

PATENT SPECIFICATION

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(72) Inventor JOANNES BAPTISTA WIJFFELS

(54) A PROCESS AND APPARATUS FOR HYDROTREATING A LIQUID PETROLEUM FRACTION



(71) We, SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V., a Company organised under the laws of The Netherlands, of 30 Carel van Bylandtlaan, The Hague, The Netherlands, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a process for hydrotreating a liquid petroleum fraction, in which this fraction in the presence of hydrogen is passed downwardly through a reactor which contains spaced apart, fixed catalyst beds and means for the supply of cold hydrogen-rich gas above each bed and in which the treated fraction is discharged at the bottom of the reactor. The present invention also relates to apparatus in which such a process can be carried out.

Various hydrotreatments of petroleum fractions have been applied on a large scale in practice in which the envisaged catalytic reaction proceeds exothermically and takes place at such a high temperature that the risk of thermal degradation of the hydrocarbons, which are to be treated and/or which have been treated, as a result of a rise in temperature is a real problem.

It has been proposed to carry out the hydrotreatment in steps, the feed being cooled intermediately by means of fresh, relatively cold hydrogen. In that case use is made of one reactor, in the manner as stated in the preamble.

An inherent drawback of this system is that the separate steps require rather a long period of time, the catalyst beds must have a substantial length and that further the number of the beds must not be excessive on account of the cost price of the reactor. As a result the temperature nevertheless rises in these separate catalyst beds. Moreover, only at a certain depth in the

catalyst bed is the feed found to be cooled sufficiently by the relatively cold hydrogen. It appears that in the empty space above the catalyst bed only a fraction of the total cooling effect of the hydrogen is noticeable.

According to the present invention a process for hydrotreating a liquid petroleum fraction is provided, in which this fraction in the presence of hydrogen is passed downwardly through a reactor which contains spaced apart, fixed catalyst beds and means for the supply of cold hydrogen-rich gas above each bed, and in which the treated fraction is discharged at the bottom of the reactor, wherein the hydrotreatment is carried out with catalyst beds at least one of which is covered with two layers of inert ceramic particles, namely a layer of small particles having a diameter between 1 and 10 mm and on top thereof a layer of larger particles having a diameter larger than 10 mm, which layers together occupy at most 20% of the height of the catalyst bed covered thereby.

In the process of the present invention an initial difference in temperature between the petroleum fraction and the cold hydrogen-rich gas can be reduced by more than 95% by the time the petroleum fraction has passed through the lower of the two above-defined layers of particles.

The process according to the invention yields an unexpected synergistic effect. When using a single layer of particles having a diameter larger than 10 mm, the total height of the layer to obtain the desired cooling of the feed would become unacceptably high and be, for example, at least 50 cm. Although when using a single layer of particles with a diameter between 1 and 10 mm the cooling effect is already larger at a layer thickness below, for example, 25 cm, it is found that such a layer cannot be used in practice owing to the undesired channelling effect to which the layer gives rise. The channels formed in the

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layer of particles and along which the liquid petroleum fraction preferentially flows downwards result in a loss of the favourable effect of the layer on the equalization of the temperature.

The two layers of particles used in the process according to the invention have been found to ensure sufficient distribution of the liquid petroleum fraction to avoid the disadvantage of the channelling effect, sufficient cooling of the petroleum fraction also being obtained in the two layers.

According to the invention the gases preferably flow through the catalyst beds in the same direction as the petroleum fraction. In this manner the hydrogen separately supplied is coldest when it contacts the petroleum fraction in the layers of ceramic particles applied on the top of the catalyst bed. The petroleum fraction is then cooled before coming into contact with the catalyst itself. Under the latter conditions, the gases are also preferably discharged at the bottom of the reactor together with the petroleum fraction.

The invention can be applied advantageously especially in the hydrogenation, the hydrodesulphurization, the hydrocracking and in the hydrodealkylation of liquid petroleum fractions. However, the invention can also be used advantageously in other hydrotreatments of an exothermic nature in which thermally critical conditions must be considered.

The hydrotreatment according to the invention will in many cases be carried out at elevated temperature and pressure. When the hydrotreatment is carried out at elevated temperature, which is almost invariably the case, cooling can be effected with hydrogen at room temperature. As is known, it is no unusual that in hydrotreatments the reactor pressure is for example about 160 atm. Under such circumstances it is advisable to prevent too high a local rise in the reactor temperature. The present invention provides the means therefor.

According to the invention a layer of relatively small particles with diameters between 3 and 6 mm is preferably used. On the one hand these particles are small enough to effect a good heat transfer between the hydrogen-rich gas and the liquid petroleum fraction and on the other hand they are not so small that the pressure drop across the reactor becomes too high.

By preference, use is made of a layer of relatively large particles having a largest dimension between 20 and 30 mm. An upper layer of particles of such dimensions has been found to give a good distribution of the liquid, so that the channelling effect

does not occur in the two layers and the catalyst bed itself.

As relatively large particles Raschig rings or saddle-shaped particles may for example be chosen. Inert ceramic bodies of this shape are generally available in the dimensions required, since they are used as catalyst carriers.

In most cases good results will be obtained if use is made of a layer of relatively large particles with a thickness between 10 and 40 cm and a layer of relatively small particles having a thickness between 5 and 20 cm. The reactors usually contain two to five catalyst beds, the thickness of which lies between 1 and 5 m. The dimensions of the reactor, the catalyst beds and the upper layers to be applied thereon according to the invention, highly depend on the type of hydrotreatment, the desired capacity and the activity of the catalyst.

The invention can e.g. successfully be applied in the treatment of a lubricating oil fraction with hydrogen at a temperature between 350 and 500°C and a pressure of at least 100 atm. Under such circumstances the lubricating oil is very sensitive to fluctuations in temperature during the contact with the catalyst. In the event of an excessive fluctuation, such as a 10°C deviation from the desired value, an unacceptable change in viscosity may occur. Such a treatment of lubricating oil, for example hydrotreating or hydrofinishing, is usually carried out with a catalyst consisting of Co or Ni and Mo or W on an alumina carrier.

According to the invention some of the hydrogen-rich gas required is preferably supplied near the top of the reactor and the remaining hydrogen-rich gas required is supplied to the reactor into the spaces between the reactor beds, which are located one above another in the reactor, all the catalyst beds in the reactor, or all said beds except the top catalyst bed, being covered with the two layers of inert ceramic particles.

In this connection it will be clear that the top catalyst bed need not be covered with two layers of particles, since the liquid feed need not yet be cooled. In principle, within certain limits all the hydrogen not required for cooling can be introduced at the top of the reactor, in order to ensure stable operation.

At least half the hydrogen-rich gas is advantageously introduced near the top of the reactor. It is generally possible to vary widely the supply of hydrogen-rich gas above the various catalyst beds. It is thus possible to vary the cooling effect.

According to an embodiment of the invention, in which a lubricating oil fraction

is treated with hydrogen at a temperature between 350°C and 500°C and a pressure of at least 100 atm., at least such a quantity of hydrogen-rich gas per ton of lubricating oil intake is introduced near the top into the reactor and at least such a quantity of hydrogen-rich gas per ton of lubricating oil intake per space is introducing into the spaces between the catalyst beds that it is possible to treat the lubricating oil fraction at a temperature which invariably deviates from the desired value by less than 25°C.

In such a treatment of a lubricating oil fraction the linear space velocity of the lubricating oil is preferably at least 0.1 kg per litre of catalyst per hour.

Also, according to the present invention an apparatus for use in carrying out the hydrotreating of a liquid petroleum fraction, comprises a reactor containing spaced apart, fixed catalyst beds and means for the supply of cold hydrogen-rich gas above each bed, or above each bed except the first bed, the top of the reactor being provided with a supply line for the petroleum fraction and a supply line for hydrogen-rich gas and the bottom with a discharge line for the petroleum fraction, wherein all the catalyst beds, or all the beds except the first bed, are covered with two layers of inert ceramic particles, namely a layer of small particles with a diameter between 1 and 10 mm and on top thereof a layer of larger particles with a diameter larger than 10 mm, which layers together occupy at most 20% of the height of the catalyst bed covered thereby.

The discharge line for the petroleum fraction at the bottom of the reactor is preferably also designed for the discharge of gas.

The invention is illustrated by the following embodiment which will be described with reference to the accompanying drawing, which is a diagrammatic vertical cross-section, in which some parts are not shown to scale, of a reactor according to the present invention.

With the reactor shown in the drawing a conventional deasphalted Basrah oil is treated with hydrogen under hydrotreating conditions at about 455°C and 170 atm.

The reactor consists of a reactor vessel 1 in which a supply line 2 for lubricating oil to be treated and hydrogen-rich gas and a discharge line 3 for treated lubricating oil and spent gas as well as a discharge line 4 for the removal of catalyst from the reactor are provided.

The reactor contains four catalyst beds 5—8, inclusive, having respective approximate lengths of 2.5 m, 3.4 m, 3.4 m and 3.5 m. At the level of the catalyst beds

the reactor is not shown to scale. The diameter of the reactor is about 1.5 m.

A distribution tray 9 is provided above each catalyst bed, which contributes to a good distribution of the oil over the total cross-section of the catalyst bed located below the tray.

Below each of the distribution trays a 25 cm layer of inert ceramic Raschig rings having a largest dimension of 25 mm is provided. For the catalyst beds 6, 7 and 8, a 10 cm high layer of inert ceramic spheres 11 with a diameter of 3 mm is also provided below the layer of Raschig rings 10.

The catalyst beds rest on supports 12 and between each support 12 and the layer 10 covering the underlying catalyst bed there is an about 50 cm high empty space which contains the said distribution tray 9. Above these trays 9 are annular elements 13 for the supply of relatively cold hydrogen-rich gas. The radius of the annular element is about 50 cm.

No element 13 but a sedimentation tray 14 is located above the top catalyst bed.

The temperature of the hydrogen-rich gas originating from the refinery, which contains hydrogen sulphide and C₁—C₄ hydrocarbons in addition to hydrogen, is less than 50°C.

The catalyst used contains 8% by weight of Ni and 13% by weight of Mo on alumina (based on dry matter).

The linear space velocity of the lubricating oil is about 1 kg of oil per litre of catalyst per hour.

It has now been found that at a gas supply of 1,000 Nm³ of gas per ton of feed via the supply 2 and a gas supply of 100 Nm³ of gas per ton of feed via each of the elements 13, a rise in temperature of about 25°C occurs across the first catalyst bed, of 20°C across the second catalyst bed, of 10°C across the third catalyst bed and of 5°C across the fourth catalyst bed.

However, owing to the provisions according to the invention, the temperature of the feed at the beginning of the catalyst bed proper has invariably been found to deviate by less than 5°C from the desired value, which is 430°C.

If the special process of intermediate cooling has not been applied, the temperature of the feed at the end of the reactor would have risen to at least 470°C.

WHAT WE CLAIM IS:—

1. A process for hydrotreating a liquid petroleum fraction, in which this fraction in the presence of hydrogen is passed downwardly through a reactor which contains spaced apart, fixed catalyst beds and means for the supply of cold hydrogen-rich gas above each bed, and in which the treated fraction is discharged at the bottom

is treated with hydrogen at a temperature between 350°C and 500°C and a pressure of at least 100 atm., at least such a quantity of hydrogen-rich gas per ton of lubricating oil intake is introduced near the top into the reactor and at least such a quantity of hydrogen-rich gas per ton of lubricating oil intake per space is introducing into the spaces between the catalyst beds that it is possible to treat the lubricating oil fraction at a temperature which invariably deviates from the desired value by less than 25°C.

In such a treatment of a lubricating oil fraction the linear space velocity of the lubricating oil is preferably at least 0.1 kg per litre of catalyst per hour.

Also, according to the present invention an apparatus for use in carrying out the hydrotreating of a liquid petroleum fraction, comprises a reactor containing spaced apart, fixed catalyst beds and means for the supply of cold hydrogen-rich gas above each bed, or above each bed except the first bed, the top of the reactor being provided with a supply line for the petroleum fraction and a supply line for hydrogen-rich gas and the bottom with a discharge line for the petroleum fraction, wherein all the catalyst beds, or all the beds except the first bed, are covered with two layers of inert ceramic particles, namely a layer of small particles with a diameter between 1 and 10 mm and on top thereof a layer of larger particles with a diameter larger than 10 mm, which layers together occupy at most 20% of the height of the catalyst bed covered thereby.

The discharge line for the petroleum fraction at the bottom of the reactor is preferably also designed for the discharge of gas.

The invention is illustrated by the following embodiment which will be described with reference to the accompanying drawing, which is a diagrammatic vertical cross-section, in which some parts are not shown to scale, of a reactor according to the present invention.

With the reactor shown in the drawing a conventional deasphalted Basrah oil is treated with hydrogen under hydrotreating conditions at about 455°C and 170 atm.

The reactor consists of a reactor vessel 1 in which a supply line 2 for lubricating oil to be treated and hydrogen-rich gas and a discharge line 3 for treated lubricating oil and spent gas as well as a discharge line 4 for the removal of catalyst from the reactor are provided.

The reactor contains four catalyst beds 5—8, inclusive, having respective approximate lengths of 2.5 m, 3.4 m, 3.4 m and 3.5 m. At the level of the catalyst beds

the reactor is not shown to scale. The diameter of the reactor is about 1.5 m.

A distribution tray 9 is provided above each catalyst bed, which contributes to a good distribution of the oil over the total cross-section of the catalyst bed located below the tray.

Below each of the distribution trays a 25 cm layer of inert ceramic Raschig rings having a largest dimension of 25 mm is provided. For the catalyst beds 6, 7 and 8, a 10 cm high layer of inert ceramic spheres 11 with a diameter of 3 mm is also provided below the layer of Raschig rings 10.

The catalyst beds rest on supports 12 and between each support 12 and the layer 10 covering the underlying catalyst bed there is an about 50 cm high empty space which contains the said distribution tray 9. Above these trays 9 are annular elements 13 for the supply of relatively cold hydrogen-rich gas. The radius of the annular element is about 50 cm.

No element 13 but a sedimentation tray 14 is located above the top catalyst bed.

The temperature of the hydrogen-rich gas originating from the refinery, which contains hydrogen sulphide and C_1 — C_4 hydrocarbons in addition to hydrogen, is less than 50°C.

The catalyst used contains 8% by weight of Ni and 13% by weight of Mo on alumina (based on dry matter).

The linear space velocity of the lubricating oil is about 1 kg of oil per litre of catalyst per hour.

It has now been found that at a gas supply of 1,000 Nm³ of gas per ton of feed via the supply 2 and a gas supply of 100 Nm³ of gas per ton of feed via each of the elements 13, a rise in temperature of about 25°C occurs across the first catalyst bed, of 20°C across the second catalyst bed, of 10°C across the third catalyst bed and of 5°C across the fourth catalyst bed.

However, owing to the provisions according to the invention, the temperature of the feed at the beginning of the catalyst bed proper has invariably been found to deviate by less than 5°C from the desired value, which is 430°C.

If the special process of intermediate cooling has not been applied, the temperature of the feed at the end of the reactor would have risen to at least 470°C.

WHAT WE CLAIM IS:—

1. A process for hydrotreating a liquid petroleum fraction, in which this fraction in the presence of hydrogen is passed downwardly through a reactor which contains spaced apart, fixed catalyst beds and means for the supply of cold hydrogen-rich gas above each bed, and in which the treated fraction is discharged at the bottom



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5 of the reactor, wherein the treatment is carried out with catalyst beds at least one of which is covered with two layers of inert ceramic particles, namely a layer of small particles with a diameter between 1 and 10 mm and on top thereof a layer of larger particles with a diameter larger than 10 mm, which layers together occupy at most 20% of the height of the catalyst bed covered thereby.

10 2. A process as claimed in Claim 1, wherein the gases flow through the catalyst beds in the same direction as the petroleum fraction.

15 3. A process as claimed in Claim 2, wherein the gases are discharged at the bottom of the reactor together with the petroleum fraction.

20 4. A process as claimed in any one of the preceding claims, wherein the treatment is carried out at elevated temperature and pressure.

25 5. A process as claimed in any one of the preceding claims, wherein the layer of small particles consists of particles with diameters between 3 and 6 mm.

30 6. A process as claimed in any one of the preceding claims, wherein the layer of larger particles consists of particles having a largest dimension between 20 and 30 mm.

35 7. A process as claimed in any one of the preceding claims, wherein said larger particles are Raschig rings or saddle-shaped particles.

40 8. A process as claimed in any one of the preceding claims, wherein the layer of larger particles has a thickness between 10 and 40 cm and the layer of small particles has a thickness between 5 and 20 cm.

45 9. A process as claimed in any one of the preceding claims, wherein a lubricating oil fraction is treated with hydrogen at a temperature between 350 and 500°C and a pressure of at least 100 atm.

50 10. A process as claimed in any one of the preceding claims, wherein some of the hydrogen-rich gas required is introduced near the top of the reactor and the remaining hydrogen-rich gas required is supplied to the reactor into the spaces between the reactor beds, which are located one above another in the reactor, all the catalyst beds in the reactor, or all said beds except the top catalyst bed, being covered with the two layers of particles.

55 11. A process as claimed in Claim 10, wherein at least half of the hydrogen-rich gas is supplied near the top of the reactor.

12. A process as claimed in any one of Claims 9—11, wherein the linear space velocity of the lubricating oil is at least 0.1 kg per litre of catalyst per hour.

13. A process as claimed in Claim 1 and substantially as hereinbefore described with reference to the Example.

14. An apparatus for use in carrying out the hydrotreating of a liquid petroleum fraction, comprising a reactor containing spaced apart, fixed catalyst beds and means for the supply of cold hydrogen-rich gas above each bed, or above each bed except the first bed, the top of the reactor being provided with a supply line for the petroleum fraction and a supply line for hydrogen-rich gas and the bottom with a discharge line for the petroleum fraction, wherein all the catalyst beds, or all the beds except the first bed, are covered with two layers of inert ceramic particles, namely a layer of small particles with a diameter between 1 and 10 mm and on top thereof a layer of larger particles with a diameter larger than 10 mm, which layers together occupy at most 20% of the height of the catalyst bed covered thereby.

15. An apparatus as claimed in Claim 14, wherein the discharge line for the petroleum fraction at the bottom of the reactor is also designed for the discharge of gas.

16. An apparatus as claimed in Claim 14 or 15, wherein the small particles have a diameter between 3 and 6 mm.

17. An apparatus as claimed in Claim 14, 15 or 16, wherein the larger particles have a largest dimension between 20 and 30 mm.

18. An apparatus as claimed in any one of Claims 14—17, wherein the larger particles are Raschig rings or saddle-shaped particles.

19. An apparatus as claimed in any one of Claims 14—18, wherein the layer of larger particles has a thickness between 10 and 40 cm and the layer of small particles has a thickness between 5 and 20 cm.

20. An apparatus as claimed in Claim 14 and substantially as hereinbefore described with reference to the accompanying drawing.

R. C. ROGERS,
Chartered Patent Agent,
Shell Centre,
London, S.E.1.,
Agent for the Applicants.