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Description

The present invention relates to a process for the conversion of a heavy hydrocarbon oil by contacting the hydrocarbon oil with solid particles in the presence of hydrogen at elevated temperature and moderate pressure.

Various processes have been developed in order to convert heavy hydrocarbons into valuable light fractions. These processes can be roughly divided into carbon rejecting type of processes, e.g. thermal cracking, and hydrogen addition type of processes, e.g. hydrocracking.

Thermal cracking of residual material is usually performed at a relatively low or moderate pressure (usually 5 to 30 bar) and at a relatively high temperature (420-520 °C) without the use of a catalyst and in the absence of hydrogen. The middle distillates obtained from thermal cracking of high boiling residues are of good quality as far as the ignition properties are concerned. The high content of olefins and heteroatoms (especially sulphur and nitrogen), however, make a hydrofinishing treatment necessary for many applications. An intrinsic problem of thermal cracking is the occurrence of condensation reactions which lead to the formation of polyaromatics and at high severity can lead to coke in the cracked residue.

Hydrocracking is usually performed at a relatively high hydrogen partial pressure (usually 100-140 bar) and a relatively low temperature (usually 300 to 400 °C). The catalyst used in this reaction has several functions: acid catalyzed cracking of the hydrocarbon molecules and activation of hydrogen and hydrogenation. A long reaction time is used (usually 0.3 to 2 l/l/h liquid hourly space velocity). Due to the high hydrogen pressure only small amounts of coke are deposited on the catalyst which makes it possible to use the catalyst for 0.5 to 2 years in a fixed bed operation without regeneration. The product slates obtained in this process are dependent on the mode of operation. In one mode of operation, predominantly naphtha and lighter products are obtained. The naphtha fraction contains paraffins with a high iso/normal ratio, making it a valuable gasoline blending component. In a mode for heavier products, kerosene and gas oil are mainly obtained. In spite of the extensive hydrogenation, the quality of these products is rather moderate, due to the presence of remaining aromatics together with an undesired high iso/normal ratio of the paraffins among others.

At the present there is much interest in processes combining carbon rejection with hydrogen addition. Conceptually, these processes combine the benefits of carbon rejection and hydrogen addition, both contributing to the desired hydrogen/carbon ratio of the valuable distillate products. Such processes could be very attractive because of controlled production of coke and simultaneous upgrading of the distillates obtained.

Further, in general it is advantageous when a process can be operated in the absence of a catalyst as catalysts tend to become deactivated in heavy hydrocarbon conversion processes, due to the presence of asphaltenes and metals therein. Deactivated catalyst must then be regenerated, involving metal removal and catalyst rejuvenation, which leads to higher operating costs.

Therefore, an object of the present invention is to provide a non-catalytic process wherein the production of liquid hydrocarbons together with substantial amounts of coke can be controlled and optimized. Furthermore, it is highly advantageous when part or all of the coke produced can be used in the production of energy or hydrogen containing streams for further use in e.g. refineries.

A process has now been found which is especially suitable for the conversion of heavy hydrocarbon oils with the help of non-catalytic solid particles in the presence of hydrogen and at elevated temperature and moderate pressure. The solid particles and hydrogen-containing gas must be of such a temperature when in contact with the hydrocarbon oil that at least part of the hydrogen is thermally dissociated. In this way hydrogenation of hydrocarbons takes place and condensation reactions resulting in the formation of aromatic components are suppressed. Thus, this process combines the favourable aspects of carbon rejection and hydrogen addition in one process step.

The present invention relates to a process for the conversion of a heavy hydrocarbon oil, which process comprises:

(i) contacting non-catalytic solid particles of a temperature of at least 600 °C with a hydrogen-containing gas and a heavy hydrocarbon oil in a reactor which is operated at a hydrogen partial pressure of between 10 and 80 bar and a temperature of between 450 and 850 °C, whereby the coke make calculated on Conradson Carbon content of the feedstock is between 0.5 and 1.4 weight/weight and in which reactor the bulk temperature is substantially uniform,

(ii) withdrawing coked solid particles from the reactor and removing coke from said particles, and

(iii) recycling particles from which coke has been removed in step (ii), to the reactor.

The earlier application EP-A-0 400 743 discloses catalytic and non-catalytic processes for the conversion of heavy hydrocarbon oils at the same hydrogen partial pressures and reactor temperatures.

In British patent specification 1,460,615 a process is described for cracking heavy hydrocarbons in a reactor, in which feed is introduced together with granular solid in an upper zone, which is maintained at a tem-

perature of not higher than 550 °C, and preheated hydrogen-containing gas is introduced in a lower zone. Gaseous components are withdrawn from the top of the reactor. In this way an upper zone is created in which heavy hydrocarbons are converted under non-hydrogenating conditions and a lower zone in which hydrogen addition takes place of heavy material. The required temperature differences within the reactor will present large difficulties, both because of the operating conditions which need to be such that separate reaction zones are maintained and because of the reactor which has to be made such that it can stand such differences in process temperature.

Another non-catalytic process is the so-called Dynacracking Process, described for example in Hydrocarbon Processing, May 1981 pp. 86-92, which is in essence a thermal hydroconversion process carried out in a moving particles system. The feed is thermally converted in the presence of hydrogen in the upper part of the system in the presence of synthesis gas producing substantial amounts of coke which are deposited on inert carrier material. In the lower part of the system coke on the inert material is gasified to synthesis gas with steam and oxygen. The problems to be faced in designing and operating such reactor would seem to be quite formidable.

A further process is the Fluidized Thermal Cracking (FTC) process which is, for instance, described in US patent specification 4,668,378. The process is carried out in a fluidized system in which residual feedstock is contacted with fine porous catalytically inactive particles, which particles are fluidized by steam or a hydrogen-containing gas at a rather low (hydrogen) partial pressure.

The conversion in the present process leading to molecular weight reduction is essentially determined by the hydrogen dissociating role of the solid particles of high temperature and the hydrogen partial pressure of between 10 and 80 bar. The coke make, calculated on Conradson Carbon Content of the feedstock, varies between 0.5 and 1.4 weight/weight, respectively. The dissociated hydrogen apparently participates in the radical reaction mechanisms and contributes to the saturation of the larger hydrocarbyl radicals resulting in less condensed aromatic structures and finally a lower coke make.

The middle distillates obtained in the present process are of good quality due to the high amount of n-paraffins and the low amount of olefins although they may contain a certain amount of aromatic compounds. The hydrogen consumption of the process is relatively low compared to pure hydrogen-addition processes, as the aromatic components are not substantially hydrogenated. A large part of the metals and nitrogen components present in the feed is deposited on the solid particles leaving a high quality distillate with a low metal(s) and nitrogen content which makes the distillate very suitable for product blending or as a feedstock for further upgrading in, for instance, catalytic cracking or hydrocracking units.

When compared with a usual thermal cracking process a higher middle distillate yield is produced with a comparable product quality, assuming that the thermal cracking product is subjected to an additional hydrofinishing treatment.

When compared with the Dynacracking and FTC processes as described hereinbefore and the process described in British patent specification 1,460,615, the present process has the important advantage that a considerable hydrogenation takes place in the presence of the dissociated hydrogen at relatively elevated hydrogen partial pressure. This results in a higher middle distillate yield of a higher quality and a lower and controllable coke production on feed.

With regard to the usual hydrocracking process, the process of the present invention is relatively insensitive to feedstock impurities, as there are no catalytic sites needed.

A feedstock which can suitably be applied in the present process is a heavy hydrocarbon oil comprising at least 35 %wt of material boiling above 520 °C, and usually more than 15 %wt of material boiling above 620 °C. Vacuum distillates, catalytically cracked cycle oils and slurry oils, deasphalted oils, atmospheric and vacuum residues, thermally cracked residues, asphalts originating from various kinds of deasphalting processes, synthetic residues and hydrocarbon oils originating from tar sands and shale oils of any source can suitably be converted as such or in mixtures in the process according to the present invention. Preference is given to hydrocarbon oils which comprise at least 50 %wt of material boiling above 520 °C, in particular to hydrocarbon oils comprising at least 90 %wt of material boiling above 520 °C. Feedstocks comprising at least 3 %wt of asphaltenic constituents, in particular at least 10 %wt, can suitably be processed. With the asphaltenic constituents mentioned hereinbefore "C_7-asphaltenes" are meant, i.e. the asphaltenic fraction removed from the oil fraction by precipitation with heptane.

The solid particles to be applied in the present process can comprise any non-catalytic solid material which can withstand the high temperatures applied, e.g. coke, alumina, silica and zirconia. Preferably, the particles substantially consist of coke. Suitably, the process is initially carried out with the help of ex-situ coke particles on which in-situ coke deposits during the reaction, which in-situ coke is thereafter (partly) removed. Before recycling, the particles may be ground and sieved in order to obtain particles of a preferred diameter. When the non-catalytic solid particles are contacted with the hydrogen-containing gas and the heavy hydrocarbon

oil, the particles should have a temperature of at least 600 °C, in order to dissociate the hydrogen present. Preferably, the particles have a temperature of at least 650 °C.

The process according to the present invention is suitably carried out at a hydrogen partial pressure of between 10 and 80 bar, preferably between 12 and 50 bar, and a temperature of between 450 and 850 °C and at a substantially uniform bulk temperature within the reactor. Suitably a difference in bulk temperature of not more than 100 °C can be measured within the reactor, more specifically not more than 50 °C.

It will be appreciated that a higher conversion will be obtained when the temperature is higher, as the rate of cracking of hydrocarbons will be higher at higher temperatures.

The process according to the present invention: can suitably be carried out in various types of moving bed reactors: a fluidized bed reactor and a riser reactor. Each type of moving bed reactor has its specifically preferred reaction conditions.

In case the process according to the present invention is carried out in a fluidized bed reactor, i.e. in which part or all of the feed is sprayed on the non-catalytic solid particles, a suitable temperature is between 450 and 650 °C, preferably between 470 and 600 °C. The hydrogen partial pressure is then suitably chosen between 10 and 80 bar, preferably between 12 and 50 bar, more preferably between 15 and 40 bar. The non-catalytic solid particles/oil ratio can suitably be chosen between 1-20 weight/weight, preferably between 2-12 weight/weight, more preferably between 2-8 weight/weight. Suitably the particles residence time in the fluidized bed reactor is chosen between 0.2 and 10 minutes, preferably between 0.4 and 5 minutes. A hydrogen containing gaseous stream is supplied to the fluidized bed reactor to provide the hydrogen required for the desired reactions and to maintain a good fluidization, this is suitably achieved at a superficial gas velocity between 0.01 and 3.50 m/s.

If the present process is carried out in a riser reactor, in which the liquid feed is sprayed onto the incoming hot non-catalytic solid particles, the temperature is suitably between 450 and 850 °C, preferably between 500 and 750 °C. The hydrogen partial pressure is suitably chosen between 10 and 80 bar, preferably between 12 and 50 bar, most preferably between 15 and 40 bar. The non-catalytic solid particles/oil ratio is suitably chosen between 1-20 weight/weight, preferably between 2 and 12 weight/weight, most preferably between 2 and 8 weight/weight. Suitably, the particles residence time in the riser reactor is below 2 minutes, preferably between 0.1 and 10.0 seconds. The hydrogen containing gaseous stream is suitably supplied to the riser reactor at a superficial gas velocity of between 0.6 and 3.5 m/s to provide the hydrogen required for the desired process reactions and to maintain a good fluidization and aeration.

The hydrogen-containing gas applied in the present process suitably comprises molecular hydrogen. Hydrogen containing refinery streams can be applied. They may also contain lower hydrocarbons, steam and/or mixtures thereof.

Removal of coke from the coked non-catalytic solid particles can suitably be carried out by burning off or gasifying coke. The synthesis gas obtained in the gasification of the coke can suitably be used as a refinery fuel gas or as a hydrogen source for hydro-processes in the refinery, or as a feedstock for hydrocarbon synthesis processes. If desired, the removal step can suitably be carried out by supplying the heat required for gasification via hot particles which preferably have a larger diameter and a higher density than the solid particles from which coke is to be removed. The use of relatively large particles (e.g. 3-20 times the diameter of the solid particles from which coke is to be removed) allows easy separation by fluidization and/or centrifugation in a cyclone. The hot particles which provide the external heat for the removal step are suitably brought to the desired temperature by heating in a combustive atmosphere (e.g. in an air/fuel gas system).

In order to prevent accumulation of contaminants, such as metals originally present in the heavy hydrocarbon oils, it is preferred to continuously remove a small amount of coked particles from the process of the present invention. Such coked particles are preferably replaced by fresh solid particles. Preferably, at least 90 % of the coked solid particles being withdrawn from the reactor is replaced by particles from which coke has been removed.

The present invention will now be illustrated by means of the following Example.

EXAMPLE

An Arabian light vacuum residue and a Maya vacuum residue, respectively, were used as feedstock to demonstrate the conversion process according to the present invention. The feed properties are described in Table 1.

Experiments were carried out using coke particles having a diameter between 0.01 and 5 mm.

The feedstock and the liquid product were analyzed for the boiling point distribution using a TBP-GLC (true boiling point measured by gas liquid chromatography) method. On basis thereof conversions and product yields were calculated. The 520 °C$^+$ conversion has been defined as the amount of 520 °C$^+$ material present

in the feedstock minus the amount of 520 °C$^+$ material present in the total liquid product, divided by the amount of 520 °C$^+$ material present in the feedstock. The product slate was split up into gas (C_1-C_4), the total liquid product (C_5^+) and the coke deposited on the catalyst. The respective fractions have been calculated as the amount of product in question, divided by the total amount of products. The following experiments were carried out:

Experiment 1

The Arabian light vacuum residue was contacted with coke particles having a temperature of 650 °C. The reaction was carried out at a temperature of 500 °C, a hydrogen partial pressure of 25 bar and at substantially uniform bulk temperature. The product obtained is described in Table 2.

Experiment 2

The Arabian light vacuum residue was contacted with coke particles having a temperature of 650 °C. The reaction was carried out at a temperature of 500 °C, a hydrogen partial pressure of 50 bar and at substantially uniform bulk temperature. The product obtained is described in Table 2.

Experiment 3

The Maya vacuum residue was contacted with coke particles having a temperature of 700 °C. The reaction was carried out at a temperature of 540 °C, a hydrogen partial pressure of 25 bar and at substantially uniform bulk temperature. The product obtained is described in Table 2.

Experiment 4

The Maya vacuum residue was contacted with coke particles having a temperature of 700 °C. The reaction was carried out at a temperature of 540 °C, a hydrogen partial pressure of 50 bar and at substantially uniform bulk temperature. The product obtained is described in Table 2.

TABLE 1

	Arabian light vacuum residue	Maya vacuum residue
Specific gravity (d 15/4)	1.014	1.052
Sulphur content (%wt)	4.11	5.24
Nitrogen content (%wt)	0.4303	0.9401
Vanadium content (%wt)	0.0078	0.0615
C_7-asphaltenes (%wt)	6.7	23.0
Conradson Carbon test (%wt)	15.62	26.7
Viscosity at 100 °C (cSt)	618.5	-
Viscosity at 150 °C (cSt)	-	1226.7
Distillation TBP/GLC:		
350 °C - 520 °C	9.8	4.7
520 °C$^+$	90.2	95.3

TABLE 2

Experiment	1	2	3	4
520 °C$^+$ Conversion (%w)	93.6	94.5	96.8	97.0
Product yields:				
Total gas make (%w)	5.5	5.6	11.2	10.9
H_2S (%w)	1.1	1.4	3.1	3.8
C_1-C_4 (%w)	4.4	4.2	8.1	7.1
Total liquid product:	72.6	78.2	73.0	75.0
C_5-250 °C (%w)	14.4	17.3	23.8	27.8
250-370 °C (%w)	19.6	24.3	26.4	28.2
370-520 °C (%w)	32.8	31.6	19.7	16.2
520 °C$^+$ (%w)	5.8	5.0	3.1	2.8
Coke (%w)	21.9	16.2	15.8	14.1

Claims

1. Process for the conversion of a heavy hydrocarbon oil, which process comprises:
   (i) contacting non-catalytic solid particles of a temperature of at least 600 °C with a hydrogen-containing gas and a heavy hydrocarbon oil in a reactor which is operated at a hydrogen partial pressure of between 10 and 80 bar and a temperature of between 450 and 850 °C, whereby the coke make calculated on Conradson Carbon Content of the feedstock is between 0.5 and 1.4 weight/weight and in which reactor the bulk temperature is substantially uniform;
   (ii) withdrawing coked solid particles from the reactor and removing coke from said particles; and
   (iii) recycling particles from which coke has been removed in step (ii), to the reactor.

2. Process according to claim 1, wherein the heavy hydrocarbon oil comprises at least 35 %wt of material boiling above 520 °C.

3. Process according to claim 1 or 2, wherein the heavy hydrocarbon oil comprises at least 3 %wt of asphaltenic constituents, preferably at least 10 %wt.

4. Process according to any one of claims 1-3, wherein a difference in bulk temperature of not more than 100 °C can be measured within the reactor, preferably not more than 50 °C.

5. Process according to any one of claims 1-4, wherein the non-catalytic solid particles substantially consist of coke.

6. Process according to any one of claims 1-5, wherein the solid particles have a temperature of at least 650 °C.

7. Process according to any one of claims 1-6, wherein in the reactor the hydrogen partial pressure is between 12 and 50 bar.

8. Process according to any one of claims 1-7, wherein coke is removed from the coked non-catalytic solid particles by burning off or gasifying coke.

9. Process according to any one of claims 1-8, wherein at least 90 % of the coked solid particles being withdrawn from the reactor is replaced by particles from which coke has been removed.

10. Process according to any one of claims 1-9, wherein the reaction is carried out in a fluidized bed reactor at a temperature of between 450 and 650 °C, and wherein the non-catalytic solid particles have a residence time of between 0.2 and 10 minutes.

11. Process according to any one of claims 1-9, wherein the reaction is carried out in a riser reactor at a temperature of between 450 and 850 °C and wherein the non-catalytic solid particles have a residence time below 2 minutes.

Patentansprüche

1. Verfahren zur Umwandlung eines schweren Kohlenwasserstofföls, welches die folgenden Stufen umfaßt:
(i) Kontaktieren von nicht-katalytischen festen Teilchen mit einer Temperatur von mindestens 600°C mit einem wasserstoffhaltigen Gas und einem schweren Kohlenwasserstofföl in einem Reaktor, der bei einem Wasserstoffpartialdruck zwischen 10 und 80 Bar und einer Temperatur zwischen 450 und 850°C betrieben wird, wobei die Koksbildung, berechnet nach dem Conradson-Kohlenstoffgehalt des Ausgangsmaterials zwischen 0,5 und 1,4 Gewicht/Gewicht liegt, und in welchem Reaktor die Massetemperatur im wesentlichen gleichförmig ist,
(ii) Abziehen der verkoksten Teilchen aus dem Reaktor und Entfernen von Koks von den genannten Teilchen, und
(iii) Rückführen im Kreislauf der Teilchen, von welchen in Stufe (ii) Koks entfernt worden ist, zu dem Reaktor.

2. Verfahren nach Anspruch 1, in welchem das schwere Kohlenwasserstofföl mindestens 35 Gewichtsprozent an Material mit einem Siedepunkt oberhalb 520°C enthält.

3. Verfahren nach Anspruch 1 oder 2, in welchem das schwere Kohlenwasserstofföl mindestens 3 Gewichtsprozent und vorzugsweise mindestens 10 Gewichtsprozent an Asphaltenbestandteilen enthält.

4. Verfahren nach einem der Ansprüche 1 bis 3, in welchem ein Unterschied in der Massetemperatur von nicht mehr als 100°C , vorzugsweise von nicht mehr als 50°C innerhalb des Reaktors gemessen wird.

5. Verfahren nach einem der Ansprüche 1 bis 4, in welchem die nicht-katalytischen festen Teilchen im wesentlichen aus Koks bestehen.

6. Verfahren nach einem der Ansprüche 1 bis 5, in welchem die festen Teilchen eine Temperatur von mindestens 650°C aufweisen.

7. Verfahren nach einem der Ansprüche 1 bis 6, in welchem der Wasserstoffpartialdruck im Reaktor zwischen 12 und 50 Bar beträgt.

8. Verfahren nach einem der Ansprüche 1 bis 7, in welchem Koks durch Abbrennen oder Vergasen von den verkoksten nicht-katalytischen festen Teilchen entfernt wird.

9. Verfahren nach einem der Ansprüche 1 bis 8, in welchem mindestens 90% der verkoksten festen Teilchen, die aus dem Reaktor abgezogen werden, durch Teilchen ersetzt werden, von welchen Koks entfernt worden ist.

10. Verfahren nach einem der Ansprüche 1 bis 9, in welchem die Reaktion in einem Wirbelschichtbettreaktor bei einer Temperatur zwischen 450 und 650°C durchgeführt wird und in welchem die nicht-katalytischen festen Teilchen eine Verweilzeit von 0,2 bis 10 Minuten aufweisen.

11. Verfahren nach einem der Ansprüche 1 bis 9, in welchem die Reaktion in einem Steigrohrreaktor bei einer Temperatur von 450 bis 850°C durchgeführt wird und in welchem die nicht-katalytischen festen Teilchen eine Verweilzeit von weniger als 2 Minuten aufweisen.

Revendications

1. Procédé de conversion d'une huile lourde d'hydrocarbures, qui comprend :
   (1) la mise en contact de particules solides non-catalytiques d'une température d'au moins 600°C avec un gaz contenant de l'hydrogène et une huile lourde d'hydrocarbures dans un réacteur que l'on fait fonctionner à une pression partielle d'hydrogène comprise entre 10 et 80 bars et à une température comprise entre 450 et 850°C, de façon que la production de coke calculée par rapport à la teneur en carbone Conradson de la charge de départ soit comprise entre 0,5 et 1,4 % en poids, la température apparente étant substantiellement uniforme dans le réacteur ;
   (2) l'évacuation du réacteur des particules solides revêtues de coke et l'enlèvement du coke de ces particules ; et
   (3) le recyclage au réacteur des particules desquelles le coke a été enlevé dans l'étape (2).

2. Procédé selon la revendication 1, dans lequel l'huile lourde d'hydrocarbures comprend au moins 35 % en poids de matière bouillant au-dessus de 520°C.

3. Procédé selon la revendication 1 ou 2, dans lequel l'huile lourde d'hydrocarbures comprend au moins 3 % en poids de constituants asphalténiques, de préférence au moins 10 % en poids.

4. Procédé selon l'une quelconque des revendications 1-3, dans lequel on ne peut pas mesurer dans le réacteur une différence de température apparente de plus de 100°C, de préférence pas plus de 50°C.

5. Procédé selon l'une quelconque des revendications 1-4, dans lequel les particules solides non-catalytiques sont constituées essentiellement de coke.

6. Procédé selon l'une quelconque des revendications 1-5, dans lequel les particules solides ont une température d'au moins 650°C.

7. Procédé selon l'une quelconque des revendications 1-6, dans lequel la pression partielle d'hydrogène dans le réacteur est comprise entre 12 et 50 bars.

8. Procédé selon l'une quelconque des revendications 1-7, dans lequel on enlève le coke des particules solides non-catalytiques revêtues de coke en faisant brûler le coke ou en le gazéifiant.

9. Procédé selon l'une quelconque des revendications 1-8, dans lequel au moins 90 % des particules solides revêtues de coke qui sont évacuées du réacteur sont remplacées par des particules dont le coke a été enlevé.

10. Procédé selon l'une quelconque des revendications 1-9, dans lequel la réaction est conduite dans un réacteur à lit fluidisé à une température comprise entre 450 et 650°C, et dans lequel les particules solides non-catalytiques ont un temps de séjour compris entre 0,2 et 10 minutes.

11. Procédé selon l'une quelconque des revendications 1-9, dans lequel la réaction est conduite dans un réacteur à colonne montante à une température comprise entre 450 et 850°C et dans lequel les particules solides non-catalytiques ont un temps de séjour inférieur à 2 minutes.