuous operation and productivity viewpoint, it is desirable to dispose at least two second adsorption treatment zones and thereby enable feed line changeover by operating a directional control valve disposed in the piping from the downstream of the first adsorption treatment zones when the adsorptivity in one second adsorption treatment zone is found decreased. The connecting pipe from the downstream of the first adsorption treatment zones may be directly connected to the single second adsorption treatment zone or to at least two second adsorption treatment zones so that either one can serve as the upstream side and the other as the downstream side, as in the piping system for the first adsorption treatment zones.

For the contact of the liquid hydrocarbon with the adsorbents for trace metals in the first adsorption treatment zones and second adsorption treatment zone or zones, any of the fixed bed, moving bed, fluidized bed and ebullated bed systems can be employed. The fixed bed system is preferred, however, since the structure of each adsorption zone becomes simple and the operability is good.

Each fixed adsorbent bed can be prepared by packing the adsorption zone with the adsorbent having a powdery, ground, cylindrical, spherical, fibrous or honeycomb form. It is fixedly placed in position in the conventional manner. The trace metal-containing liquid hydrocarbon may be brought into contact with the adsorbent of trace

metals in the fixed bed either from above as a descending stream or from bottom as an ascending stream. From the viewpoint of stability of the adsorbent in the adsorption bed, however, feeding as a descending stream is preferred.

When such process and apparatus as mentioned above are employed in removing trace metals in liquid hydrocarbons, in particular 10 to 5,000 ppb of mercury contained in asphaltene-containing natural gas condensates, the first adsorption treatment zones mainly remove asphaltene by adsorption. In particular, since said apparatus comprises at least two first adsorption treatment zones disposed in parallel and connected in series, frequent checking for the state of adsorption of asphaltene is no more necessary if data on the course of adsorption of asphaltene are available in advance; it is only required to change periodically the liquid hydrocarbon feeding to the first adsorption treatment zones disposed in parallel from the upstream side to the downstream side. Even when the asphaltene content in the feedstock varies, i.e. increases, backup adsorption is possible in the first adsorption treatment zones connected in series. Furthermore, adsorbent exchange or regeneration is easy.

In the second adsorption treatment zone or zones, trace metals, in particular mercury, in liquid hydrocarbons can be removed by adsorption with high efficiency and good productivity, since asphaltene and like undesirable substances occurring in liquid hydrocarbons along with the trace metals are removed beforehand in the first adsorption treatment zones.

PREFERRED EMBODIMENTS

Now, referring to the drawing, the invention is described. Fig. 1 is a schematic flowchart illustrating an embodiment of the invention in

which two first adsorption treatment zones and one second adsorption treatment zone are combined. According to Fig. 1, an asphaltene- and mercury-containing liquid hydrocarbon (natural gas condensate) is fed through pipe 3, a three-way valve 4 and a pipe 5 to an adsorbent (activated clay)-packed first fixed bed 6 in a first adsorption treatment zone 1 in the form of a descending stream. The natural gas condensate after such asphaltene adsorption treatment is drawn out through a pipe 7 and fed, via a three-way valve 8, a pipe 9, a three-way valve 10 and a pipe 11, to an adsorbent-packed second fixed bed 12 connected in series in the first adsorption treatment zone 1, in the form of a descending stream. The adsorbent-packed second fixed bed 12 contains the same adsorbent as that in the adsorbent-packed first fixed bed 6 and serves to adsorb that portion of asphaltene and the like which has not been adsorbed on the adsorbent-packed first fixed bed 6. The mercury-containing natural gas condensate, now free of asphaltene, is drawn out via a pipe 13 and fed, via a three-way valve 14 and a pipe 15, to a mercury-adsorbing fixed bed 16 packed with activated carbon, in the form of a descending stream. The posttreatment natural gas condensate deprived of mercury by activated carbon is drawn out via a pipe 17.

When the adsorptivity of the adsorbent-packed first fixed bed 6 is found decreased, the three-way valve 4 for natural gas condensate feeding and other three-way valves 8, 10 and 14 are operated, so that the raw natural gas condensate can be fed, via a pipe 3', to the adsorbent-packed second fixed bed 12. The natural gas condensate deprived of asphaltene by adsorption is drawn out via the pipe 13 and fed, via the three-way valve 14 and the pipe 15, to the mercury-adsorbing fixed bed 16 for treatment in the same manner as mentioned above.

After completion of adsorbent exchange or regeneration in the adsorbent-packed first fixed bed, the three-way valves 8, 10 and 14 are operated, so that the natural gas condensate can be fed from adsorbent-packed second fixed bed to the adsorbent-packed first fixed bed 12 via pipes 6, 9 and 11'. The oil is thus again treated in two adsorbent-packed fixed beds and thereafter fed, via a pipe 13', the three-way valve 14 and the pipe 15, to the mercury-adsorbing fixed bed 16 for treatment in the same manner as mentioned above.

In cases where both adsorbents in the first adsorption treatment zone and the adsorbent in the second adsorption treatment zone are each in the form of a fixed bed, the natural gas condensate to be fed to each adsorption treatment zone may be fed in the form of an ascending stream, in lieu of the descending stream mentioned above, for passage through each packing, although this operation mode is not shown in Fig. 1.

The following example illustrates the invention in further detail.

EXAMPLE

A natural gas condensate (specific gravity 15/4 °C 0.75, initial boiling point 25 °C, end point 330 °C) containing 27 ppb of mercury, 3 ppm of asphaltene and 300 ppm of sulfur was subjected to treatment for removing mercury by treatment in the following first and second adsorption treatment zones under the conditions mentioned below.

First adsorption treatment zone:

- (1) Containers for adsorbent: Glass-made, 20 mm (dia.) × 800 mm × 2 containers.
- (2) Adsorbent: Activated clay produced by sulfuric acid treatment of acid clay, 200 ml × 2.
- (3) Adsorbent-packed fixed beds: The above containers each packed

with the above activated clay and further with glass wool at both ends were connected in series, as shown in Fig. 1, via a piping.

Second adsorption treatment zone:

- (1) Container for adsorbent: Glass-made, 10 mm (dia.) $\times$ 400 mm $\times$ 1 container.
- (2) Adsorbent: Activated carbon with specific surface area 1,200 m²/g (mean grain size 1.7 mm), 24 ml.
- (3) Adsorbent-packed fixed bed: The above container packed with activated carbon and further with glass wool at both ends was connected via a piping to the downstream end of the activated clay-packed container mentioned above, as shown in Fig. 1.

Adsorption conditions:

- (1) Temperature: 25 °C.
- (2) Flow rate: 1 ml/minute.
- (3) Adsorption treatment in first adsorption treatment zone: The upstream side and downstream side adsorbent-packed fixed beds were connected in series and adsorption treatment was carried out. The natural gas condensate feeding was changed from the upstream side to the downstream side at 2-hour intervals. During activated clay exchange in the upstream side adsorbent-packed fixed bed, the downstream side adsorbent-packed fixed bed alone was operated for adsorption treatment. Exchange of the adsorbent activated clay was completed within 2 hours, and the upstream side adsorbent-packed fixed bed was connected to the downstream side of the downstream side adsorbent-packed fixed bed so that the latter bed then could serve as the upstream side one. This adsorption treatment procedure was repeated.

Then, the natural gas condensate after adsorption treatment in the adsorbent-packed fixed beds in the first adsorption treatment zone

as drawn out from the downstream end was fed to the entrance of the adsorbent-packed fixed bed in the second adsorption treatment zone connected for further adsorption treatment.

For comparison, the above adsorption procedure was followed in the same manner except that only one adsorbent-packed container was used in the first adsorption treatment zone and adsorption treatment was performed continuously without changeover.

When the above process and apparatus of the invention were used, the mercury content in the condensate after adsorption treatment remained below 1 ppb over 10 days (operation period). With the comparative process and apparatus, said content exceeded 1 ppb in half a day.

The process and apparatus of the invention can remove trace metals occurring in liquid hydrocarbons, in particular asphaltene-containing natural gas condensates, with high efficiency without being affected by the adsorption of asphaltene. Furthermore, since changeover operation between the first adsorption treatment zones is possible, operation interruption otherwise caused by adsorbent exchange which becomes necessary due to a decrease in adsorbent's performance can be avoided and, as a result, good productivity can be attained.

BRIEF DESCRIPTION OF THE DRAWING

Fig. 1 is a flowchart illustrating an embodiment of the invention. The reference numeral 1 indicates a first adsorption treatment zone, 2 - a second adsorption treatment zone, 6 and 12 each - a first adsorbent-packed fixed bed, and 16 - a second adsorbent-packed fixed bed.

CLAIMS

1. A process for removing trace metals in liquid hydrocarbons by adsorption using a first adsorption treatment zone comprising a bed packed with a porous inorganic adsorbent and a second adsorption treatment zone comprising a bed packed with a porous carbonaceous material, which process comprises the steps of:

- (1) using at least two such first adsorption zones, connecting the same to each other in series such that either one is on the upstream side and the other is on the downstream side, and feeding a trace metal-containing liquid hydrocarbon to the upstream side first adsorption treatment zone,
- (2) contacting said liquid hydrocarbon with said porous inorganic adsorbent in said upstream side first adsorption treatment zone,
- (3) passing the adsorption-treated liquid hydrocarbon from said upstream side first adsorption treatment zone through the downstream side first adsorption treatment zone,
- (4) exchanging the adsorbent in said upstream side first treatment zone while continuing the adsorption treatment in said downstream side first adsorption treatment zone,
- (5) then changing the connection so that the first adsorption treatment zone in which the adsorbent exchange has been finished can now serve as the downstream side one,
- (6) feeding said liquid hydrocarbon treated in said first adsorption treatment zone(s) to said second adsorption treatment zone, and
- (7) contacting said liquid hydrocarbon with the porous carbonaceous material in said second adsorption treatment zone.

2. The process for removing trace metals in liquid hydrocarbons by adsorption as claimed in claim 1, wherein said porous inorganic adsorbent is at least one member selected from the group consisting of



activated clay, silica gel, zeolites, alumina and silica alumina and said porous carbonaceous material is active carbon.

3. The process for removing trace metals in liquid hydrocarbons by adsorption as claimed in claim 1 or 2, wherein said liquid hydrocarbon is a condensate oil containing asphaltene and a trace of mercury.

4. The process for removing trace metals in liquid hydrocarbons by adsorption as claimed in claim 1, wherein said first adsorption treatment zones are disposed in parallel each other.

5. An apparatus for removing trace metals in liquid hydrocarbons by adsorption using a first adsorption treatment zone comprising a bed packed with a porous inorganic adsorbent and a second adsorption treatment zone comprising a bed packed with a porous carbonaceous material, which apparatus comprises:

- (1) at least two such first adsorption treatment zones connected via a piping to each other in series such that either one is on the upstream side and the other is on the downstream side,
- (2) a piping for feeding liquid hydrocarbons to either of said at least two first adsorption treatment zones such that the adsorbent in said upstream side first adsorption treatment zone can be exchanged while continuing the adsorption treatment in said downstream side first adsorption treatment zone, and a piping between said at least two first adsorption treatment zones which piping has directional control valves,
- (3) a piping connecting the downstream end of either of said first adsorption treatment zones to said second adsorption treatment zone or to one of a plurality of such second adsorption treatment zones, and
- (4) a directional control valve disposed in said piping for feeding liquid hydrocarbons from the downstream end of either of said first adsorption



treatment zones to said second adsorption treatment zone or zones.

6. The apparatus for removing trace metals by adsorption in liquid hydrocarbons as claimed in claim 5, wherein the packed bed volume in the first adsorption treatment zones comprising said bed packed with a porous inorganic absorbent is 5 to 30 times the packed bed volume in the second adsorption treatment zone or zones.

7. The apparatus for removing trace metals by adsorption in liquid hydrocarbons claimed in claim 5, wherein the first adsorption treatment zones are disposed in parallel each other.

