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(54) **A METHOD OF UPGRADING CRUDE OIL**

(57) The present invention provides a method of upgrading crude oil, the method at least comprising the steps of:

- (a) providing an olefin-containing crude oil stream;
- (b) adding an olefin-containing stream to the olefin-containing crude oil stream provided in step (a), thereby obtaining an olefin-enriched stream;
- (c) subjecting the olefin-enriched stream obtained in step

(b) to an olefin metathesis reaction in the presence of one or more metathesis catalysts thereby obtaining a metathesis product, the metathesis product containing at least 20 wt.% of a fraction having a boiling point between 50-380°C at atmospheric pressure;

(d) removing at least partly the fraction having a boiling point between 50-380°C from the metathesis product as obtained in step (c).

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Description

[0001] The present invention relates to upgrading crude oil.

[0002] In crude oil processing, there is a growing demand for so-called 'middle distillates' (such as kerosene, heating oil, jet fuel, etc.), whereas at the same time the supply of crude oils shifts to more heavy crude oils. The upgrading of crude oils has traditionally been performed via thermal cracking, catalytic cracking or hydrocracking, all using high temperatures and resulting in unselective reactions. Hence, there has been a continuous desire in developing alternative processes that convert crude oils, in particular heavy crude oils, into middle distillate fractions.

[0003] It is an object of the present invention to provide an alternative method for upgrading crude oil, in particular heavy crude oil. It is a further object of the present invention to provide a method for upgrading crude oil, which can be performed at a relatively low temperature, such as below 300°C.

[0004] One or more of the above or other objects can be achieved by providing a method of upgrading crude oil, the method at least comprising the steps of:

- (a) providing an olefin-containing crude oil stream;
- (b) adding an olefin-containing stream to the olefin-containing crude oil stream provided in step (a), thereby obtaining an olefin-enriched stream;
- (c) subjecting the olefin-enriched stream obtained in step (b) to an olefin metathesis reaction in the presence of one or more metathesis catalysts thereby obtaining a metathesis product, the metathesis product containing at least 20 wt.% of a fraction having a boiling point between 50-380°C at atmospheric pressure;
- (d) removing at least partly the fraction having a boiling point between 50-380°C from the metathesis product as obtained in step (c).

[0005] It has surprisingly been found according to the present invention that the upgrading of crude oil, in particular heavy crude oil, can be achieved by an olefin metathesis reaction. Olefin metathesis is a well-known reaction and has been subject to a Nobel Prize in Chemistry in 2005 (in particular for the discovery of a variety of highly efficient and selective catalysts). Because of the relative simplicity of olefin metathesis it often creates fewer undesired by-products than alternative organic reactions. The olefin metathesis reaction typically provides for the redistribution of fragments of olefins by the scission and regeneration of carbon-carbon double bonds. The olefin metathesis reaction can be carried out at room and elevated temperatures using a wide variety of catalysts.

[0006] The present inventors have now surprisingly found that the presence of contaminants commonly present in crude oil (such as nitrogen, oxygen and/or sulphur compounds, and/or metal contaminants such as nickel and vanadium compounds), in particular in heavy crude oils, do not hamper or detrimentally retard the olefin metathesis reaction. Also, the present inventors have surprisingly found that the metathesis catalysts used survive the presence of typical contaminants as present in crude oil, in particular heavy crude oil.

[0007] In step (a), an olefin-containing crude oil stream is provided. Although the olefin-containing crude oil stream is not particularly limited, it typically is from a mineral or fossil (hence non-vegetable and non-synthetic) origin. The olefin-containing crude oil stream may have been obtained as a fraction during processing and refining crude oil. Preferably, at least 10 wt.%, more preferably, at least 20 wt.%, even more preferably at least 50 wt.% or even more than 80 wt.% or even 100 wt.% of the olefin-containing crude oil stream is from a mineral origin.

[0008] Preferably, the olefin-containing crude oil stream provided in step (a) has an aromatic content of at least 10 wt.%, preferably at least 20 wt.%, as determined by ¹H-NMR. Further, it is preferred that the olefin-containing crude oil stream provided in step (a) has a sulphur content of at least 0.1 wt.%, preferably at least 0.5 wt.%, more preferably at least 1.0 wt.%, even more preferably at least 2.0 wt.%, as determined by ASTM D2622. Also, it is preferred that the olefin-containing crude oil stream provided in step (a) has an API gravity of at most 19, as determined according to ASTM D 6822 at 15°C. Further it is preferred that the olefin-containing crude oil stream provided in step (a) has a total Ni/V/Fe content of at least 50 ppm, preferably at least 100 ppm, as determined by ASTM D5863. Also, it is preferred that the olefin-containing crude oil stream provided in step (a) has an asphaltene content of at least 0.04 gram per 100 gram, as determined by ASTM D2007. Further, it is preferred that the olefin-containing crude oil stream provided in step (a) has an Micro-Carbon Residue ('MCR') of at least 0.02 gram per 100 gram as determined by ASTM D4530.

[0009] According to a preferred embodiment of the present invention, at least 50 wt.%, preferably at least 90 wt.%, of the olefin-containing crude oil stream provided in step (a) has a boiling point of above 250°C at atmospheric pressure, preferably above 300°C, more preferably above 330°C, even more preferably above 360°C, yet even more preferably above 390°C. Further, it is preferred that the olefin-containing crude oil stream provided in step (a) contains at least 2.0 wt.%, preferably at least 5.0 wt.%, more preferably at least 10.0 wt.%, even more preferably at least 20 wt.% olefins. Typically, the content of olefins can be determined by ¹H NMR or by bromine number according to ASTM D2710.

[0010] In step (b), an olefin-containing stream is added to the olefin-containing crude oil stream provided in step (a), thereby obtaining an olefin-enriched stream. Although the olefin-containing stream added in step (b) is not particularly

limited, it typically contains lighter olefins than the olefins present in the olefin-containing crude oil stream provided in step (a).

[0011] Preferably, at least 50 wt.%, preferably at least 90 wt.%, of the olefin-containing stream added in step (b) has a boiling point of below 150°C at atmospheric pressure, preferably below 100°C, more preferably below 80°C, even more preferably below 50°C.

[0012] Further it is preferred that the olefin-containing stream added in step (b) contains at least 2.0 wt.%, preferably at least 5.0 wt.%, more preferably at least 10.0 wt.%, even more preferably at least 20 wt.% olefins.

[0013] According to an especially preferred embodiment according to the present invention, at least 90 wt.% of the olefins of the olefin-containing stream added in step (b) are selected from the group consisting of ethylene, propylene, butenes and mixtures thereof.

[0014] In step (c), the olefin-enriched stream obtained in step (b) is subjected to an olefin metathesis reaction in the presence of one or more metathesis catalysts thereby obtaining a metathesis product, the metathesis product containing at least 20 wt.% of a fraction having a boiling point between 50-380°C at atmospheric pressure.

[0015] As the person skilled in the art is familiar with the olefin metathesis reaction and suitable metathesis catalysts and conditions, this is not discussed here in detail.

[0016] Suitable metathesis catalysts include the so-called 'Schrock catalysts' (molybdenum(IV)- and tungsten(IV)-based) and 'Grubbs' catalysts' (ruthenium(II) carbenoid complexes). Suitable metathesis catalysts have been described in detail in paragraphs [0041]-[0091] of WO 2010/062958, the teaching of which is hereby incorporated by specific reference.

[0017] Preferably, the one or more metathesis catalysts to be used according to the present invention are metal carbene catalysts based on the group consisting of ruthenium, molybdenum, osmium, chromium, rhenium and tungsten and a combination thereof; preferably metal carbene catalysts based on the group consisting of ruthenium, molybdenum, tungsten and a combination thereof; more preferably heterogeneous catalysts based on molybdenum. There is also a preference for iron oxide catalysts.

[0018] Typically, the olefin-enriched stream is subjected to the olefin metathesis reaction in step (c) at a temperature between 10°C and 400°C, more typically above 20°C, even more typically above 50°C, preferably above 70°C. Preferably, the olefin-enriched stream is subjected to the olefin metathesis reaction in step (c) at a temperature below 300°C, preferably below 200°C, more preferably below 160°C.

[0019] Furthermore, the olefin-enriched stream is typically subjected to the olefin metathesis reaction in step (c) at a pressure above 2.0 bar, more typically above 5 bar, more typically above 20 bar, preferably above 50 bar.

[0020] As mentioned above, the metathesis product contains at least 20 wt.% of a fraction having a boiling point between 50-380°C at atmospheric pressure. Preferably, the metathesis product obtained in step (c) contains at least 25 wt.%, more preferably at least 30 wt.%, even more preferably at least 40 wt.%, yet even more preferably at least 50 wt.%, of a fraction having a boiling point between 50-380°C at atmospheric pressure.

[0021] According to an especially preferred embodiment according to the present invention, the metathesis product obtained in step (c) comprises at least 5.0 wt.% more of a fraction having a boiling point between 50-380°C at atmospheric pressure, when compared to the olefin-enriched stream as obtained in step (b), preferably at least 7.0 wt.% more, more preferably at least 10 wt.% more, or even at least 20 wt.% more.

[0022] In step (d), the fraction having a boiling point between 50-380°C is at least partly removed from the metathesis product as obtained in step (c), typically by distillation. The fraction having a boiling point between 50-380°C can be suitably used as a middle distillate.

[0023] Preferably, the fraction having a boiling point between 50-380°C as removed at least partly in step (d) contains at least 20 wt.%, preferably at least 50 wt.% olefins, more preferably at least 80 wt.% olefins.

[0024] Hereinafter the invention will be further illustrated by the following non-limiting examples.

Examples

Example 1

[0025] A dehydrogenated vacuum gas oil (VGO) with the composition and properties as given in Table 1 was obtained.

Table 1. Properties and composition of VGO

Property / component	Amount	Measuring method
Specific gravity 15/4C	0.898	
Hydrogen [wt.%]	12.4	
Carbon [wt.%]	3.3	

(continued)

Property / component	Amount	Measuring method
H/C ratio	1.74	
Oxygen [wt.%]	0.071	
Total nitrogen [ppmw]	706	
Sulfur content [wt.%]	2.121	ASTM D2622
Basic nitrogen [ppmw]	232	
Mono aromatic nuclei [wt.%]	4.72	
Di aromatic nuclei [wt.%]	3.77	
Tri aromatic nuclei [wt.%]	3.13	
Tetra+ aromatic nuclei [wt.%]	2.49	
Total aromatic nuclei [wt.%]	14.1	
Micro Carbon Residue (MCR) [wt.%]	0.33	ASTM D4530
Bromine number	6.9	
Fraction of carbon atoms in naphthenic structure [wt.%]	25.4	
Fraction of carbon atoms in aromatic structure [wt.%]	14.4	¹ H-NMR
Fraction of carbon atoms in paraffinic structure [wt.%]	45.5	
Total amount of olefins [wt.%]	45	¹ H-NMR
Iron [ppmw]	0.55	
Sodium [ppmw]	0.11	
Nickel [ppmw]	0.08	
Vanadium [ppmw]	0.38	
Ni/V/Fe content [ppmw]	1.01	ASTM D5863
Asphaltene content [wt.%]		ASTM D2007
Viscosity at 100°C [cSt]	3.33	
V50	19.4	
UOPK	11.89	

[0026] A 272 mg sample of the above VGO and 503 mg catalyst potassium-promoted iron oxide catalyst (as prepared according to the general synthesis procedure as described on page 2119 of S.C. Ndlela et al., "Reducibility of Potassium-Promoted Iron Oxide under Hydrogen Conditions", Ind. Eng. Chem. Res. 42, 2112-2121 (2003)), were fed into an 8 ml Hastelloy C autoclave. The autoclave was charged with ethylene (62 bar, 47 mol. equivalents) and was heated to 150°C. The sample was kept isothermal for 3 hours, after which it was cooled down. The pressure loss from the reaction was 6.0 bar. The gas cap was collected and measured with GC. The obtained liquid (being the metathesis product) was washed off the catalyst with n-pentane (1 ml) and was measured by GC, SimDist, and NMR analysis. The results are given in Table 2.

Table 2. Change in boiling range properties by metathesis reaction.

Boiling range [°C]	Before metathesis reaction [wt.%]	After metathesis reaction [wt.%]	Difference [wt.%]
50-380	61.4	68.9	+7.6
380-615	38.6	31.1	-7.6
25-100	0.44	3.26	+2.82
100-200	6.74	9.33	+2.59

(continued)

Boiling range [°C]	Before metathesis reaction [wt. %]	After metathesis reaction [wt. %]	Difference [wt. %]
200-300	21.57	26.61	+3.04
300-400	40.22	38.59	-1.63
400-500	25.26	20.03	-5.23
500-600	5.77	4.18	-1.59

Table 2 shows an increase of material having a boiling point of 50-380°C and a decrease in material having a boiling point from 380-615°C. This is indicative for that higher-boiling olefins in the (ethylene-enriched) VGO sample have been converted into lower-boiling olefins in the metathesis product.

[0027] Using atmospheric distillation a fraction having a boiling point between 50-380°C at atmospheric pressure was removed from the metathesis product. The removed fraction may be suitably used as a middle distillate.

Discussion

[0028] As can be seen from the Example, the present invention provides a method for upgrading crude oil.

[0029] The person skilled in the art will readily understand that many modifications may be made without departing from the scope of the invention.

Claims

1. A method of upgrading crude oil, the method at least comprising the steps of:

- (a) providing an olefin-containing crude oil stream;
- (b) adding an olefin-containing stream to the olefin-containing crude oil stream provided in step (a), thereby obtaining an olefin-enriched stream;
- (c) subjecting the olefin-enriched stream obtained in step (b) to an olefin metathesis reaction in the presence of one or more metathesis catalysts thereby obtaining a metathesis product, the metathesis product containing at least 20 wt.% of a fraction having a boiling point between 50-380°C at atmospheric pressure;
- (d) removing at least partly the fraction having a boiling point between 50-380°C from the metathesis product as obtained in step (c).

2. The method according to any of the preceding claims, wherein the olefin-containing crude oil stream provided in step (a) has an aromatic content of at least 10 wt.%, as determined by ¹H-NMR.

3. The method according to claim 1 or 2, wherein the olefin-containing crude oil stream provided in step (a) has a sulphur content of at least 0.1 wt.% as determined by ASTM D2622.

4. The method according to any of the preceding claims, wherein the olefin-containing crude oil stream provided in step (a) has an API gravity of at most 19, as determined according to ASTM D 6822 at 15°C

5. The method according to any of the preceding claims, wherein at least 50 wt.%, preferably at least 90 wt.%, of the olefin-containing crude oil stream provided in step (a) has a boiling point of above 250°C at atmospheric pressure, preferably above 300°C, more preferably above 330°C, even more preferably above 360°C, yet even more preferably above 390°C.

6. The method according to any of the preceding claims, wherein the olefin-containing crude oil stream provided in step (a) contains at least 2.0 wt.%, preferably at least 5.0 wt.%, more preferably at least 10.0 wt.%, even more preferably at least 20 wt.% olefins.

7. The method according to any of the preceding claims, wherein at least 50 wt.%, preferably at least 90 wt.%, of the olefin-containing stream added in step (b) has a boiling point of below 150°C at atmospheric pressure, preferably below 100°C, more preferably below 80°C, even more preferably below 50°C.

8. The method according to any of the preceding claims, wherein the olefin-containing stream added in step (b) contains at least 2.0 wt.%, preferably at least 5.0 wt.%, more preferably at least 10.0 wt.%, even more preferably at least 20 wt.% olefins.
- 5 9. The method according to any of the preceding claims, wherein the olefin-enriched stream is subjected to the olefin metathesis reaction in step (c) at a temperature below 300°C, preferably below 200°C, more preferably below 160°C.
- 10 10. The method according to any of the preceding claims, wherein the metathesis product obtained in step (c) comprises at least 5.0 wt.% more of a fraction having a boiling point between 50-380°C at atmospheric pressure, when compared to the olefin-enriched stream as obtained in step (b).
- 15 11. The method according to any of the preceding claims, wherein the fraction having a boiling point between 50-380°C as at least partly removed in step (d) contains at least 20 wt.%, preferably at least 50 wt.% olefins, more preferably at least 80 wt.% olefins.



EUROPEAN SEARCH REPORT

Application Number
EP 16 15 1925

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			TECHNICAL FIELDS SEARCHED (IPC)
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The present search report has been drawn up for all claims			
Place of search The Hague		Date of completion of the search 11 July 2016	Examiner Galleiske, Anke
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

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**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

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