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HYDROTREATING PROCESS

The present process relates to a process for hydrotreating of a heavy residual oil fraction.

At the moment much work is carried out on whitening of the barrel, especially on conversion of the residual material into lighter and more valuable products. Many suitable residue conversion processes are known, which are generally carried out at high temperature and in the presence of hydrogen. Nevertheless, at the end of the conversion line there will be an amount of residual heavy material which has not been converted into lighter products. It has been found that especially when the conversion process has been a very severe one, such unconverted heavy material contains a large amount of contaminants such as sulphur, and flocculated asphaltenes and/or toluene insolubles. Because of these contaminants, the unconverted heavy material does not qualify for use as fuel. Therefore it has to be disposed of in a commercially less attractive way, such as gasification in a refinery.

Surprisingly, it has now been found that if a heavy residual oil fraction which remained after a residue conversion process, is subjected to a relatively mild hydrotreating process, a product of lower sulphur content is obtained. This is the case even if the residue conversion process had already been carried out at severe process conditions. Severe conversion conditions comprise those in which at least 50% by weight of the fraction boiling above 520 °C of the residue is converted. It has further been found that the present hydrotreating process can be operated for a fairly long time which is contrary to expectations, as one would expect that further treatment of such heavy material would lead to unacceptable coke make. Further, the product obtained is of such quality that it can suitably be used as low-sulphur refinery fuel.

The present invention relates to a process for hydrotreating a heavy residual oil fraction, in which process a heavy residual oil

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hydrotreated at a temperature which is lower than the temperature at which the residue conversion process was carried out.

Especially good results in both the sulphur content of the product obtained and the life time of the catalyst, can be obtained by operating the hydrotreating process at a hydrogen partial pressure which is higher than the hydrogen partial pressure at which the residue conversion has been carried out.

The residue which is subjected to the residue conversion process can be any hydrocarbon oil of which a substantial fraction boils above 350 °C, preferably above 520 °C. A typical residue could comprise more than 90% by weight of hydrocarbons boiling above 520 °C.

The residue conversion process can be any hydrocarbon conversion process known to be suitable for conversion of such residual hydrocarbon fractions. The process can be carried out in the presence of a catalyst or in the absence of it. If a catalyst is present it can be a normally active, low active or inactive material. The process will generally be carried out at elevated temperature and pressure, such as a temperature of between 350 and 500 °C, preferably between 360 and 450 °C, and a total pressure which can vary widely, for example between 5 and 300 bar. In general, hydrogen will be present at the residue conversion process.

The heavy residual oil fraction can be separated from the effluent of the residue conversion process in any suitable manner, such as fractional distillation and flash distillation. The heavy residual fraction which is to be subjected to hydrotreating can comprise a certain amount of distillates, i.e. material boiling below 520 °C. Generally, at least 90% by weight of the heavy residual oil fraction will boil above 520 °C, more specifically at least 95%. Its sulphur content will be more than 0.5% by weight on total amount of hydrocarbon oil, more specifically more than 1.0% by weight, and can be more than 1.5% by weight. Due to the fact that the heavy residual oil fraction has already been subjected to at least one conversion process, the amount of metal contaminants

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fraction separated from effluent of a residue conversion process is present in the fraction will be relatively low. Generally, at most 400 parts per million by weight (ppm) of nickel and vanadium will be present, preferably at most 200 ppm, more preferably at most 80 ppm.

Further, the heavy residual oil fraction will contain relatively large amounts of organic contaminants, such as flocculated asphaltenes and/or toluene insolubles. The heavy residual oil fraction will generally have a C5-asphaltenes content of more than 10% by weight, more specifically more than 15% by weight and it can even be more than 20% by weight. Further, the Conradson carbon residue of a heavy residual oil fraction suitable to be hydrotreated according to the present invention will be normally be more than 15% by weight, more specifically more than 20% by weight and it can even be more than 25% by weight.

The hydrotreating process of the present invention is carried out at a temperature which is lower than the temperature at which the residue conversion process is carried out. The temperature of the hydrotreatment step can be between 340 and 450 °C, preferably it is between 370 and 430 °C, more preferably between 380 and 410 °C. Further, the temperature at which the hydrotreating process of the present invention is carried out is preferably more than 10 °C lower than the temperature at which the residue conversion process is carried out, more preferably more than 15 °C lower, even more preferably more than 20 °C lower. The hydrogen partial pressure at which the hydrotreating process is carried out is preferably higher than the pressure at which the residue conversion process has been carried out. The hydrogen partial pressure at which the hydrotreating process is carried out can be between 100 and 300 bar, preferably between 125 and 250 bar, more preferably between 140 and 225 bar. Suitably, the hydrogen partial pressure of the hydrotreating process is 10 bar higher than the hydrogen partial pressure of the residue conversion process, preferably 15 bar.

Commercially available hydrotreating catalysts can be used in

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the hydrotreating step of the present invention. Catalysts which can be applied can comprise as hydrogenating metals a Group VI and/or VIII metal, suitably on an amorphous carrier. Preferred catalysts comprise as hydrogenating metals cobalt and/or nickel, and further tungsten and/or molybdenum, on a carrier consisting of alumina and/or silica. It can be advantageous if the catalyst further contains phosphorus. The catalyst can comprise between 4 and 25% by weight of hydrogenating metal on amount of carrier, preferably between 6 and 18% by weight.

The product obtained in the process according to the present invention has a reduced content of contaminants, which makes that it qualifies to be used as fuel. Products containing less than 0.25% by weight of sulphur can be obtained, which products can be applied as low-sulphur refinery fuel or they can be blended with another oil fraction and be used as feed for a downstream conversion process such as cat cracking.

Hereinafter, the invention will be further elucidated by way of an example.

EXAMPLE

An Arabian Heavy atmospheric residue has been used, having an initial boiling point above 364 °C and of which 95% by weight boils above 520 °C. Further, the residue contained 23.8% by weight of C5-asphaltenes, 202 ppm of nickel and vanadium and 5.4% by weight of sulphur. The residue was subjected to a residue conversion process at an average reactor bed temperature of 435 °C, a hydrogen partial pressure of 150 bar, a WHSV of 0.2 kg/l/h and with the help of a combination of conventional residue conversion catalysts, comprising a first catalyst containing nickel and vanadium on silica, and a subsequent catalyst containing molybdenum on silica.

The product obtained was flashed at a Maxwell Bonnell temperature of 530 °C. The initial boiling point of the residue was 454 °C, 88% by weight of the residue boiled above 520 °C and 39% by weight boiled above 620 °C. The residue obtained comprised 1.8% by weight of sulphur, 18 ppmw of nickel and vanadium and 29.0% by weight of C5-asphaltenes.

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The residue obtained was subjected to hydrotreating with the help of a commercially available hydrotreating catalyst (C 227 ex Criterion Catalyst Co. LP.), at a temperature of 400 °C, a hydrogen partial pressure of 180 bar and a WHSV of 0.1 kg/l/h.

The product obtained comprised 0.2% by weight of sulphur and 5 ppmw of nickel and vanadium.

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1. Process for hydrotreating a heavy residual oil fraction, in which process a heavy residual oil fraction separated from effluent of a residue conversion process is hydrotreated at a temperature which is lower than the temperature at which the residue conversion process was carried out.

2. Process according to claim 1, in which the heavy residual fraction is hydrotreated at a pressure which is higher than the pressure at which the residue conversion process was carried out.

3. Process according to claim 1 and/or 2, in which at least 90% by weight of the heavy residual oil fraction boils above 520 °C, its sulphur content is at least 0.5% by weight on total amount of hydrocarbon oil and its nickel and vanadium content is at most 400 ppm.

4. Process according to any one of the preceding claims, in which the heavy residual oil fraction has a C5-asphaltenes content of more than 10% by weight and a Conradson carbon residue of more than 15% by weight.

5. Process according to any one of the preceding claims, in which the hydrotreating process is carried out at at a temperature between 370 and 430 °C and a hydrogen partial pressure of between 100 and 300 bar.

6. Process according to any one of the preceding claims, in which the hydrotreating process is carried out at a temperature which is at least 10 °C lower than the temperature at which the residue conversion process is carried out.

7. Process according to any one of the preceding claims, in which the catalyst applied in the hydrotreating process comprises as hydrogenating metals cobalt and/or nickel, and molybdenum and/or tungsten, on a carrier consisting of alumina and/or silica.

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8. Process according to claim 6 or 7, in which the catalyst comprises between 6 and 18% by weight of hydrogenating metal on amount of carrier.

9. Low-sulphur refinery fuel produced by a process as described in any of the preceding claims.

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