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(54) **Coking residuum in the presence of hydrogen donor.**

(57) The present invention provides a method for treating heavy hydrocarbonaceous oil feedstock, comprising:

(a) heating said feedstock to a temperature from 420°C to 500°C in a heating zone to form a reaction mass;

(b) maintaining said reaction in a coking zone at a temperature from 400°C to 490°C and pressure from 101 kPa to 600 kPa for a residence time of from 5 to 60 minutes; and

(c) recovering liquid hydrocarbon products and coke from said coking zone.

characterised in that: prior to said heating step, said heavy hydrocarbonaceous feedstock is mixed with a hydrogen-donating hydrocarbon diluent boiling in a range from 180°C to 400°C at atmospheric pressure in a ratio to said feedstock of .02:1 to 1.0:1 by weight in a mixing zone.

DESCRIPTION

COKING RESIDUUM IN THE PRESENCE OF HYDROGEN DONOR

The present invention relates to a process for obtaining increased yields of liquid hydrocarbons from coking feedstocks by introducing hydrogen-donating hydrocarbon material together with the feedstock. In known delayed coking processes a gas oil and/or residuum is heated rapidly to coking temperature, initiating thermal breakdown, and passed into a coking drum, where the hot material continues thermal breakdown and conversion to lighter hydrocarbons and coke. Coke yields in such processes can be as large as 30% or more, and the production of large amounts of this low-valued material is uneconomic.

Processes known in the art include the manufacture of premium coke, that is, coke having a low coefficient of thermal expansion (CTE), which is higher-valued than conventional coke.

For example, in U.S. Patent 4 176 046, McConaghy described a process in which vacuum residuum was hydrogen donor diluent cracked, the cracking effluent was hydrodesulphurised and partially hydrogenated, and the bottoms were delay-coked. The coker gas oil, boiling from 316°C to 480°C, was recycled to be used as donor diluent. The predominantly aromatic nature of the bottoms fed to the coker accounted for the low CTE of the product coke.

An alternative approach was described by Kegler et al in U.S. Patent 3 960 704, in which residuum was oxidised at a temperature from 260°C to 316°C and the resulting blown residuum was coked at 454°C to 510°C with or without a viscosity-reducing diluent, for example premium coker gas oil. The function of the gas oil was strictly to reduce the viscosity of the feedstock, which was said to render the coke product easier to handle than coke made without diluent blended with the feedstock.

The patent of Sooter, U.S. Patent 4 385 980, described the coking of pulverised coal with a hydrogen donor, fractionating the overhead products

of the coking reaction and partially hydrogenating a "heavy recycle gas oil" fraction of use as donor in the coker. The operating temperature of the coker was said to be in the range 450°C to 550°C. No disclosure of the use of donor diluent with other than pulverised coal was given.

5           In U.S. Patent 4 213 846, Sooter et al showed the reduction of the CTE of delayed coke by using recycled hydrotreated gas oil with premium coker feedstock in a delayed coker. The gas oil stream of unspecified boiling range was obtained from the coker liquids, and the coker was operated at a transfer line temperature of 505°C to 525°C instead of a normal (i.e. non-  
10 donor) temperature of 470°C to 505°C. It was stated at column 2, lines 48-50 that there would have been no reason to carry out recycle hydrotreating if regular, as opposed to premium, coke was being produced. No comment was made concerning coke yield.

          Wilson et al, in U.S. Patent 3 617 513, disclosed a process for  
15 converting coal into liquid hydrocarbon products. Coal was slurried with a hydrogen donor solvent boiling in the range from 177°C to 482°C, liquefied and the bottoms, containing liquid liquefaction products, non-liquefied solid coal particles and unconsumed hydrogen-donor solvent was passed to a fluid coking zone. No temperature range of operation of the fluid coking zone was  
20 disclosed, but the examples of the process were each operated at 538°C. Delayed coking was suggested as an alternative to fluid coking, but no operating conditions were disclosed.

          In U.S. Patent 2 953 513, Langer disclosed the upgrading of petroleum residua by contact with hydrogen-donating hydrocarbons boiling in a  
25 temperature range from 371°C to the initial boiling point of the residua to be upgraded, the reaction being carried on in the liquid phase, at temperatures from 427°C to 504°C and pressures from 1.4 MPa to 6.9 MPa.

          Despite these disclosures, there remained a need for a process for upgrading residua at low pressures with a reduced production of coke. The

present invention provides a method for treating heavy hydrocarbonaceous oil feedstock, comprising:

- 5 (a) mixing said heavy hydrocarbonaceous oil feedstock and a hydrogen-donating hydrocarbon diluent boiling in a range from 180°C to 400°C at atmospheric pressure, in a ratio compared to said feedstock of 0.02:1 to 1.0:1 by weight in a mixing zone;
- (b) heating said mixture of feedstock and hydrogen-donating hydrocarbon diluent to a temperature from 420°C to 500°C in a heating zone to form a reaction mass;
- 10 (c) maintaining said reaction mass in a coking zone at a temperature from 400°C to 490°C and pressure from 101 kPa to 600 kPa for a residence time of from 5 to 60 minutes; and
- (d) recovering liquid hydrocarbon products and coke from said coking zone.

15 The invention also resides in a method for reducing the amount of coke production in the coking of heavy hydrocarbonaceous oil feedstock, comprising the steps as listed above.

In this disclosure and claims, all references to percentages and proportions are references to percentages and proportions by weight, and  
20 boiling temperatures refer to atmospheric pressure, unless otherwise indicated.

The process of the invention utilises a hydrogen-donating hydrocarbon diluent to provide sufficient hydrogen to add to at least a portion of the radicals that are created from the residuum feedstock when it is  
25 exposed to temperatures in the coking range, i.e. from 420°C to 500°C: The hydrogen-donating diluent has a boiling range from 180°C to 400°C, preferably from 200°C to 350°C, at atmospheric pressure. Advantageously, the donor diluent can be a highly aromatic light cycle oil generated in a catalytic

cracking process; the oil is partially hydrogenated by known methods to produce a hydrogen donor diluent containing, for example, tetralin and substituted tetralins. Preferably, hydrogen-donating compounds and hydrogen donor precursors together comprise at least 40 percent of the hydrogen donor diluent. Hydrocarbons boiling in the upper portion of the aforementioned broad boiling range, that is, boiling from about 350°C to 400°C, generally participate to a minor degree, if at all, as hydrogen-donating materials during donor hydrocracking. Some of those hydrocarbons, called herein hydrogen donor precursors, are converted during donor hydrocracking into compounds that can be partially hydrogenated to hydrogen-donating compounds boiling in the aforementioned broad boiling range. Thus where a donor recycle is used as will be described below, the hydrogen-donating diluent can advantageously include materials boiling up to 400°C. Compounds included in the hydrogen-donating diluent that do not actually supply hydrogen nevertheless have some usefulness in the process in that they act as diluents to reduce the viscosity of the reaction mass and thereby assist in checking deposition of coke on the furnace tube walls. The proportion of hydrogen-donating hydrocarbon diluent in relation to the residuum feedstock can be from about 0.02:1 to 1.0:1, preferably from 0.15:1 to 0.5:1. Optionally, a portion of the hydrogen donor requirement can be supplied by recycled hydrogen donor material obtained by fractionating the coker liquids product and partially hydrogenating at least a portion of a 180°C to 400°C donor precursor fraction, or preferably a 200°C to 350°C fraction, to produce a recycle hydrogen donor material. The ratio of recycle hydrogen donor material to fresh hydrogen donor material can be from 0.1:1 to 2:1.

The temperature of the reaction mass entering the coker from a transfer tube can be in the range from 420°C to 500°C, preferably from 450°C to 500°C. The relationship of time in the heating zone and temperature of

that zone is governed by the nature of the heavy hydrocarbonaceous oil being treated. Oils that tend to crack easily are kept for a shorter residence time or at a lower temperature, or both, than oils that are more refractory. The heavy hydrocarbonaceous oil feedstock can comprise a residuum from atmospheric or vacuum distillation of conventional crude oil, or an atmospheric or vacuum residuum of heavy oil or bitumen. Where the content of naphthas and distillates is low, as in oil sands bitumens, whole bitumen can be used as the feedstock oil. Mixtures of the above-mentioned oils can also be fed to the process. In general, in treating a given heavy feedstock, a high temperature requires a short residence time in the heating zone, as is known to those skilled in the art. The temperature maintained in a coke drum is generally lower than the material in the transfer tube, and can be from 400°C to 490°C, preferably from 425°C to 480°C. Operating pressure can be from atmospheric, i.e. 101 kPa, to about 600 kPa, preferably from 200 kPa to 400 kPa.

The liquid product material obtained from an overhead stream off the coke drum can be fractionated. At least a portion of a material boiling in the heavy gas oil range, i.e. above 400°C, can be recycled to be mixed with fresh residuum feedstock. The bottoms recycle-to-fresh residuum feed ratio can be up to about 0.4:1. In refinery operation, a bottoms recycle-to-fresh feed ratio of 0.1:1 to 0.3:1 is generally sufficient to remove the entire heavy gas oil product. Optionally, both hydrogen donor material and heavy gas oil can be recycled.

The hold time of reaction mass in the coke drum can be from 5 minutes to 60 minutes. In a typical refinery, delayed coking according to the invention is performed using two coke drums alternately. When one of the drums is filled with coke, it is disconnected from the preheating furnace and the coke product is discharged while the other drum is being filled with

reaction mass from a preheating furnace via a transfer tube. The initial reaction mass entering either coke drum after startup of that drum is subjected to a longer period of exposure to coking conditions than the last reaction mass prior to shutdown of that drum. The method of the invention  
5 can be performed in such refinery conditions.

Figure 1, the single drawing, represents a preferred form of apparatus for carrying out the process of the invention.

Referring to the drawing figure, in a preferred embodiment of the process of the invention, vacuum residuum feedstock is fed by lines 11 and 13  
10 to surge drum 2. Partially hydrogenated light cycle oil is fed by line 12, and blended with residuum to be fed into drum 2 by line 13, and optionally recycled gas oil is added by line 17. The resulting blend is taken through line 14 to coker preheating furnace 6 where it is heated to coking temperature, typically 420°C to 500°C, thence by line 15 to coke drum 7 or coke drum 7a. The drum  
15 not being filled at the time is cut off from the system by valves 3 and 4 or 3a and 4a. After a suitable holding period in the coke drum, at a temperature preferably from 400°C to 480°C, and a pressure substantially lower than the pressure in the preheating furnace 6, during which period coker overheads are removed by line 16 to fractionator 8 from which products from gases to heavy  
20 gas oil are withdrawn by lines 21 to 24, the drum is taken out of service and its coke content removed via line 18 or 18a. Optionally at least a portion of heavy gas oil boiling above 400°C can be recycled via line 17 for further treatment in the coker, and if desired, all of the heavy gas oil can be thus converted to lighter petroleum products or to coke. Where such stream is not  
25 recycled, it can advantageously be fed to a fluid catalytic cracking zone. Optionally a portion of the hydrogen donor requirement can be satisfied by passing through line 19 at least a portion of the gas oil fraction in line 23 boiling between 180°C and 400°C, preferably between 200°C and 350°C,

partially hydrogenating the gas oil in hydrogenation zone 9 and recycling the resulting recycle hydrogen donor material through line 20 to blend with fresh donor fed by line 12.

### Example 1

5 Four parts by volume of a vacuum residuum of conventional crude oil boiling above 510°C was blended with one part of a mildly hydrotreated light cycle oil boiling from 180°C to 390°C and one part of coker recycle gas oil boiling above 400°C. The gas oil served as a diluent providing a lower viscosity to the reaction mixture, and also entered into the donor coking  
10 reaction to some extent. Hydrogen-donating species, ie. tetralin and substituted tetralins, comprised about 35% by weight of the cycle oil. The blend was heated to 493°C in a commercial-scale coker furnace at 1.48 MPa (absolute) and passed through a pressure reducing valve into a coke drum where the reaction mass was held at 471°C and 240 kPa as the coke drum  
15 filled with coke. Coker overheads were taken off the fractionator with yields (net of the added cycle oil) shown as Run 1 in Table 1. The coke product contained 12 percent Volatile Combustible Matter (VCM). A similar run was done with no added cycle oil, and product yields are shown as Run 2.

TABLE 1

| 20 | <u>Conditions</u>                                   | <u>Run 1</u> | <u>Run 2</u> |
|----|-----------------------------------------------------|--------------|--------------|
|    | Coke Drum Temp., °C                                 | 471          | 471          |
|    | Hydrotreated Cycle Oil addition,<br>% of total feed | 16.7         | none         |
| 25 | Product Yield, % on residuum feed                   |              |              |
|    | Vapours (to C4)                                     | 10.7         | 10.8         |
|    | Gasoline (C5-190°C)                                 | 3.3          | 4.2          |
|    | Distillate (190-320°C)                              | 29.9         | 35.1         |
|    | Gas Oil (320-480°C)                                 | 37.5         | 25.4         |
| 30 | Coke (12% VCM)                                      | 19.6         | 24.5         |

During the operation in Run 1 according to the invention, about 12.5 m<sup>3</sup>/m<sup>3</sup> (70 SCFB) of hydrogen was transferred to the residuum products. The Bromine Number of the gasoline boiling range product was decreased from 52 in the prior art operation of Run 2, to 43 in the process of the invention, illustrating a significant improvement in the saturation of the gasoline.

### Examples 2-3

In a laboratory apparatus, a series of simulated delayed coking runs was performed. The apparatus consisted of a single reactor vessel, provided with means for temperature and pressure control. Each reactor charge was held at 427°C and 1.1 MPa for five minutes, then the pressure was reduced to 233 kPa and the treatment was continued at the above temperature for another 20 minutes. The coke yield was normalized to 12% volatile combustible matter (VCM) content for the coke product of each run. The results are summarized in Table 2.

| <u>TABLE 2</u>                                                                                 |                             |                            |                            |
|------------------------------------------------------------------------------------------------|-----------------------------|----------------------------|----------------------------|
| <u>Conditions</u>                                                                              | <u>Run 3<br/>Comparison</u> | <u>Run 4<br/>Example 2</u> | <u>Run 5<br/>Example 3</u> |
| Hydrotreated cycle oil<br>addition to recycle<br>gas oil to residuum<br>feed, ratios by weight | 0:1:4                       | 1:1:4                      | 2:0:4                      |
| Coke yield, % by weight<br>on residuum feed                                                    | 26.5                        | 20.9                       | 16.1                       |
| Coke yield reduction,<br>compared to Run 3, %                                                  | -                           | 21                         | 39                         |

The process of the invention is thus shown to be effective in lowering the production of coke on both laboratory-scale and commercial-scale apparatus. Additional advantages are that the process produces a more saturated gasoline product than conventional processes, and reduces fouling of furnace tubes in the heating zone.

CLAIMS

1. A method for treating heavy hydrocarbonaceous oil feedstock, comprising:

- (a) heating said feedstock to a temperature from  
5 420°C to 500°C in a heating zone to form a reaction mass;  
(b) maintaining said reaction in a coking zone at  
a temperature from 400°C to 490°C and pressure from 101 kPa  
to 600 kPa for a residence time of from 5 to 60 minutes; and  
(c) recovering liquid hydrocarbon products and coke  
10 from said coking zone;  
characterised in that; prior to said heating step, said  
heavy hydrocarbonaceous feedstock is mixed with a  
hydrogen-donating hydrocarbon diluent boiling in a range  
from 180°C to 400°C at atmospheric pressure in a ratio  
15 to said feedstock of .02:1 to 1.0:1 by weight in a mixing  
zone.

2. A method according to Claim 1, wherein said  
hydrogen-donating diluent comprises a partially hydrogenated  
light cycle oil, wherein hydrogen-donating hydrocarbons  
20 and hydrogen donor precursors together comprise at least  
40 percent of said light cycle oil.

3. A method according to Claim 1 or 2, wherein  
said hydrogen-donating diluent boils in a range from  
200°C to 350°C at atmospheric pressure.

25 4. A method according to any of Claims 1 to 3,  
wherein said hydrogen-donating hydrocarbon diluent is  
mixed with said heavy hydrocarbonaceous oil feedstock in  
a ratio to said feedstock of 0.15:1 to 0.5:1.

5. A method according to any of claims 1 to 4,  
30 wherein said heating zone conditions include a temperature  
in the range from 450°C to 500°C.

6. A method according to any of Claims 1 to 5, wherein  
said pressure in said coking zone is from 200 kPa to 400  
kPa.

7. A method according to any of Claims 1 to 6, further characterised by:

(a) fractionating said recovered liquid hydrocarbon products to separate therefrom hydrocarbon streams boiling  
5 below 400°C, to produce a heavy gas oil fraction boiling in a range above 400°C; and

(b) recycling at least a portion of said heavy gas oil fraction to said mixing zone.

8. A method according to claim 7, wherein the ratio  
10 of said recycled heavy gas oil fraction to said heavy hydrocarbonaceous oil feedstock is from 0.1:1 to 0.3:1.

9. A method according to claim 7 or 8, wherein the entire amount of said heavy gas oil fraction is recycled to said mixing zone.

15 10. A method according to any of claims 1 to 9 characterised by:

(a) fractionating said recovered liquid hydrocarbon products to separate therefrom a donor precursor fraction boiling in a range from about 180°C to 400°C.

20 (b) partially hydrogenating at least a portion of said donor precursor fraction to produce a recycle hydrogen-donating material; and

(c) recycling said recycle hydrogen-donating material to form at least a portion of said hydrogen-donating  
25 diluent.

11. A method according to claim 10, wherein said recycle hydrogen-donating material is used in a ratio to fresh hydrogen-donating diluent from 0.1:1 to 2:1.

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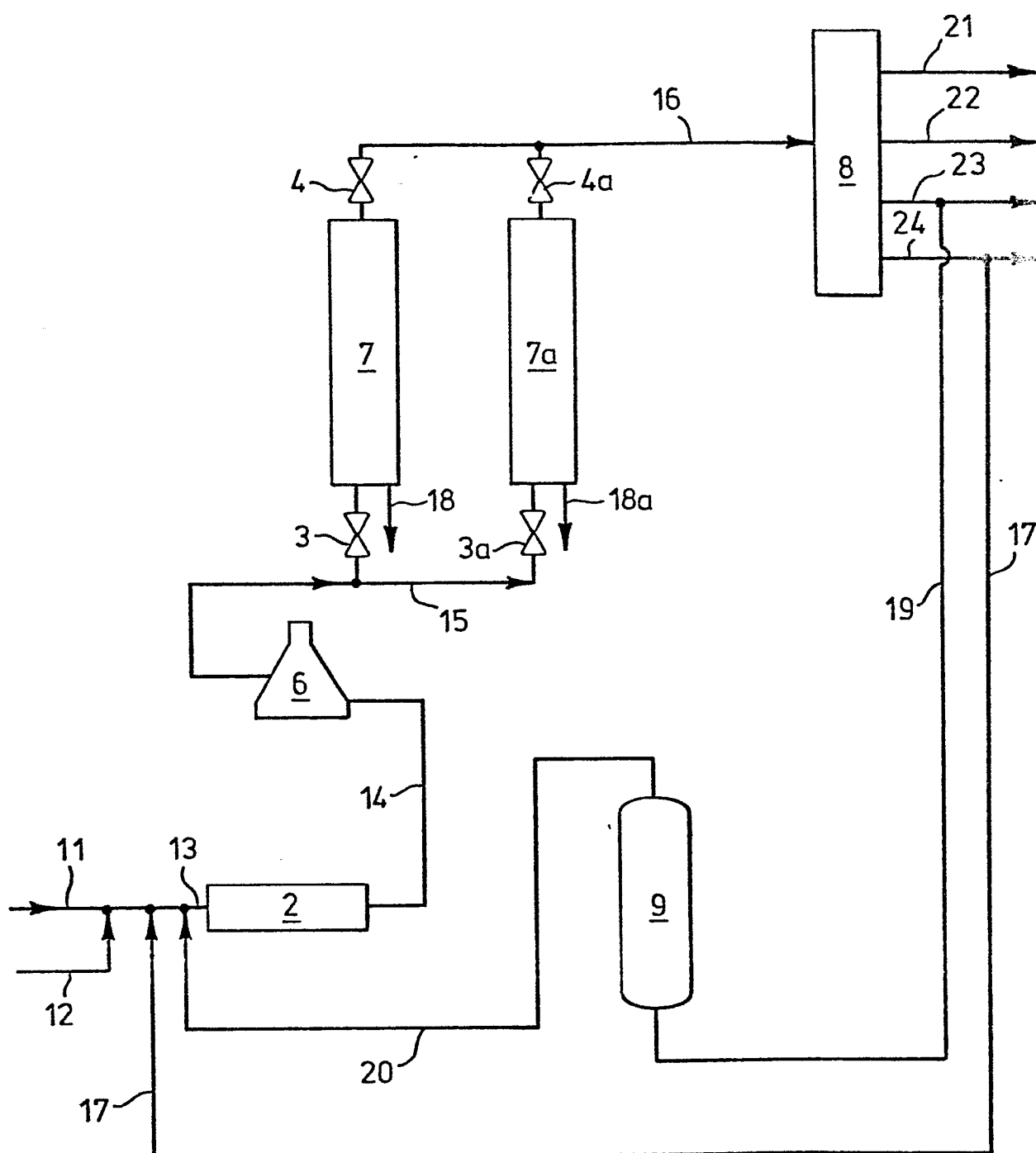


FIG. 1