

RENEWABLE STABILIZED NAPHTHA-RANGE HYDROCARBON FEED, THERMAL CRACKING METHOD AND PRODUCTS THEREOF

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Technical Field

The present invention relates to a method comprising thermal cracking, a renewable stabilized naphtha-range hydrocarbon feed usable in such a method and products obtainable by use of such a method.

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Background of the Invention

Thermal cracking, such as steam cracking, is a well-known and established route for upgrading conventional (mineral oil based) material. In recent times, thermal cracking of biogenic material has been investigated, while it was usually tried to achieve direct cracking of a biogenic feed (usually having high oxygen content) or to mimic conventional (fossil) feeds.

High value chemicals produced in the thermal cracking process (such as steam cracking) are ethylene, propylene, butadiene, olefinic C4, benzene, xylene and toluene. Of these high value chemicals light olefins, specifically ethylene and propylene are the most sought after in industry.

C4 olefins are also valuable products but may require additional refining steps to extract chemical and polymer grades of each individual component. Aromatics are of less importance as there are other routes to their manufacture such as reforming of fossil naphtha. In addition, in steam cracking operations benzene may enrich in a pyrolysis gasoline fraction of the cracking effluent which is typically valorised in fuels. Since there are stringent limitations in the amount of benzene allowable in such fuel products (due to its carcinogenic effects) it may even become an unwanted by-product which requires removal.

In order to introduce bio molecules to the petrochemical value chain, and in view of the above considerations, it is useful to employ a process that

maximises the yields to light olefins while suppressing formation of aromatics, in particular benzene.

Brief description of the invention

5 The present invention was made in view of the above-mentioned problems and it is an object of the present invention to provide a renewable stabilized naphtha-range hydrocarbon feed, a thermal cracking method employing the renewable stabilized naphtha-range hydrocarbon feed and products emerging from the method as well as their use and further processing.

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The problem underlying the invention is solved by the subject-matters set forth in the independent claims. Further beneficial developments are set forth in dependent claims.

15 In brief, the present invention relates to one or more of the following items:

1. A method comprising

(a) a step of providing a renewable stabilized naphtha-range hydrocarbon feed,

20 (b) a step of thermally cracking the renewable stabilized naphtha-range hydrocarbon feed in a thermal cracking furnace, optionally together with co-feed(s) and/or additive(s), and

(c) a step of subjecting the effluent of the thermal cracking furnace of step (b) to a separation treatment to provide at least a light olefin(s) fraction.

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2. The method according to item 1, wherein the thermal cracking step (b) is conducted at a coil outlet temperature (COT) selected from the range from 780°C to 880°C, preferably from 800°C to 860°C, more preferably from 820°C to 850°C.

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3. The method according to item 1 or 2, wherein the thermal cracking step (b) is conducted at a coil outlet pressure (COP) selected from the range from 1.3 bar to 6.0 bar, preferably from 1.3 bar to 3.0 bar.
- 5 4. The method according to any one of the preceding items, wherein the thermal cracking step (b) is a steam cracking step.
5. The method according to any one of the preceding items, wherein the thermal cracking step (b) is conducted in the presence of a thermal cracking
10 diluent at a dilution within a range from 0.10 to 0.85, preferably from 0.25 to 0.60, such as 0.35 to 0.55.
6. The method according to any one of the preceding items, comprising a purification treatment to remove at least one of methyl acetylene,
15 propadiene, CO, CO₂ and C₂H₂, preferably at least one of CO, CO₂ and C₂H₂, as a purification stage (c') in the step (c) of separating at least the light olefin(s) fraction from the effluent of the thermal cracking furnace of step (b).
7. The method according to any one of the preceding items, comprising
20 performing one or more further cracking operation(s) to provide further cracking effluent(s), wherein
step (c) further comprises adding the further effluent(s) and/or fraction(s) thereof to the effluent of the thermal cracking furnace of step (b) before and/or during the separation treatment.
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8. The method according to any one of the preceding items, wherein the thermal cracking in step (b) is carried out in the presence of co-feed(s).
9. The method according to the preceding item, wherein the content of
30 the renewable stabilized naphtha-range hydrocarbon feed in the total cracker feed is in the range of from 10 wt.-% to 100 wt.-%, preferably 20 wt.-% to 100 wt.-%, 30 wt.-% to 100 wt.-%, 40 wt.-% to 100 wt.-%, 50 wt.-% to 100 wt.-%, 60 wt.-% to 100 wt.-%, 70 wt.-% to 100 wt.-%, 80 wt.-% to 100 wt.-%, or 90 wt.-% to 100 wt.-%, wherein the total cracker feed refers

to the renewable stabilized naphtha-range hydrocarbon feed plus optional co-feed(s) and optional additive(s).

10. The method according to any one of the preceding items, wherein the
5 co-feed(s) comprise a fossil hydrocarbon co-feed.

11. The method according to any one of the preceding items, wherein the co-feed(s) comprise a naphtha range feed.

10 12. The method according to any one of the preceding items, wherein the total cracker feed has a sulphur content in the range from 20 to 300 ppm by weight, preferably 20 to 250 ppm by weight, more preferably 20 to 100 ppm by weight, and even more preferably 50 to 65 ppm by weight.

15 13. The method according to any one of the preceding items, wherein the step (a) of providing the renewable stabilized naphtha-range hydrocarbon feed comprises

a stage of subjecting an oxygenate bio-renewable feed to hydrotreatment comprising at least hydrodeoxygenation to provide at least a
20 liquid hydrocarbon stream, and

a stage of subjecting at least part of the liquid hydrocarbon stream to fractionation and recovering at least the renewable stabilized naphtha-range hydrocarbon feed.

25 14. The method according to item 13, wherein the hydrotreatment comprises at least the hydrodeoxygenation to provide a hydrotreatment effluent, and the hydrotreatment effluent is subjected to gas-liquid separation to provide a gaseous stream and a first liquid hydrocarbon stream, and

at least part of the first liquid hydrocarbon stream is subjected to a
30 further hydrotreatment comprising at least hydroisomerisation, followed by optional further gas-liquid separation, to provide at least a second liquid hydrocarbon stream, and subjecting at least part of the second liquid hydrocarbon stream as the liquid hydrocarbon stream to the fractionation and

recovering of at least the renewable stabilized naphtha-range hydrocarbon feed.

15. The method according to item 14, wherein at least a part of the first
5 liquid hydrocarbon stream and/or of the second liquid hydrotreatment stream
is recycled back to the hydrotreatment comprising at least
hydrodeoxygenation.

16. The method according to item 14 or 15, further comprising subjecting
10 the gaseous stream to a propane separation process to provide a stream
enriched in propane and a stream depleted in propane.

17. The method according to item 16, further comprising subjecting at
least part of the propane from the stream enriched in propane to
15 dehydrogenation, preferably catalytic dehydrogenation, to produce
propylene.

18. The method according to any one of items 13 to 17, wherein
the stage of subjecting at least part of the liquid hydrocarbon stream
20 to fractionation and recovering at least the renewable stabilized naphtha-
range hydrocarbon feed further comprises recovering a heavy liquid
hydrocarbon fraction.

19. The method according to item 18, wherein
25 the heavy liquid hydrocarbon fraction is subjected to further
fractionation to provide at least an aviation fuel range fraction and a bottoms
fraction.

20. The method according to any one of items 13 to 17, wherein
30 the stage of subjecting at least part of the liquid hydrocarbon stream
to fractionation and recovering at least the renewable stabilized naphtha-
range hydrocarbon feed further comprises recovering at least an aviation fuel
range fraction and/or a diesel range fraction.

21. The method according to any one of items 18 to 20, wherein the diesel range fraction, the aviation fuel range fraction, the heavy liquid hydrocarbon fraction and/or the bottoms fraction has an iso-paraffins content of at least 65 wt.-%, preferably at least 70 wt.-%, at least 75 wt.-%, at least 80 wt.-%, at least 85 wt.-% or at least 90 wt.-%.

22. The method according to any one of items 13 to 21, wherein the stage of subjecting at least part of the liquid hydrocarbon stream to fractionation and recovering at least the renewable stabilized naphtha-range hydrocarbon feed comprises at least

subjecting at least part of the liquid hydrocarbon stream to fractionation to provide a naphtha range fraction, and

subjecting the naphtha range fraction to stabilization, wherein the stabilisation comprises removing, preferably by means of a distillation technique, at least part of components boiling below 20°C, preferably at least part of components boiling below 25°C, at least part of components boiling below 30°C, at least part of components boiling below 40°C or at least part of components boiling below 50°C.

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23. The method according to any one of items 18 to 20, wherein the heavy liquid hydrocarbon fraction and/or the diesel range fraction has an iso-paraffins content of less than 65 wt.-%.

24. The method according to any one of the preceding items, wherein the step (a) of providing a renewable stabilized naphtha-range hydrocarbon feed comprises:

subjecting an oxygenate bio-renewable feed to hydrotreatment comprising at least hydrodeoxygenation to provide a hydrotreatment effluent,

subjecting at least part of the hydrotreatment effluent to gas-liquid separation to provide a gaseous stream and a first liquid hydrocarbon stream,

providing the first liquid hydrocarbon stream as a liquid hydrocarbon stream or subjecting at least part of the first liquid hydrocarbon stream to a

further hydrotreatment comprising at least hydroisomerisation, followed by optional further gas-liquid separation, to provide at least a second liquid hydrocarbon stream as the liquid hydrocarbon stream, and

5 feeding at least part of the liquid hydrocarbon stream to a first distillation column, preferably a first stabilisation column, to obtain a first overhead fraction and a stabilised heavy liquid hydrocarbon fraction,

optionally using at least part of the stabilised heavy liquid hydrocarbon fraction in diesel fuel and/or recovering from at least part of the stabilised heavy liquid hydrocarbon fraction at least an aviation fuel range fraction and
10 a bottoms fraction,

separating from the first overhead fraction at least a fuel gas fraction and a naphtha range fraction,

refluxing a portion, preferably at least 50 wt.-%, more preferably at least 70 wt.-%, even more preferably at least 85 wt.-% of the naphtha range
15 fraction back to the first distillation column,

feeding at least a portion of the naphtha range fraction to a second distillation column, preferably a second stabilisation column, to obtain a second overhead fraction, preferably comprising at least part of components boiling below 20°C, and a stabilised naphtha range fraction,

20 separating from the second overhead fraction at least a further fuel gas fraction and light liquid hydrocarbons, and

refluxing at least a portion, preferably at least 50 wt.-%, more preferably at least 70 wt.-%, even more preferably at least 85 wt.-% of the light liquid hydrocarbons back to the second distillation column, and

25 recovering at least a portion of the stabilised naphtha range fraction as the renewable stabilized naphtha-range hydrocarbon feed.

25. The method according to any one of items 13 to 24, wherein the hydrotreatment comprising at least hydrodeoxygenation further comprises
30 hydroisomerisation.

26. The method according to any one of the preceding items, further comprising derivatisation of at least part of the light olefin(s) to obtain one

or more derivate(s) of the light olefin(s) as bio-monomer(s), such as acrylic acid, acrylonitrile, acrolein, propylene oxide, ethylene oxide, 1,4-butanediol, 1,2-butanediol, 1,3-butanediol, 2,3-butanediol, adiponitrile, hexamethylene diamine (HMDA), hexamethylene diisocyanate (HDI), (methyl)methacrylate, ethylidene norbornene, 1,5,9-cyclododecatriene, sulfolane, 1,4-hexadiene, tetrahydrophthalic anhydride, valeraldehyde, 1,2-butyloxide, n-butyl mercaptan, o-sec-butylphenol, octene and sec-butyl alcohol.

27. The method according to any one of the preceding items, further comprising

(d) a step of (co)polymerizing at least one of the light olefin(s) separated in step (c) and/or at least one of the bio-monomer(s), optionally together with other (co)monomer(s) and/or after optional further purification, to produce a biopolymer composition.

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28. The method according to item 27, wherein the biopolymer composition is further processed to produce a sanitary article, a construction material, a packaging material, a coating composition, a paint, a decorative material, such as a panel, an interior part of a vehicle, such as an interior part of a car, a rubber composition, a tire or tire component, a toner, a personal health care article, a part of a consumer good, a part or a housing of an electronic device, a film, a moulded product, a gasket, optionally together with other components.

29. A renewable stabilized naphtha-range hydrocarbon feed for thermal cracking.

30. The renewable stabilized naphtha-range hydrocarbon feed according to item 29, wherein the renewable stabilized naphtha-range hydrocarbon feed has a content of naphthenes in the range of from 0.1 wt.-% to 10.0 wt.-% based on the total weight of the renewable stabilized naphtha-range hydrocarbon feed.

31. The renewable stabilized naphtha-range hydrocarbon feed according to item 29 or 30, wherein the renewable stabilized naphtha-range hydrocarbon feed has a content of naphthenes of 0.2-10.0 wt.-%, such as 0.5-8.0 wt.-%, 0.5-6.0 wt.-%, 0.6 to 5.8 wt.-%, 0.8 to 5.8 wt.-%, 1.0 to 5.6 wt.-% or 1.2 to 5.6 wt.-%.

32. The renewable stabilized naphtha-range hydrocarbon feed according to any one of items 29 to 31, wherein the renewable stabilized naphtha-range hydrocarbon feed has a content of olefins of 0.50 wt.-% or less, preferably 0.40 wt.-% or less, 0.30 wt.-% or less, 0.25 wt.-% or less, 0.20 wt.-% or less, 0.15 wt.-% or less, 0.12 wt.-% or less, 0.10 wt.-% or less, 0.07 wt.-% or less, or 0.05 wt.-% or less.

33. The renewable stabilized naphtha-range hydrocarbon feed according to any one of items 29 to 32, wherein the renewable stabilized naphtha-range hydrocarbon feed has a total content of olefins and naphthenes in the range from 0.1 wt.-% to 10.0 wt.-%.

34. The renewable stabilized naphtha-range hydrocarbon feed according to any one of items 29 to 33, wherein the renewable stabilized naphtha-range hydrocarbon feed has a total content of olefins and naphthenes of 0.1 wt.-% to 8.0 wt.-%, such as 0.1 wt.-% to 6.5 wt.-%, 0.1 wt.-% to 6.0 wt.-%, 0.2 wt.-% to 5.5 wt.-%, 0.5 wt.-% to 5.5 wt.-%, 0.5 wt.-% to 5.0 wt.-%, 0.8 wt.-% to 5.0 wt.-%, 0.9 wt.-% to 5.0 wt.-%, 1.0 wt.-% to 5.0 wt.-%, 1.1 wt.-% to 5.0 wt.-%, or 1.2 wt.-% to 5.0 wt.-%.

35. The renewable stabilized naphtha-range hydrocarbon feed according to any one of items 29 to 34, wherein the renewable stabilized naphtha-range hydrocarbon feed has a content of aromatics of 0.80 wt.-% or less, preferably 0.70 wt.-% or less, 0.60 wt.-% or less, 0.50 wt.-% or less, 0.40 wt.-% or less, 0.35 wt.-% or less, 0.30 wt.-% or less, 0.25 wt.-% or less, 0.20 wt.-% or less, or 0.15 wt.-% or less.

36. The renewable stabilized naphtha-range hydrocarbon feed according to any one of items 29 to 35, wherein the renewable stabilized naphtha-range hydrocarbon feed has a ratio between the content of naphthenes and the content of aromatics of 1 or more, preferably 10 or more, 50 or more, or 100 or more.

37. The renewable stabilized naphtha-range hydrocarbon feed according to any one of items 29 to 36, wherein the renewable stabilized naphtha-range hydrocarbon feed has a total content of olefins, aromatics and naphthenes of 0.1 wt.-% to 10.0 wt.-%, preferably 0.1 wt.-% to 8.0 wt.-%, 0.1 wt.-% to 6.5 wt.-%, 0.2 wt.-% to 6.0 wt.-%, 0.5 wt.-% to 5.5 wt.-%, 0.5 wt.-% to 5.0 wt.-%, 0.8 wt.-% to 5.0 wt.-%, 0.9 wt.-% to 5.0 wt.-%, 1.0 wt.-% to 5.0 wt.-%, 1.1 wt.-% to 5.0 wt.-%, or 1.2 wt.-% to 5.0 wt.-%.

38. The renewable stabilized naphtha-range hydrocarbon feed according to any one of items 29 to 37, wherein the renewable stabilized naphtha-range hydrocarbon feed has a content of oxygenates of 1000 wt.-ppm or less, preferably 700 wt.-ppm or less, 500 wt.-ppm or less, 300 wt.-ppm or less, 100 wt.-ppm or less, 80 wt.-ppm or less, 60 wt.-ppm or less, 50 wt.-ppm or less, 40 wt.-ppm or less, or 30 wt.-ppm or less.

39. The renewable stabilized naphtha-range hydrocarbon feed according to any one of items 29 to 38, wherein the renewable stabilized naphtha-range hydrocarbon feed has a content of C17 and higher carbon number compounds of 1.0 wt.-% or less, such as 0.0 to 0.9 wt.-%, preferably 0.0 to 0.8 wt.-%, more preferably 0.0 to 0.5 wt.-% or 0.0 to 0.2 wt.-%.

40. The renewable stabilized naphtha-range hydrocarbon feed according to any one of items 29 to 39, wherein the renewable stabilized naphtha-range hydrocarbon feed has a carbon range of 10 or less, preferably 8 or less, 7 or less, 6 or less, or 5 or less, and the carbon range is 1 or more, such as from 1 to 10, 2 to 10, 3 to 10, 3 to 8, 3 to 7, or 3 to 6.

41. The renewable stabilized naphtha-range hydrocarbon feed according to any one of items 29 to 40, wherein the renewable stabilized naphtha-range hydrocarbon feed has an interventile carbon number range (IVR) of 6.5 or less, preferably 5.0 or less, 4.5 or less, 4.0 or less or 3.8 or less.

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42. The renewable stabilized naphtha-range hydrocarbon feed according to any one of items 29 to 41, wherein the renewable stabilized naphtha-range hydrocarbon feed has an interdecile carbon number range (IDR) of 4.5 or less, preferably 4.0 or less, 3.5 or less, or 3.0 or less.

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43. The renewable stabilized naphtha-range hydrocarbon feed according to any one of items 29 to 42, wherein the renewable stabilized naphtha-range hydrocarbon feed has an interquartile carbon number range (IQR) of 2.5 or less, preferably 2.0 or less, 1.8 or less, or 1.5 or less.

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44. The renewable stabilized naphtha-range hydrocarbon feed according to any one of items 29 to 43, wherein the renewable stabilized naphtha-range hydrocarbon feed has a content of C11 and higher carbon number components of less than 5.0 wt.-%, preferably 4.5 wt.-% or less, 4.0 wt.-% or less, 3.5 wt.-% or less, 3.0 wt.-% or less, 2.5 wt.-% or less or 2.0 wt.-% or less.

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45. The renewable stabilized naphtha-range hydrocarbon feed according to any one of items 29 to 44, wherein the renewable stabilized naphtha-range hydrocarbon feed has a T95 temperature of 220°C or less, preferably 200°C or less, 180°C or less, 160°C or less, or 140°C or less.

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46. The renewable stabilized naphtha-range hydrocarbon feed according to any one of items 29 to 45, wherein the renewable stabilized naphtha-range hydrocarbon feed has a T99 temperature of 220°C or less, preferably 200°C or less, 180°C or less, 160°C or less, or 140°C or less.

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47. The renewable stabilized naphtha-range hydrocarbon feed according to any one of items 29 to 46, wherein the renewable stabilized naphtha-range hydrocarbon feed has a final boiling point of 220°C or less, preferably 200°C or less, 180°C or less, or 160°C or less.

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48. The renewable stabilized naphtha-range hydrocarbon feed according to any one of items 29 to 47, wherein the renewable stabilized naphtha-range hydrocarbon feed has an initial boiling point of 20°C or more, preferably 20°C to 60°C, such as 30°C to 50°C or 30°C to 45°C.

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49. The renewable stabilized naphtha-range hydrocarbon feed according to any one of items 29 to 48, wherein the renewable stabilized naphtha-range hydrocarbon feed has a T5 temperature of 40°C or more, preferably 45°C or more, 50°C or more, 55°C or more, or 60°C or more.

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50. The renewable stabilized naphtha-range hydrocarbon feed according to any one of items 29 to 49, wherein the difference between the T10 temperature and the T90 temperature of the renewable stabilized naphtha-range hydrocarbon feed is less than 100°C, preferably less than 80°C, such as 20°C to 75°C, 30°C to 70°C, or 40°C to 70°C.

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51. The renewable stabilized naphtha-range hydrocarbon feed according to any one of items 29 to 50, wherein the renewable stabilized naphtha-range hydrocarbon feed has a total paraffins content of 90 wt.-% or more, preferably 92 wt.-% or more, 93 wt.-% or more, 94 wt.-% or more or 95 wt.-% or more.

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52. The renewable stabilized naphtha-range hydrocarbon feed according to any one of items 29 to 51, wherein the renewable stabilized naphtha-range hydrocarbon feed has a content ratio of i-paraffins to n-paraffins in the range of 1.7 or less, preferably 1.5 or less, such as 0.5 to 1.7, or 0.7 to 1.5.

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53. The renewable stabilized naphtha-range hydrocarbon feed according to any one of items 29 to 52, wherein the renewable stabilized naphtha-range hydrocarbon feed has a content ratio of i-paraffins to n-paraffins in the range of 2.0 or more, preferably 2.2 or more.

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54. The renewable stabilized naphtha-range hydrocarbon feed according to any one of items 29 to 53, wherein the renewable stabilized naphtha-range hydrocarbon feed is obtainable by a method comprising subjecting an oxygenate bio-renewable feed to hydrotreatment comprising at least hydrodeoxygenation, and optionally to hydroisomerisation.

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55. The renewable stabilized naphtha-range hydrocarbon feed according to item 54, wherein the method comprises the hydroisomerisation.

15 56. The renewable stabilized naphtha-range hydrocarbon feed according to any one of items 29 to 55 obtainable by a method comprising:

subjecting an oxygenate bio-renewable feed to hydrotreatment comprising at least hydrodeoxygenation to provide a hydrotreatment effluent,

20 subjecting at least part of the hydrotreatment effluent to gas-liquid separation to provide a gaseous stream and a first liquid hydrocarbon stream,

providing the first liquid hydrocarbon stream as a liquid hydrocarbon stream or subjecting at least part of the first liquid hydrocarbon stream to a further hydrotreatment comprising at least hydroisomerisation, followed by optional further gas-liquid separation, to provide at least a second liquid hydrocarbon stream as the liquid hydrocarbon stream, and

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feeding at least part of the liquid hydrocarbon stream to a first distillation column, preferably a first stabilisation column, to obtain a first overhead fraction and a stabilised heavy liquid hydrocarbon fraction,

30 separating from the first overhead fraction at least a fuel gas fraction and a naphtha range fraction,

refluxing a portion, preferably at least 50 wt.-%, more preferably at least 70 wt.-%, even more preferably at least 85 wt.-% of the naphtha range fraction back to the first distillation column,

feeding at least a portion of the naphtha range fraction to a second distillation column, preferably a second stabilisation column, to obtain a second overhead fraction, preferably comprising at least part of components boiling below 20°C, and a stabilised naphtha range fraction,

5 separating from the second overhead fraction at least a further fuel gas fraction and light liquid hydrocarbons, and

refluxing at least a portion, preferably at least 50 wt.-%, more preferably at least 70 wt.-%, even more preferably at least 85 wt.-% of the light liquid hydrocarbons back to the second distillation column, and

10 recovering at least a portion of the stabilised naphtha range fraction as the renewable stabilized naphtha-range hydrocarbon feed.

57. The renewable stabilized naphtha-range hydrocarbon feed according to item 56, wherein the hydrotreatment comprising at least
15 hydrodeoxygenation further comprises hydroisomerisation.

58. The renewable stabilized naphtha-range hydrocarbon feed according to any one of items 29 to 57, having a content of C4 and lower carbon number compounds of 5.0 wt.-% or less, preferably 2.5 wt.-% or less, more
20 preferably 2.0 wt.-% or less, even more preferably 1.5 wt.-% or less

59. The method according to any one of items 1 to 25, wherein the renewable stabilized naphtha-range hydrocarbon feed is the renewable stabilized naphtha-range hydrocarbon feed according to any one of items 29
25 to 58.

60. A renewable thermal cracking effluent having a benzene content of 6.0 wt.-% or less, a total content of ethylene and propylene of 45.0 wt.-% or more and a carbon monoxide content of 0.25 wt.-% or less.

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61. The renewable thermal cracking effluent according to item 60, having a benzene content of 0.01 wt.-% to 6.0 wt.-%, such as 0.1 wt.-% to 4.0 wt.-%, 0.1 wt.-% to 3.6 wt.-%, 0.1 wt.-% to 3.4 wt.-%, 0.1 wt.-% to 3.2 wt.-%

%, 0.1 wt.-% to 3.0 wt.-%, 0.1 wt.-% to 2.8 wt.-%, 0.1 wt.-% to 2.6 wt.-%, 0.2 wt.-% to 2.4 wt.-%, 0.3 wt.-% to 2.2 wt.-%, or 0.5 wt.-% to 2.0 wt.-% or less.

- 5 62. The renewable thermal cracking effluent according to item 60 or 61, wherein the renewable thermal cracking effluent has a total content of ethylene and propylene of 45 wt.-% to 65 wt.-%, preferably 46.0 wt.-% to 65.0 wt.-%, 47.0 wt.-% to 65.0 wt.-%, 48.0 wt.-% to 65.0 wt.-%, 49.0 wt.-% to 65.0 wt.-%, 50.0 wt.-% to 60.0 wt.-%, or 50.0 wt.-% to 55.0 wt.-%.

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63. The renewable thermal cracking effluent according to any one of items 60 to 62, wherein the renewable thermal cracking effluent has a total content of C4 olefins of at least 5.0 wt.-%, such as 5.0 wt.-% to 20.0 wt.-%, preferably at least 8.0 wt.-%, at least 10.0 wt.-%, at least 11.0 wt.-%, at least 12.0 wt.-%, at least 12.6 wt.-%, at least 13.0 wt.-%, or at least 13.5 wt.-%.

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64. The renewable thermal cracking effluent according to any one of items 60 to 63, wherein the renewable thermal cracking effluent is the effluent of the thermal cracking furnace of step (b) of the method according to any one of items 1 to 25.

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65. The renewable thermal cracking effluent according to any one of items 60 to 64, wherein the renewable thermal cracking effluent has a carbon monoxide content of 0.23 wt.-% or less, preferably 0.21 wt.-% or less, 0.20 wt.-% or less, 0.19 wt.-% or less, 0.18 wt.-% or less, 0.17 wt.-% or less, 0.16 wt.-% or less, 0.15 wt.-% or less, 0.14 wt.-% or less, 0.13 wt.-% or less, 0.12 wt.-% or less, 0.11 wt.-% or less, 0.10 wt.-% or less, or 0.09 wt.-% or less.

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66. The renewable thermal cracking effluent according to any one of items 60 to 65, wherein the renewable thermal cracking effluent has a C4

monoolefin content of 6.0 wt.-% or more, preferably 6.5 wt.-% or more, 6.8 wt.-% or more, 7.0 wt.-% or more, 7.2 wt.-% or more, or 7.4 wt.-% or more.

67. The renewable thermal cracking effluent according to any one of items
5 60 to 66, wherein the renewable thermal cracking effluent has a C4 monoolefin content of at most 15.0 wt.-%, or at most 13.0 wt.-%.

68. The renewable thermal cracking effluent according to any one of items
60 to 67, wherein the renewable thermal cracking effluent has a 1,3-
10 butadiene content of at least 5.0 wt.-%, preferably at least 5.5 wt.-%, at least 6.0 wt.-% or at least 6.2 wt.-%.

69. The renewable thermal cracking effluent according to any one of items
60 to 68, wherein the renewable thermal cracking effluent has a 1,3-
15 butadiene content of at most 15.0 wt.-%, at most 13.0 wt.-%, or at most 11.0 wt.-%.

70. The renewable thermal cracking effluent according to any one of items
60 to 69, wherein the renewable thermal cracking effluent has an isobutene
20 content of least 2.0 wt.-%, preferably at least 2.4 wt.-%, at least 3.0 wt.-%, or at least 3.2 wt.-%.

71. The renewable thermal cracking effluent according to any one of items
60 to 70, wherein the renewable thermal cracking effluent has an isobutene
25 content of at most 10.0 wt.-%, at most 9.0 wt.-%, or at most 8.0 wt.-%.

72. The renewable thermal cracking effluent according to any one of items
60 to 71, wherein the renewable thermal cracking effluent has a content of
n-C4 monoolefins of 3.0 wt.-% or more, preferably 3.5 wt.-% or more, or 4.0
30 wt.-% or more.

73. The renewable thermal cracking effluent according to any one of items
60 to 72, wherein the renewable thermal cracking effluent has a content of

n-C4 monoolefins of at most 15.0 wt.-%, at most 12.0 wt.-%, or at most 10.0 wt.-%.

74. The renewable thermal cracking effluent according to any one of items
5 60 to 73, wherein the renewable thermal cracking effluent has a total content of C2-C4 paraffins of more than 4.0 wt.-%, preferably 4.2 wt.-% or more, more preferably 4.3 wt.-% or more.

75. The renewable thermal cracking effluent according to any one of items
10 60 to 74, wherein the renewable thermal cracking effluent has a total content of C2-C4 paraffins of at most 15.0 wt.-%, at most 12.0 wt.-% or at most 10.0 wt.-%.

76. The renewable thermal cracking effluent according to any one of items
15 60 to 75, wherein the renewable thermal cracking effluent has a content of pyrolysis fuel oil (C10 and heavier compounds, abbreviated "PFO") of less than 1.5 wt.-%, preferably less than 1.2 wt.-%, more preferably less than 1.0 wt.-%.

77. The renewable thermal cracking effluent according to any one of items
20 60 to 76, wherein the renewable thermal cracking effluent has a toluene content in the range of from 0.2 wt.-% to 1.8 wt.-%, preferably 0.2 wt.-% to 1.6 wt.-%, 0.2 wt.-% to 1.4 wt.-%, 0.2 wt.-% to 1.2 wt.-%, 0.2 wt.-% to 1.0 wt.-%, 0.2 wt.-% to 0.9 wt.-%, 0.2 wt.-% to 0.8 wt.-%, 0.2 wt.-% to
25 0.7 wt.-%, or 0.3 wt.-% to 0.6 wt.-%.

78. The renewable thermal cracking effluent according to any one of items
60 to 77, wherein the renewable thermal cracking effluent has a total content of ethylene and propylene of 50.0 wt.-% or more, a benzene content of
30 4.0 wt.-% or less, and a toluene content in the range of from 0.2 wt.-% to 0.6 wt.-%

79. The renewable thermal cracking effluent according to any one of items 60 to 78, wherein the renewable thermal cracking effluent has a total content of ethylene and propylene and total C4 olefins of 45 wt.-% to 80 wt.-%, preferably 50 wt.-% to 75 wt.-%, 50 wt.-% to 70 wt.-%, 50 wt.-% to 65 wt.-%, or 55 wt.-% to 65 wt.-%.

80. A biopolymer composition obtainable by the method according to item 27.

10 **Brief description of drawings**

FIG. 1 illustrates linear interpolation for obtaining c₅₀ value.

Detailed description of the invention

In the present invention, unless specified otherwise, contents and content ratios are provided on a weight basis.

Furthermore, i-paraffins (also referred to as iso-paraffins) refer to branched non-cyclic alkanes, and n-paraffins (also referred to as normal-paraffins) refer to linear non-cyclic alkanes. Total paraffins content refers to the summed content of i-paraffins and n-paraffins. Similarly, olefins refer to linear or branched non-cyclic alkenes, including multiple unsaturated. Naphthenes refer to cyclic non-aromatic branched or non-branched alkanes, alkenes or alkynes, including multiple unsaturated. Aromatics refer to compounds having at least one aromatic ring.

Contents of n-paraffins, i-paraffins, olefins, naphthenes and aromatics can be determined using the PIONA method, which is a GCxGC analysis method, as published by Pyl et al in Journal of Chromatography A, 1218 (2011) 3217–3223 for the GCxGC description. Regarding this publication, for samples that have been subjected to high severity hydroisomerisation the primary column and secondary column are preferably reversed to enhance separation and identification of the isoparaffins from n-paraffins.

In the present context, the term "renewable" or "bio-based" or "bio-" refers to a material which is derived from renewable or biological sources in full or in part. Carbon atoms of renewable or biological origin comprise a higher number of unstable radiocarbon (^{14}C) atoms compared to carbon atoms of fossil origin. Therefore, it is possible to distinguish between carbon compounds derived from renewable or biological sources or raw material and carbon compounds derived from fossil sources or raw material by analysing the ratio of ^{12}C and ^{14}C isotopes. Thus, a particular ratio of said isotopes (yielding the "biogenic carbon content") can be used as a "tag" to identify renewable carbon compounds and differentiate them from non-renewable carbon compounds. The isotope ratio does not change in the course of chemical reactions. Examples of a suitable method for analysing the biogenic carbon content are DIN 51637 (2014), ASTM D6866 (2020) and EN 16640 (2017). The content of carbon from biological or renewable sources is expressed as the biogenic carbon content meaning the amount of biogenic carbon in the material as a weight percent of the total carbon (TC) in the material. As used herein, the biogenic carbon content is determined in accordance with EN 16640 (2017). In the present invention, the term "renewable" or "bio-based" or "bio-" preferably refers to a material having a biogenic carbon content in the range of from 1% to 100%.

In particular, the biogenic carbon content of the renewable stabilized naphtha-range hydrocarbon feed, which may also be referred to as bio-based cracker feed is preferably more than 5 % and up to 100%, such as more than 20 %, more than 40%, more than 50 %, more than 60 % or more than 70 %, more than 80 %, more than 90 %, or more than 95 %, and may even be about 100 %. The biogenic carbon content of the oxygenate bio-renewable feed is preferably more than 50 % and up to 100%, preferably more than 60 % or more than 70 %, preferably more than 80 %, more preferably more than 90 % or more than 95 %, even more preferably about 100 %.

The biogenic carbon content of the renewable thermal cracking effluent of the present invention may be below 1 %, but is preferably at least 1 % and up

to 100 %, such as at least 2 %, at least 5 %, at least 10 %, at least 20 %, at least 40 %, at least 50 %, at least 75 %, at least 90 %, or about 100 %.

5 The biogenic carbon content of the effluent of the thermal cracking furnace of step (b), and of products and intermediates downstream the cracking step (b) may be below 1 %, but is preferably at least 1 % and up to 100 %, such as at least 2 %, at least 5 %, at least 10 %, at least 20 %, at least 40 %, at least 50 %, at least 75 %, at least 90 %, or about 100 %.

10 In particular, the biogenic carbon content of the light olefin(s) (fraction) and/or the bio-monomer and/or the biopolymer composition may be below 1 %, but is preferably at least 1 % and up to 100 %, such as at least 2 %, at least 5 %, at least 10 %, at least 20 %, at least 40 %, at least 50 %, at least 75 %, at least 90 %, or about 100 %.

15

By the term "optionally" or "optional", a characteristic, feature or step that may be present, but is not necessarily required for carrying out the invention, is meant.

20 Unless indicated otherwise, all test method standards referred to in this text are the latest versions available on December 1, 2021.

Thermal cracking method

The method of the present invention will be described first.

25

The method of the present invention comprises a step (a) of providing a renewable stabilized naphtha-range hydrocarbon feed, a step (b) of thermally cracking the renewable stabilized naphtha-range hydrocarbon feed in a thermal cracking furnace, optionally together with co-feed(s) and/or additive(s), and a step (c) of subjecting the effluent of the thermal cracking furnace of step (b) to a separation treatment to provide at least a light olefin(s) fraction.

30

The method of the present invention provides a light olefin(s) fraction. The method may comprise further purification of the light olefin(s) fraction to provide one or more light olefins, preferably of industry grade or even polymer grade.

5

The step (b) of thermally cracking may be referred to as "thermal cracking step".

10

The renewable stabilized naphtha-range hydrocarbon feed preferably has an initial boiling point of 20°C or more, preferably within 20°C to 50°C. The initial boiling point is more preferably within 30°C to 45°C. The renewable stabilized naphtha-range hydrocarbon feed preferably has a T95 temperature (95 vol-% recovered) of 220°C or less, preferably 200°C or less, 180°C or less, 160°C or less, or 140°C or less. The renewable stabilized naphtha-range hydrocarbon feed may have a T99 temperature (99 vol-% recovered) of 220°C or less, preferably 200°C or less, 180°C or less, 160°C or less, or 140°C or less, or a final boiling point of 220°C or less, preferably 200°C or less, 180°C or less, or 160°C or less.

15

20

The difference between initial boiling point and T95 temperature (T95-IBP) of the renewable stabilized naphtha-range hydrocarbon feed is preferably at least 50°C, such as at least 80°C. For example, the difference between initial boiling point and T95 temperature may be 50°C to 155°C, preferably 60°C to 120°C, 60°C to 100°C or 65°C to 90°C.

25

The boiling points and T## temperature(s), such as T95 temperature, are as determined in accordance with EN ISO 3405-2019. EN ISO 3405-2019 refers to the determination of distillation characteristics at atmospheric pressure, suitable for products boiling between 0°C and 400°C.

30

An initial boiling point of more than 20°C improves the suitability of the stabilized naphtha-range hydrocarbon feed for cracking in conventional steam cracking procedures. On the other hand, if the initial boiling point

exceeds 50°C, a large amount of usable hydrocarbons may be lost (i.e. not valorised), which is not desired.

5 The term "stabilized" in the expression "stabilized naphtha-range" means that the content of C4 and lower carbon number compounds is 5.0 wt.-% or less, preferably 2.5 wt.-% or less, more preferably 2.0 wt.-% or less, even more preferably 1.5 wt.-% or less.

10 In the present invention, the "*renewable stabilized naphtha-range hydrocarbon feed*" contains at least 98.5 wt.-% hydrocarbons, preferably at least 99.5 wt.-%. In other words, at least 98.5 wt.-% of the feed are made up of hydrocarbons. Herein, hydrocarbons mean compounds containing only C and H (carbon atoms and hydrogen atoms). This means that at most 1.5 wt.-%, preferably at most 0.5 wt.-% of the hydrocarbon feed may be made
15 up of non-hydrocarbon species, such as heteroatom containing impurities or free water (free water according to ASTM D1364). The non-hydrocarbon species may specifically be free water and/or species containing carbon atoms, hydrogen atoms and a heteroatom, such as at least one of oxygen, nitrogen, sulphur or phosphorous. Such low levels of non-hydrocarbon
20 species makes the renewable stabilized naphtha-range hydrocarbon feed particularly suitable for conventional cracking apparatuses so that no special arrangements are required.

The thermal cracking step (b) may be a steam cracking step. Steam cracking
25 is tolerant to possible impurities which are common in renewable material. In addition, the method of the present invention has shown to provide particularly good results when employing steam cracking.

Preferably, the thermal cracking step (b) is conducted at a coil outlet
30 temperature (COT) selected from the range from 780°C to 880°C, preferably from 800°C to 860°C, more preferably from 820°C to 850°C.

The thermal cracking step (b) may be conducted at a coil outlet pressure (COP) selected from the range from 1.3 bar to 6.0 bar, preferably from 1.3 bar to 3.0 bar. In the present invention, a pressure value or range refers to absolute pressure, unless otherwise specified.

5

The thermal cracking step (b) is preferably conducted in the presence of a thermal cracking diluent. Any conventional thermal cracking diluent(s) may be used in the thermal cracking step (b). Examples of such thermal cracking diluents comprise steam, molecular nitrogen (N₂), or a mixture thereof.

10 Dilution of the thermal cracker feed lowers the hydrocarbon partial pressure in the thermal cracking coils and favours formation of primary reaction products, such as ethylene and propylene. The thermal cracking diluent preferably comprises steam.

15 The thermal cracking step (b) is preferably conducted in the presence of a thermal cracking diluent at dilution within a range from 0.10 to 0.85, preferably from 0.25 to 0.60, such as 0.35 to 0.55. The dilution refers to a flow rate ratio between thermal cracking diluent and the total cracker feed (flow rate of thermal cracking diluent [kg/h] / flow rate of total cracker feed
20 [kg/h]). The total cracker feed refers to the renewable stabilized naphtha-range hydrocarbon feed plus optional co-feed(s) and optional additive(s), but excluding diluent.

The individual components of the total cracker feed as well as the diluent(s)
25 may be fed to the thermal cracking furnace as a pre-formed mixture, as separate streams or as a combination of separate stream(s) and pre-formed mixture(s).

The method may comprise a purification treatment to remove at least one of methyl acetylene, propadiene, CO, CO₂ and C₂H₂, preferably at least one of
30 CO, CO₂ and C₂H₂, as a purification stage (c') in the step (c) of separating at least the light olefin(s) fraction from the effluent of the thermal cracking furnace of step (b).

The step (c) may comprise quenching and cooling the effluent of the thermal cracking furnace of step (b). Typically, at least a portion of CO, CO₂, C₂H₂, or a combination thereof, is removed from the effluent of the thermal cracking furnace of step (b) during the quenching and cooling. In certain embodiments, the step (c) comprises fractionating the effluent of the thermal cracking furnace of step (b). The fractionation may comprise separating from the cracking effluent a fuel oil fraction, a PyGas fraction, a hydrogen fraction, a methane fraction, a fuel gas fraction, and the light olefin(s) fraction, such as a C₂ fraction (ethylene fraction), C₃ fraction (propylene fraction), and/or a C₄ fraction. The fractionation may be carried out in a single stage or as a series of fractionations, such as first separating a C₂/C₃ fraction and then recovering a C₂ fraction and a C₃ fraction by a second-stage fractionation. The C₂ fraction (ethylene fraction) and the C₃ fraction (propylene fraction) are particularly suitable to be used for producing polymers, such as a biopolymer composition. Thus, in certain embodiments, the method comprises, in step (c), separating from the effluent of the thermal cracking furnace of step (b) a C₂ fraction, or a C₃ fraction, or both a C₂ fraction and a C₃ fraction, or a C₂/C₃ fraction comprising C₂ and C₃ as a light olefin(s) fraction, and optionally subjecting at least ethylene derived from the C₂ fraction, at least propylene derived the C₃ fraction, or both ethylene and propylene to a polymerisation treatment. The ethylene and/or propylene may be derived from the C₂ and/or C₃ fraction by further purification treatment(s) to obtain polymer grade material.

25

In a preferred embodiment, a fraction rich in C₂ hydrocarbons (C₂ fraction) is separated and this fraction is then further separated at least into a fraction comprising ethene and a fraction comprising ethane. Such separation of a fraction rich C₂ hydrocarbons, e.g. a fraction comprising 30 wt.-% to 100 wt.-%, preferably at least 40 wt.-% C₂ hydrocarbons, may be forwarded to a C₂ splitter to provide a fraction comprising ethene and a fraction comprising ethane. Similarly, a fraction rich in C₃ hydrocarbons may be separated and this fraction is then further separated at least into a fraction comprising

30

propene and a fraction comprising propane. Such separation of a fraction rich C3 hydrocarbons (C3 fraction), e.g. a fraction comprising 30 wt.-% to 100 wt.-%, preferably at least 40 wt.-% C3 hydrocarbons, may be forwarded to a C3 splitter to provide a fraction comprising propene and a fraction comprising propane. The fraction rich C3 hydrocarbons may be separated after the fraction rich C2 hydrocarbons has been separated or may be separated in the same stage. Each of these fraction may be recovered as a product fraction of the method or may be further purified or post-processes to give a product fraction of the method.

10

The method may comprise subjecting at least a portion of the effluent of the thermal cracking furnace of step (b) to a purification treatment (c') within step (c) to remove at least one of CO, CO₂, or C₂H₂. This is particularly advantageous in embodiments where at least a portion of the cracking effluent is subjected to a polymerisation treatment. CO, CO₂, and C₂H₂ are polymerisation catalyst poisons and thus undesirable in a polymerisation process. An absorbent, an adsorbent, a reactant, a molecular sieve and/or a purification catalyst may be used in the purification treatment to remove at least one of CO, CO₂, or C₂H₂, and decreases the regeneration frequency of the active material.

20

The purification treatment to which at least a portion of the effluent of the thermal cracking furnace of step (b) may be subjected can be any purification treatment suitable for removing at least one of CO, CO₂, or C₂H₂. Examples of such purification treatments are described in EP 2679656 A1, WO 2016023973 A1, WO 2003048087 A1, and US 2010331502 A1, all of which are incorporated herein by reference in their entirety.

25

In certain embodiments, the purification treatment comprises contacting at least a portion of the cracking effluent with an active material, such as an absorbent, an adsorbent, a purification catalyst, a reactant, a molecular sieve, or a combination thereof, to remove at least one of CO, CO₂, or C₂H₂.

30

The active material may comprise, for example, copper oxide or a copper oxide catalyst, oxides of Pt, Pd, Ag, V, Cr, Mn, Fe, Co, or Ni optionally supported on alumina, Au/CeC optionally supported on alumina, zeolites, in particular type A and/or type X zeolites, alumina based absorbents or catalysts, such as a Selexsorb™ COS or Selexord™ CD, a molecular sieve comprising alumina, aluminosilicates, aluminophosphates or mixtures thereof, or any combination thereof.

The active material may comprise an adsorbent or adsorbents as described in WO 03/048087 A1 on p. 11, 11. 12 - p. 12, 11. 3; p. 12, 11. 18 - p. 15, 11. 29, and/or p. 17, 11. 21 - p. 21, 11. 2 and/or a molecular sieve or molecular sieves as described in WO 03/048087 A1 on p. 21, 11. 3 - p. 22 11. 26. The active material may comprise a purification catalyst or catalysts as described in US 2010/0331502 A1, paragraphs [0105] to [0116], or a molecular sieve or molecular sieves as described in US 2010/0331502 A1, paragraphs [0117] to [0119]. The active material may comprise a purification catalyst or catalysts as described in WO 2016/023973 A1, paragraph [0061], [0062], [0063], and/or [0064]

The purification treatment may be a purification treatment as described in EP 2679656 A1, paragraphs [0043] to [0082]. The purification treatment may be a purification treatment as described in US 2010/0331502 A1, paragraphs [0092] to [0119], and/or paragraph [0126], and/or Example 2. The purification treatment may be a purification treatment as described in WO 2016/023973 A1, paragraphs [0056] to [0067]. The purification treatment may be a purification treatment as described in WO 03/048087 A1, p. 11, 11. 12 - p. 15, 11. 29, and/or p. 16, 11. 1 - p. 21, 11. 2, and/or p. 23, 11. 14 - p. 24, 11. 13, and/or Example 1 and/or Example 2.

Typically, impurities deactivate or foul the active material during purification treatment. Thus, the active material may be regenerated to at least partially regain its purification activity.

In certain embodiments, the purification treatment comprises at least one of the following steps: i) contacting at least a portion of the cracking effluent with a CuO catalyst to remove oxygen, ii) contacting at least a portion of the cracking effluent with H₂ to remove C₂H₂ by hydrogenation, iii) contacting at least a portion of the cracking effluent with a CuO₂ catalyst to remove CO by oxidation, or iv) contacting at least a portion of the cracking effluent with a zeolitic molecular sieve to remove CO₂. Optionally, the purification treatment may comprises removing secondary impurities, such as at least one of COS, H₂S, or CS₂, by contacting at least a portion of the cracking effluent with an activated alumina catalyst, such as Selexorb™.

The method may comprise performing one or more further cracking operation(s) to provide further cracking effluent(s), wherein step (c) further comprises adding the further effluent(s) and/or fraction(s) thereof before and/or during the separation treatment.

Specifically, the cracking effluent obtained in step (b) may be combined with other stream(s), such as effluent(s) from further cracking process(s) produced in other thermal cracking furnace(s), i.e. further cracking effluent(s) and/or fraction(s) thereof, in step (c). The further cracking effluent(s) and/or fraction(s) thereof may simply be referred to as co-feed(s) of step (c). In this case, the effluent of the thermal cracking furnace of step (b) preferably amounts to 10 wt.-% to 100 wt.-%, preferably 20 wt.-% to 100 wt.-%, 30 wt.-% to 100 wt.-%, 40 wt.-% to 100 wt.-%, 50 wt.-% to 100 wt.-%, 60 wt.-% to 100 wt.-%, 70 wt.-% to 100 wt.-%, 80 wt.-% to 100 wt.-%, or 90 wt.-% to 100 wt.-% relative to the summed amount of effluent of the thermal cracking furnace of step (b) and the co-feed(s) of step (c). A minimum value of 10 wt.-%, for example, ensures the presence of a certain share of material of biological origin, thus contributing to sustainability. Nevertheless, even minimum contents of material of biological origin being subjected to step (c) contribute to sustainability.

The one or more further cracking operation(s) are preferably carried out in one or more further cracking furnace(s). The one or more further cracking operation(s) may be thermal cracking operation(s) and/or cracking operation(s) other than thermal cracking, such as FCC (fluidized catalytic cracking).

The further cracking operation(s) may be carried out with any suitable feed, including fossil feed (crude oil-based feed), renewable feed or a combination thereof. The further cracking operation(s) are preferably carried out under conditions differing from step (b) in at least one of total cracker feed composition and cracking condition(s), such as COT, COP, or dilution.

The further cracking effluent(s) may be subjected to purification, gas-liquid separation and/or fractionation before being added in step (c) or may be added as such, i.e. as crude effluent(s). The addition may be carried out before the separation treatment of step (c). In this case, the further cracking effluent(s) is/are subjected to the separation treatment. This option is particularly suitable if a crude effluent is added as the further effluent. The addition may be carried during or after the separation treatment of step (c). In this case, it is favourable for the further cracking effluent to be at least partially subjected to purification, gas-liquid separation and/or fractionation before being added in step (c).

The thermal cracking in step (b) is preferably carried out in the presence of co-feed(s).

Preferably, the content of the renewable stabilized naphtha-range hydrocarbon feed in the total cracker feed is in the range of from 10 wt.-% to 100 wt.-%, preferably 20 wt.-% to 100 wt.-%, 30 wt.-% to 100 wt.-%, 40 wt.-% to 100 wt.-%, 50 wt.-% to 100 wt.-%, 60 wt.-% to 100 wt.-%, 70 wt.-% to 100 wt.-%, 80 wt.-% to 100 wt.-%, or 90 wt.-% to 100 wt.-%. The upper limit may also be 90 wt.-% or 80 wt.-%, i.e. the content may for

example be in the range of from 10 wt.-% to 90 wt.-% or from 10 wt.-% to 80 wt.-%.

Employing at least 10 wt.-% renewable stabilized naphtha-range hydrocarbon feed ensures that the effects of the present invention are remarkably pronounced. The total cracker feed may consist of the renewable stabilized naphtha-range hydrocarbon feed, i.e. the content thereof may be 100 wt.-%.

10 The co-feed(s) may comprise a fossil hydrocarbon co-feed. Fossil co-feeds, in particular fossil naphtha, are readily available and highly suitable for thermal cracking.

In the present invention, the "*fossil hydrocarbon co-feed*" contains at least 15 98.5 wt.-% hydrocarbons, preferably at least 99.5 wt.-%. In other words, at least 98.5 wt.-% of the co-feed are made up of hydrocarbons. This means that at most 1.5 wt.-%, preferably at most 0.5 wt.-% of the hydrocarbon co-feed may be made up of non-hydrocarbon species, such as heteroatom containing impurities, and in particular sulphur-containing impurities.

20

Preferably, the co-feed(s) comprise a naphtha range feed since this provides high compatibility with the renewable stabilized naphtha-range hydrocarbon feed. Moreover, since the renewable stabilized naphtha-range hydrocarbon feed is a well-defined (narrow-range) feed, it is preferable to employ a narrow-range co-feed, such as fossil naphtha, in order to make full use of the benefits of the present invention. A particularly preferred co-feed is light naphtha, specifically fossil light naphtha. The light naphtha preferably boils in the range of from 20°C (IBP) to 120°C (FBP), such as from 30°C (IBP) to 90°C (FBP).

30

The total cracker feed preferably has a sulphur content in the range of from 20 to 300 ppm by weight, preferably 20 to 250 ppm by weight, more

preferably 20 to 100 ppm by weight, and even more preferably 50 to 65 ppm by weight.

5 The inventors surprisingly found that a (total) cracker feed containing the renewable stabilized naphtha-range hydrocarbon feed (and optionally co-feed and/or additive) and having a sulphur content within the above-mentioned limits results in a significantly reduced coking tendency during thermal cracking.

10 As the renewable stabilized naphtha-range hydrocarbon feed typically has inherently low or no sulphur content, the sulphur may be incorporated in the total cracker feed by using a sulphur-containing co-feed, such as a fossil hydrocarbon feed. The sulphur may also originate, in part or in total, from sulphur-containing additive(s), including conventional cracking additive(s).
15 Specifically, any conventional thermal cracking additive(s) may be added to the renewable stabilized naphtha-range hydrocarbon feed of the present disclosure, to optional co-feed(s) or to a pre-formed total cracker feed or be co-fed to the thermal cracking furnace or may be added to thermal cracking diluent and thus fed to the thermal cracking furnace. Examples of such
20 conventional thermal cracking additives include sulphur containing species (sulphur additives), such as dimethyl disulphide (DMDS), or carbon disulphide (CS_2). DMDS is a particularly preferred sulphur additive. Sulphur additive(s) may be mixed with the renewable stabilized naphtha-range hydrocarbon feed, with optional co-feed(s) or with a pre-formed total cracker feed before
25 feeding to the thermal cracking furnace. Optionally, sulphur additive(s) may be added by injecting into the thermal cracking furnace a thermal cracking diluent, preferably steam, comprising sulphur additive(s).

The step (a) of providing the stabilized naphtha-range hydrocarbon feed may
30 for example comprise subjecting an oxygenate bio-renewable feed to hydrotreatment comprising at least hydrodeoxygenation, and to optional subsequent further hydrotreatment comprising at least hydroisomerisation, and conducting gas-liquid separation(s) after the hydrotreatment(s) to

provide liquid hydrocarbon stream(s) and gaseous stream(s). In a subsequent stage, the optionally isomerised liquid hydrocarbon stream may be subjected to fractionation, from which at least the renewable stabilized naphtha-range hydrocarbon feed is recovered. In addition, other fractions
5 may be recovered from the fractionation, including but not limited to a fuel gas fraction, a diesel range fraction, aviation fuel range fraction, a marine fuel fraction and an electrotechnical fluid fraction. Additionally a propane fraction may be recovered at least from the gaseous stream(s) separated from the liquid hydrocarbon stream(s).

10

An exemplary aviation fuel range fraction may boil within a range from 100°C-300°C, such as within 150°C-300°C. An exemplary gasoline fuel range fraction may boil within a range from 25°C-220°C. An exemplary diesel fuel range fraction may boil within a range from 160°C-380°C. An exemplary
15 marine fuel range fraction may boil within 180°C-600°C.

20

In general, a naphtha range fraction as disclosed herein may refer to a fraction having an initial boiling point of more than 0°C, preferably more than 20°C or more than 30°C, and a T95 temperature of 220°C or less, preferably
200°C or less, 180°C or less, 160°C or less, 140°C or less. The naphtha range fraction may have a T99 temperature of 220°C or less, preferably 200°C or less, 180°C or less, 160°C or less, 140°C or less, or a final boiling point of 220°C or less, preferably 200°C or less or 180°C or less.

25

Unless specified to the contrary, the boiling characteristics in the present invention, such as the T95 temperature (95 vol-% recovered), the T99 temperature (99 vol-% recovered), the final boiling point, the initial boiling point, the T5 temperature (5 vol-% recovered) and the T10 temperature (10 vol-% recovered) are as determined in accordance with EN ISO 3405-2019.

30

The step (a) in the above embodiment preferably may comprise the further hydrotreatment comprising at least hydroisomerisation subsequent to the hydrotreatment comprising at least hydrodeoxygenation (HDO), and/or may

comprise hydroisomerisation as a part of the hydrotreatment comprising at least HDO.

5 In other words, hydroisomerisation may be carried out in a separate further hydrotreatment after the hydrotreatment comprising at least HDO. Alternatively or in addition, hydroisomerisation may be carried out as a part of the hydrotreatment comprising at least HDO, for example by means of a catalyst or catalyst system achieving both hydrodeoxygenation and hydroisomerisation in a single step.

10

The effluent from the hydrotreatment comprising at least HDO, which is referred to as hydrotreatment effluent, may be subjected to gas-liquid separation to provide a gaseous stream and a first liquid hydrocarbon stream. At least part of the first liquid hydrocarbon stream may be provided as the liquid hydrocarbon stream mentioned above. Alternatively or in addition, at least part of the liquid hydrotreatment effluent stream may be subjected, in a subsequent stage, to the further hydrotreatment comprising at least hydroisomerisation to provide, preferably after gas-liquid separation, a second liquid hydrocarbon stream which may be provided as the liquid hydrocarbon stream mentioned above.

20

The gaseous stream obtained in a second gas-liquid separation may be combined and processed together with the gaseous stream obtained in the first gas-liquid separation. Condensable hydrocarbons, if any, may be separated from the gaseous stream(s), and combined with the liquid hydrocarbon stream.

25

At least a part of the first liquid hydrocarbon stream and/or of the second liquid hydrocarbon stream may be recycled back to the hydrotreatment comprising at least hydrodeoxygenation. Such recycling may be suited to achieve temperature control.

30

The above-mentioned gaseous stream(s) may be subjected to a propane separation process to provide a stream enriched in propane and a stream depleted in propane. At least part of the propane contained in the stream enriched in propane may be subjected to dehydrogenation, preferably
5 catalytic dehydrogenation, to produce propylene.

Propane (or a stream enriched in propane) may also be recovered from a stabilisation stage and subjected to such a dehydrogenation. The propane (or a stream enriched in propane) recovered from a stabilisation stage may be
10 subjected to dehydrogenation in a separate reactor or may be combined with propane (or a stream enriched in propane) separated after hydrotreatment so as to improve overall yields of light olefins per unit oxygenate bio-renewable feed to hydrotreatment.

15 Alternatively, or in addition, such a C3-rich stream (i.e. the stream enriched in propane recovered after hydrotreatment, the stream recovered from stabilisation or a combined stream) may be subjected to thermal cracking, such as steam cracking, in a separate furnace.

20 When a heavy liquid hydrocarbon fraction is recovered from the above-mentioned fractionation, the method may further comprise subjecting the heavy liquid hydrocarbon fraction to further fractionation to provide at least an aviation fuel range fraction and a bottoms fraction. A suitable method for fractionation, as well as usable fractionation cut-offs, resulting fractions and
25 uses thereof are set forth in WO 2021/094656 A1, the content of which is herewith incorporated in its entirety. In WO 2021/094656 A1, the bottoms fraction is referred to as an electrotechnical fluid.

Each of the diesel range fraction, the aviation fuel range fraction, heavy liquid
30 hydrocarbon fraction, the aviation fuel range fraction and the bottoms fraction may individually have an iso-paraffins content of at least 65 wt.-%, preferably at least 70 wt.-%, at least 75 wt.-%, at least 80 wt.-%, at least 85 wt.-% or at least 90 wt.-%. The iso-paraffins content is calculated relative to total

diesel range fraction or respective other fraction. High isomerisation degree of the fractions, in particular of the diesel or aviation fuel range fraction, indicates that the production process was carried out in highly isomerising mode, e.g. under severe isomerisation conditions. In such a case, the yield of naphtha range hydrocarbons tends to be higher, and the naphtha range fraction also tends to have higher iso-paraffins content. This improves overall yield of the process of the invention.

The above-mentioned stage of subjecting at least part of the liquid hydrocarbon stream to fractionation and recovering at least the renewable stabilized naphtha-range hydrocarbon feed preferably comprises a stage of subjecting at least part of the liquid hydrocarbon stream to fractionation to provide a naphtha range fraction and subjecting the naphtha range fraction to stabilization. In this respect, the stabilisation may comprise removing, preferably by means of a distillation technique, at least part of components boiling below 20°C, preferably removing at least part of components boiling below 25°C, removing at least part of components boiling below 30°C, removing at least part of components boiling below 40°C or removing at least part of components boiling below 50°C. If desired, optional additional treatments, such as stripping with N₂, H₂, or steam, to separate gases and impurities into the gaseous phase, may be performed on the liquid stream(s) during the fractionation stage.

The stabilisation stage may form a part of the fractionation from which the naphtha range fraction is recovered. Alternatively, or in addition, the stabilisation stage may be carried out as a separate stage after fractionation, i.e. removing the respective components from the recovered naphtha range fraction.

The stabilisation stage is preferably carried out by means of a distillation technique.

As used herein, distillation (or fractionation) may refer to any type of distillation, i.e. also to stripping, flashing, and any other similar separating operations based on differences in the vapour pressure of the components. Selecting suitable feed rates, operating temperatures, pressures, equipment
5 type and design, and other engineering details for the present fractionation disclosure will be within capabilities of a person skilled in the art.

The above-mentioned heavy liquid hydrocarbon fraction and/or diesel range fraction may alternatively have an iso-paraffins content of less than 65 wt.-
10 %.

The above-mentioned bottoms fraction may be subjected to a further thermal cracking, preferably steam cracking. This further cracking stage is preferably carried out separate from the thermal cracking step (b), i.e. in a different
15 furnace and/or at a different time. The cracking conditions may be different from those employed in step (b), but the same conditions as useable in step (b) may be employed as well.

The step (a) may comprise hydrotreatment of an oxygenate bio-renewable
20 feed, such as an oil and/or fat of plant origin, animal origin or other biological origin. That is, as already pointed out above, the renewable stabilized naphtha-range hydrocarbon feed may be based on a hydrotreated oxygenate feed.

25 The step (a) may comprise a step (a') of pre-treating bio-renewable oil(s) and/or fat(s) for reducing contaminants in the oil(s) and/or fat(s) to produce the oxygenate bio-renewable feed. Alternatively, the oil(s) and/or fat(s) may be employed as the oxygenate bio-renewable feed without pre-treatment.

30 The pre-treatment step (a') may be a step of reducing contaminants containing S, N and/or P in the oil(s) and/or fat(s) to produce the oxygenate bio-renewable feed. Alternatively, or in addition, the pre-treatment step (a') may be a step of reducing metal-containing contaminants in the oil(s) and/or

fat(s) to produce the oxygenate bio-renewable feed. Preferably the pre-treatment step reduces content of one or more of S, N, P, alkali metals, alkaline earth metals, Si, Al, Fe, Zn, Cu, Mn, Cd, Pb, As, Cr, Ni, V, Sn.

- 5 Suitable methods for carrying out the pre-treatment step (a') comprise one or more selected from washing, degumming, bleaching, distillation, fractionation, rendering, heat treatment, evaporation, filtering, adsorption, hydrotreatment such as hydrodeoxygenation, centrifugation or precipitation. These pre-treatment methods are simple and effective methods for removing
- 10 the potentially catalyst-poisoning S, N and P contaminants as well as metal contaminants (metals and/or metal compounds), including metalloid contaminants, such as Si-containing impurities. The pre-treatment step (a') may comprise, in the alternative or in addition, at least one of partial hydrogenation, partial deoxygenation, hydrolysis and transesterification.

15

The oxygenate bio-renewable feed may comprise fatty acid ester(s) of glycerol.

- 20 The effluent of hydrotreatment and optional isomerisation is subjected to fractionation, preferably after gas-liquid separation. The fractionation may directly yield the renewable stabilized naphtha-range hydrocarbon feed or may further be treated, such a stabilized, to provide the renewable stabilized naphtha-range hydrocarbon feed.

- 25 The total feed which may be subjected to hydrotreatment in step (a) preferably comprises a hydrotreatment diluent comprising paraffinic hydrocarbons in addition to the oxygenate bio-renewable feed. A hydrotreatment diluent is particularly suited for temperature control during hydrotreatment, specifically during hydrodeoxygenation. The hydrotreatment
- 30 diluent may comprise at least one of recycled paraffinic hydrocarbons from the hydrotreatment effluent and/or isomerisation effluent, renewable hydrocarbons obtained by Fischer-Tropsch synthesis using bio-syngas, and fossil-based hydrocarbons. Preferably, the hydrotreatment diluent comprises

- recycled paraffinic hydrocarbons from the hydrotreatment effluent and/or isomerisation effluent. When employing a hydrotreatment diluent, the hydrotreatment feed preferably contains at least 2 wt.-% of the oxygenate bio-renewable feed, such as 2 wt.-% to 100 wt.-%, preferably 3 wt.-%, at least 4 wt.-%, at least 5 wt.-%, at least 6 wt.-%, at least 7 wt.-%, at least 8 wt.-%, at least 9 wt.-%, at least 10 wt.-%, at least 11 wt.-%, at least 12 wt.-%, at least 15 wt.-%, at least 20 wt.-%, at least 25 wt.-%, at least 50 wt.-%, at least 75 wt.-%, at least 90 wt.-% or at least 95 wt.-%, or at least 99 wt.-%. The feed which is subjected to hydrotreatment in step (a) may contain 99 wt.-% or less of a oxygenate bio-renewable feed, such as 2 wt.-% to 99 wt.-%, preferably 90 wt.-% or less, 75 wt.-% or less, 50 wt.-% or less, 40 wt.-% or less, 35 wt.-% or less, 30 wt.-% or less, 25 wt.-% or less, 20 wt.-% or less, 15 wt.-% or less, or 10 wt.-% or less.
- 15 When the hydrotreatment diluent comprises recycled paraffinic hydrocarbons from the hydrotreatment step, the hydrotreatment feed preferably contains 10 wt.-% to 98 wt.-% of the recycled paraffinic hydrocarbons from the hydrotreatment step, preferably at least 25 wt.-%, at least 40 wt.-%, at least 50 wt.-%, at least 60 wt.-%, at least 70 wt.-%, at least 75 wt.-%, at least 80 wt.-%, at least 85 wt.-%, at least 90 wt.-%, or at least 92 wt.-%. The hydrotreatment feed may similarly contain 98 wt.-% or less, 95 wt.-% or less, 92 wt.-% or less, 90 wt.-% or less, 85 wt.-% or less, 80 wt.-% or less, 70 wt.-% or less, 60 wt.-% or less, 40 wt.-% or less or 25 wt.-% or less of the recycled paraffinic hydrocarbons from the hydrotreatment step, such as 10 wt.-% to 25 wt.-%. The recycled product from the hydrotreatment step is preferably a hydrocarbon, but may similarly be a material which is only partially deoxygenated and then recycled into the hydrotreatment step for further deoxygenation.
- 30 In the present invention, the hydrotreatment may involve, in addition to hydrodeoxygenation (HDO), decarbonylation and/or decarboxylation. These reactions give carbon monoxide or carbon dioxide and a hydrocarbon chain having one carbon less than the original chain.

The hydrotreatment, preferably HDO, may for example be carried out by feeding hydrogen and the natural fat or derivative thereof (co-currently or counter-currently) through a catalyst bed. A suitable process and apparatus
5 is described in EP1741767 A1, see Figure 1 and items [0061] to [0064], herewith included by reference.

The hydrotreatment, preferably HDO, is preferably carried out at a temperature between 100°C and 500°C, preferably between 250°C and
10 350°C, more preferably between 280°C and 345°C, most preferably between 280°C and 310°C. A preferred pressure is 1 MPa to 20 MPa, a more preferable one 3 MPa to 10 MPa, the most preferable one being 4 MPa to 8 MPa.

The hydrotreatment, preferably HDO, may be carried out in the presence of
15 a hydrogenation catalyst containing one or more metals from Groups 6 to 10 of the Periodic Table (IUPAC 1990), preferably a supported catalyst, more preferably the above-mentioned one or more metals supported on alumina and/or silica. Preferred hydrogenation catalysts are alumina and/or silica supported Pd, Pt, Ni, NiMo, or CoMo. The most preferred catalysts are
20 NiMo/Al₂O₃ and CoMo/Al₂O₃ in sulphided form.

In the present invention, the term "hydrotreatment" is meant to encompass removal of oxygen from organic oxygen compounds as water i.e. hydrodeoxygenation (HDO), removal of sulphur from organic sulphur
25 compounds as dihydrogen sulphide (H₂S), i.e. hydrodesulphurisation (HDS), removal of nitrogen from organic nitrogen compounds as ammonia (NH₃), i.e. hydrodenitrogenation (HDN), removal of halogens, for example chlorine from organic chloride compounds as hydrochloric acid (HCl), i.e. hydrodechlorination (HDCI), removal of metals by hydrodemetallization, and
30 hydrogenation of unsaturated bonds if present. When isomerisation is carried out together with the hydrotreatment, this may be accomplished, for example, by combined HDO and hydrocracking or by combined HDO and hydroisomerisation. Specifically, hydrocracking may be performed to increase

yield of naphtha range hydrocarbons, which is beneficial for the overall process.

5 The optional isomerisation, be it as a part of the hydrotreatment or carried out separately after hydrotreatment comprising at least hydrodeoxygenation, results in higher yield of naphtha-range hydrocarbons, thus improving the overall yield of the method. In case isomerisation is omitted, the method can be adjusted towards production of other fractions, in particular at least a diesel range fraction, while making use of the naphtha range fraction as a
10 side product. In this case, it is preferable to recover a diesel range fraction in addition to the naphtha range fraction.

The optional isomerisation, if included as a separate stage, may be carried out at a temperature selected from the range 200 °C to 500 °C, preferably
15 280 °C to 400 °C, and at a pressure selected from the range 20-150 bar (absolute), preferably 30-100 bar. The isomerization (isomerisation treatment) may be performed in the presence of known isomerization catalysts, for example, catalysts containing a molecular sieve and/or a metal selected from Group VIII of the Periodic Table and a carrier. Preferably, the
20 isomerization catalyst is a catalyst containing SAPO-11 or SAPO-41 or ZSM-22 or ZSM-23 or ferrierite and Pt, Pd, or Ni and Al₂O₃ or SiO₂. Typical isomerisation catalysts are, for example, Pt/SAPO-11/Al₂O₃, Pt/ZSM-22/Al₂O₃, Pt/ZSM-23/Al₂O₃ and/or Pt/SAPO-11/SiO₂. Catalyst deactivation may be reduced by the presence of molecular hydrogen in the isomerisation
25 treatment. Therefore, the presence of added hydrogen in the isomerisation treatment is preferred. In case the optional isomerisation is included as a separate stage, the hydrotreatment catalyst(s) and the isomerization catalyst(s) may not be in contact with the reaction feed (the oxygenate bio-renewable feed and/or the deoxygenated stream derived therefrom) at the
30 same time. For example, the hydrotreatment and the isomerisation treatment are conducted in separate reactors.

The isomerisation may be a high severity isomerisation. High severity isomerisation in the present invention is meant to refer to any technologies achieving high iso-paraffins content in the naphtha fraction, typically 50-60 wt.-% or 55-60 wt.-%. High i-paraffins content (and high ratio between i-paraffins and n-paraffins) can particularly be achieved for paraffins having longer chains, i.e. having carbon numbers near the upper carbon number limit of the naphtha range.

In case hydrotreatment and subsequent high-severity isomerisation is carried out, the following procedure may be carried out, as exemplified on triglyceride-based biomass as an oxygenate bio-renewable feed. In a first step, the triglyceride based biomass is deoxygenated over a hydrotreatment catalyst, such as NiMo catalyst supported on Al_2O_3 under hydrogen pressure. Sulphur components are preferably added to the inlet stream to keep the catalyst in the sulphided state. During the first step, triglyceride oils and fatty acids are converted to n-alkanes with minor amounts of branched alkanes (usually in the range of 1 wt.-%). Note that the oxygen content can be removed under the form of water (hydrodeoxygenation), carbon monoxide (decarbonylation) and carbon dioxide (decarboxylation). Oxygen removal by decarbonylation and decarboxylation consumes less hydrogen compared to hydrodeoxygenation but causes the resulting alkane to have one carbon atom less compared to the original fatty acid chain. In a second step, isomerisation is carried out over a molecular sieve impregnated with platinum, e.g. Pt/ZSM-22.

The method of the present invention may further comprise derivatisation of at least part of the light olefin(s) to obtain one or more derivate(s) of the light olefin(s) as bio-monomer(s), such as acrylic acid, acrylonitrile, acrolein, propylene oxide, ethylene oxide, 1,4-butanediol, 1,2-butanediol, 1,3-butanediol, 2,3-butanediol, adiponitrile, hexamethylene diamine (HMDA), hexamethylene diisocyanate (HDI), (methyl)methacrylate, ethylidene norbornene, 1,5,9-cyclododecatriene, sulfolane, 1,4-hexadiene,

tetrahydrophthalic anhydride, valeraldehyde, 1,2-butyloxy, n-butyl mercaptan, o-sec-butylphenol, propylene, octene and sec-butyl alcohol.

5 The method of the present invention may further comprise a step (d) of (co)polymerizing at least one of the light olefin(s) separated in step (c) and/or at least one of the above-mentioned bio-monomer(s), optionally together with other (co)monomer(s) and/or after optional further purification, to produce a biopolymer composition.

10 In this context, acrylic acid is meant to include any type of acrylic-based monomers, e.g. those based on (meth)acrylic acid, (meth)acrylic acid esters, and/or (meth)acrylic acid salts. Acrylic polymers are meant to include any type of acrylic-based polymers, e.g. those containing structural units derived from (meth)acrylic acid, (meth)acrylic acid esters, and/or (meth)acrylic acid
15 salts

The light olefins and/or bio-monomers may be (co)polymerized to give a biopolymer composition comprising for example polybutadiene, styrenebutadiene rubber, nitrile rubber, polychloroprene, acrylonitrile
20 butadiene styrene resin (ABS), styrene butadiene latex, TPE, nylon, such as nylon 6,6, polyurethane, methyl methacrylate-butadiene-styrene (MBS), nitrile barrier resin, butyl rubber, polyisobutylene, methyl methacrylate (MMA), MTBE/ETBE, polyolefin (co)polymers, polybutene-1, polypropylene (PP), ethylene-propylene-copolymer (EPM), polyether, polyether polyol, polyester, polymer or oligomer surfactant or ethylene-propylene-diene-
25 copolymer (EPDM).

The derivatisation may, for example, comprise at least one of oxidation and ammoxidation. Oxidation is preferably carried out by gas phase oxidation.
30

The polymerisation may be carried out in the presence of a polymerisation catalyst. The polymerisation may be initiated by means of a polymerization initiator.

The biopolymer composition may be further processed to produce a sanitary article, a construction material, a packaging material, a coating composition, a paint, a decorative material, such as a panel, an interior part of a vehicle, such as an interior part of a car, a rubber composition, a tire or tire component, a toner, a personal health care article, a part of a consumer good, a part or a housing of an electronic device, a film, a moulded product, a gasket, optionally together with other components. In particular, an acrylic polymer may be a water-absorbing polymer which may be further processed to produce a sanitary article, such as a diaper, a sanitary napkin, an incontinence draw sheet.

The present invention furthermore relates to a biopolymer composition obtainable by the embodiment of the method of the present invention including polymerisation of light olefin(s) and/or derivative(s) thereof.

Renewable stabilized naphtha-range hydrocarbon feed

The present invention furthermore relates to a renewable stabilized naphtha-range hydrocarbon feed for thermal cracking.

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Preferably, the renewable stabilized naphtha-range hydrocarbon feed has a content of naphthenes in the range of from 0.1 wt.-% to 10.0 wt.-% based on the total weight of the renewable stabilized naphtha-range hydrocarbon feed. More preferably, the renewable stabilized naphtha-range hydrocarbon feed has a content of naphthenes of 0.2-10.0 wt.-%, such as 0.5-8.0 wt.-%, 0.5-6.0 wt.-%, 0.6 to 5.8 wt.-%, 0.8 to 5.8 wt.-%, 1.0 to 5.6 wt.-% or 1.2 to 5.6 wt.-%. Naphthenes convert easily to aromatics, which are compounds possibly reacting to coke but not to desired products. Thus, it is preferred that the naphthenes content is low in the renewable stabilized naphtha-range hydrocarbon feed.

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Preferably, the renewable stabilized naphtha-range hydrocarbon feed has a content of olefins of 0.50 wt.-% or less, preferably 0.40 wt.-% or less, 0.30

wt.-% or less, 0.25 wt.-% or less, 0.20 wt.-% or less, 0.15 wt.-% or less, 0.12 wt.-% or less, 0.10 wt.-% or less, 0.07 wt.-% or less, or 0.05 wt.-% or less. Olefins are undesired components in the renewable stabilized naphtha-range hydrocarbon feed of the present invention. That is, the inventors found
5 that olefins have a strong coking tendency which is even higher than that of aromatics and, therefore, the content of olefins should be kept low. The olefins content may be 0%, i.e. no detectable amounts of olefins contained.

Preferably, the renewable stabilized naphtha-range hydrocarbon feed has a
10 total content of olefins and naphthenes in the range from 0.1 wt.-% to 10.0 wt.-%. The total content olefins and naphthenes refers to the summed content of olefins and naphthenes based on the total weight of the renewable stabilized naphtha-range hydrocarbon feed. More preferably, the renewable stabilized naphtha-range hydrocarbon feed has a total content of olefins and
15 naphthenes of 0.1 wt.-% to 8.0 wt.-%, such as 0.1 wt.-% to 6.5 wt.-%, 0.1 wt.-% to 6.0 wt.-%, 0.2 wt.-% to 5.5 wt.-%, 0.5 wt.-% to 5.5 wt.-%, 0.5 wt.-% to 5.0 wt.-%, 0.8 wt.-% to 5.0 wt.-%, 0.9 wt.-% to 5.0 wt.-%, 1.0 wt.-% to 5.0 wt.-%, 1.1 wt.-% to 5.0 wt.-%, or 1.2 wt.-% to 5.0 wt.-%.

20 Preferably, the renewable stabilized naphtha-range hydrocarbon feed has a content of aromatics of 0.80 wt.-% or less, preferably 0.70 wt.-% or less, 0.60 wt.-% or less, 0.50 wt.-% or less, 0.40 wt.-% or less, 0.35 wt.-% or less, 0.30 wt.-% or less, 0.25 wt.-% or less, 0.20 wt.-% or less, or 0.15 wt.-% or less. Aromatics, such as benzene, do not react into desired products.
25 Rather, they tend to react to coke (i.e. they are coke precursors). Their presence in the feed thus reduces the yield of the desired products and their content in the feed should be low. In the present invention, the content of aromatics is preferably low and may be 0.00%. The content of aromatics may be determined by the PIONA analysis.

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Preferably, the renewable stabilized naphtha-range hydrocarbon feed has a ratio between the content of aromatics and the content of naphthenes (content by weight of naphthenes divided by content by weight of aromatics)

of 1 or more, preferably 10 or more, 50 or more, or 100 or more. Both naphthenes and aromatics tend to increase the yield of cyclic compounds in thermal cracking. Thus, it is preferred that both are contained in low amounts. However, if both are contained, naphthenes are preferred over aromatics.

- 5 The ratio has no specific upper limit and the ratio may even be infinite in case no aromatics are contained.

Preferably, the renewable stabilized naphtha-range hydrocarbon feed has a total content of olefins, aromatics and naphthenes of 0.1 wt.-% to 10.0 wt.-%, preferably 0.1 wt.-% to 8.0 wt.-%, 0.1 wt.-% to 6.5 wt.-%, 0.2 wt.-% to 6.0 wt.-%, 0.5 wt.-% to 5.5 wt.-%, 0.5 wt.-% to 5.0 wt.-%, 0.8 wt.-% to 5.0 wt.-%, 0.9 wt.-% to 5.0 wt.-%, 1.0 wt.-% to 5.0 wt.-%, 1.1 wt.-% to 5.0 wt.-%, or 1.2 wt.-% to 5.0 wt.-%. Naphthenes, aromatics and olefins are coke precursors and their content should be low. However, since it may be laborious to strongly reduce the content of all of these components, certain contents thereof can be tolerated. Nevertheless, their total content may be down to 0%, including 0%.

Preferably, the renewable stabilized naphtha-range hydrocarbon feed has a content of oxygenates of 1000 wt.-ppm or less, preferably 700 wt.-ppm or less, 500 wt.-ppm or less, 300 wt.-ppm or less, 100 wt.-ppm or less, 80 wt.-ppm or less, 60 wt.-ppm or less, 50 wt.-ppm or less, 40 wt.-ppm or less, or 30 wt.-ppm or less. Oxygenates mean herein molecules containing carbon and hydrogen and further containing covalently bound oxygen in the structure (molecule). In the present invention, low amounts of oxygenates are preferred, including no oxygenates. On the other hand, in particular when employing e.g. 10 wt.-% or more of a low-oxygenate co-feed (e.g. a fossil hydrocarbon co-feed), higher values, such as from 100 wt.-ppm to 1000 wt.-ppm may be used. In such a case, the effort for minimizing oxygenate content is minimized which increases overall efficiency of the process. Since the renewable stabilized naphtha-range hydrocarbon feed of the present invention is a naphtha range feed, the number of possible oxygenates is limited. In accordance with the present invention, the content of oxygenates

- is determined based on ASTM D7423 (determining C2-C5 oxygenates by GC-FID, i.e. gas chromatography-flame ionisation detection), being modified to capture a longer list of oxygenates in the spectra. Specifically, the following oxygenates may be present in a renewable stabilized naphtha-range hydrocarbon feed of the present invention: ETBE (ethyl t-butyl ether), MTBE (methyl t-butyl ether), TAME (t-amyl methyl ether), DIPE (diisopropyl ether), propylether, isobutyraldehyde, butyraldehyde, isobutanol, n-butanol, sec-butanol, tert-butanol, methanol, acetone, vinyl acetate, ethyl acetate, MEK (methyl ethyl ketone), isovaleraldehyde, valeraldehyde, ethanol, isopropanol, n-propanol, allyl alcohol, diethylether, acetaldehyde, and others. The total content of all oxygenates identified by GC-FID is assumed to correspond to the total content of oxygenates in the sample, i.e. in the renewable stabilized naphtha-range hydrocarbon feed.
- 15 Preferably, the renewable stabilized naphtha-range hydrocarbon feed has a content of C17 and higher carbon number compounds of 1.0 wt.-% or less, such as 0.0 to 0.9 wt.-%, preferably 0.0 to 0.8 wt.-%, more preferably 0.0 to 0.5 wt.-%, or 0.0 to 0.2 wt.-%.
- 20 Preferably, the renewable stabilized naphtha-range hydrocarbon feed has a carbon range of 10 or less, preferably 8 or less, 7 or less, 6 or less, or 5 or less. The carbon range is preferably 1 or more, 2 or more, or 3 or more. Thus, the carbon range is preferably in a range of from 1 to 10, such as from 2 to 10, 3 to 10, 3 to 8, 3 to 7, 2 to 6, 3 to 6, 2 to 5, or 3 to 5. In the present invention, the carbon range refers to the difference between C_{max} and C_{min} (carbon range=C_{max}-C_{min}), where C_{max} (highest occurring carbon number) and C_{min} (lowest occurring carbon number) are determined by PIONA (GCxGC method described herein), and for determination of C_{min} and C_{max} carbon numbers having a measured abundance of 0.10 wt.-% or less are assumed to be absent. In other words, carbon numbers having a measured abundance of 0.10 wt.-% or less are not considered when determining C_{min} and C_{max}, and thus when determining the carbon range. The carbon range is more sensitive to low amounts of outliers in the carbon

number distribution and thus more accurate than analysis techniques based on distillation characteristics, such as those determined in accordance with EN ISO 3405-2019. In other words, the carbon range gives a good impression of the quality of the feed in terms of homogeneity.

5

Preferably, the renewable stabilized naphtha-range hydrocarbon feed has an interventile carbon number range (IVR) of 6.5 or less, preferably 5.0 or less, 4.5 or less, 4.0 or less or 3.8 or less. The IVR is the calculated carbon number range determined from a linear interpolation of data (accumulated content vs. carbon number) obtained from PIONA carbon number analysis. Similarly, IDR, IQR, and c₅₀ (and other c_{xx} values) are determined from a linear interpolation of data (accumulated content vs. carbon number) obtained from PIONA carbon number analysis.

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The IVR is the carbon number range containing 90% of the mass (i.e. from 5 wt.-% to 95 wt.-%). Similarly, the IQR (interquartile range) is the carbon number range containing 50% of mass from 25 wt.-% to 75 wt.-% and the IDR (interdecile range) is the carbon number range containing 80% of mass from 10 wt.-% to 90 wt.-%. Similarly, the IQR (interquartile range) is the carbon number range containing 50% of mass from 25 wt.-% to 75 wt.-% and the IDR (interdecile range) is the carbon number range containing 80% of mass from 10 wt.-% to 90 wt.-%. Linear interpolation means that a content range between two carbon numbers is assumed to be linear. For example a sample containing 0%C₁ (0% components having 1 carbon atom), 0%C₂, 0%C₃, 5%C₄, 5%C₅ and 8%C₆ will have a c_{2.5} value (i.e. fractional carbon number representing 2.5 wt.-% of the sample) of 3.5 (carbon number) even though C₄ is the lowest carbon number which is actually present. The c₅ value (fractional carbon number representing 5 wt.-% sample) is 4 (C₄) and the c₁₀ value (10 wt.-%) is 5 (C₅), since the accumulated amount of C₁+C₂+C₃+C₄+C₅ is exactly 10 wt.-%. The c₁₅ value (15 wt.-%) is between 5 and 6 (C₅ is 10 wt.-%, C₆ is 18 wt.-%). Linear interpolation is easily calculated such that e.g. the 15 wt.-% content carbon number (c₁₅ value) is calculated to be

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$$5 \{ \text{highest carbon number not yet contributing 15 wt.-%} \} + \\ [(15\% \{ \text{content of interest} \} - 10\% \{ \text{C5 accumulated content} \}) / \\ (18\% \{ \text{C6 accumulated content} \} - 10\% \{ \text{C5 accumulated content} \})] \\ = 5 + [5\% / 8\%] = 5 + 0.625, \text{ i.e. carbon number 5.625.}$$

- 5 In other words, for determining the c_XX value, the following equation is used:

$$\{ \text{highest carbon number not yet contributing XX wt.-%} \} + \\ [(\{ \text{content of interest: XX wt.-%} \} - \{ \text{accumulated content of highest} \\ \text{carbon number not yet contributing XX wt.-%} \}) / \\ 10 (\{ \text{accumulated content of lowest carbon number for which} \\ \text{accumulated content exceeds XX wt.-%} \} - \{ \text{accumulated content of} \\ \text{highest carbon number not yet contributing XX wt.-%} \})]$$

The linear interpolation can be easily understood from the graphical illustration of FIG. 1. In FIG. 1, the y-axis represents the accumulated content of compounds and carbon numbers are arranged on the x-axis ordered by their number. The bars represent individual content of compounds with the respective carbon number. The dots represent the accumulated content (cumulative mass fraction) for the respective carbon number and the line graph represents the linear interpolation (i.e. drawing a straight line between neighbouring dots). The carbon number where the line graph crosses the 50% cumulative mass fraction (horizontal line) is the c_50 value, which is slightly above 16 in FIG. 1, as shown by the dotted line.

- 25 The IVR, IDR and IQR ranges are less sensitive to tail effects and thus provide more stable results than the carbon range.

Preferably, the renewable stabilized naphtha-range hydrocarbon feed has an interdecile carbon number range (IDR) of 4.5 or less, preferably 4.0 or less, 30 3.5 or less, or 3.0 or less. Preferably, the renewable stabilized naphtha-range hydrocarbon feed has an interquartile carbon number range (IQR) of 2.5 or less, preferably 2.0 or less, 1.8 or less, or 1.5 or less.

Preferably, the renewable stabilized naphtha-range hydrocarbon feed has a content of C11 and higher carbon number components of less than 5.0 wt.-%, preferably 4.5 wt.-% or less, 4.0 wt.-% or less, 3.5 wt.-% or less, 3.0 wt.-% or less, 2.5 wt.-% or less or 2.0 wt.-% or less. For example, the
5 content of C11 and higher carbon number components may be 0.0 to 5.0 wt.-%, or 0.1 to 5.0 wt.-%

Preferably, the renewable stabilized naphtha-range hydrocarbon feed has a T95 temperature of 220°C or less, preferably 200°C or less, 180°C or less,
10 160°C or less, or 140°C or less.

Preferably, the renewable stabilized naphtha-range hydrocarbon feed has a T99 temperature of 220°C or less, preferably 200°C or less, 180°C or less, 160°C or less, or 140°C or less.

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Preferably, the renewable stabilized naphtha-range hydrocarbon feed has a final boiling point of 220°C or less, preferably 200°C or less, 180°C or less, or 160°C or less.

20 Preferably, the renewable stabilized naphtha-range hydrocarbon feed has an initial boiling point of 20°C or more, preferably 20°C to 60°C, such as 30°C to 50°C or 30°C to 45°C.

Preferably, the renewable stabilized naphtha-range hydrocarbon feed has a
25 T5 temperature of 40°C or more, preferably 45°C or more, 50°C or more, 55°C or more, or 60°C or more.

In the present invention, the renewable stabilized naphtha-range hydrocarbon feed has low contents of light and very light components.

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Having an initial boiling point and/or a T5 temperature within the above ranges improves the yield of valuable products, in particular propylene and

ethylene, over C3 and C4 products in the effluent of the thermal cracking furnace of step (b).

Preferably, the difference between the T10 temperature and the T90 temperature (T90-T10) of the renewable stabilized naphtha-range hydrocarbon feed is less than 100°C, preferably less than 80°C, such as 20°C to 75°C, 30°C to 70°C, or 40°C to 70°C.

The difference between T10 and T90 value largely disregards outliers (tails) in the boiling distribution and is thus a stable and very reliable measure for describing the homogeneity of a composition. Within the above limits, the renewable stabilized naphtha-range hydrocarbon feed has been found to produce favourable product distribution while still making use of a considerable amount of the material, thus contributing to high overall yield improvement.

Preferably, the renewable stabilized naphtha-range hydrocarbon feed has a total paraffins content of 90 wt.-% or more, preferably 92 wt.-% or more, 93 wt.-% or more, 94 wt.-% or more or 95 wt.-% or more.

The content of total paraffins in the renewable stabilized naphtha-range hydrocarbon feed of the present invention refers to the summed amount of n-paraffins and i-paraffins relative to the total weight of the renewable stabilized naphtha-range hydrocarbon feed. The inventors found that a high amount of total paraffins further increases the yield of valuable products and reduces coking tendency.

Preferably, the renewable stabilized naphtha-range hydrocarbon feed has a content ratio of i-paraffins to n-paraffins in the range of 1.7 or less, preferably 1.5 or less, such as 0.5 to 1.7, or 0.7 to 1.5.

An i-paraffins to n-paraffins ratio within the above limits provides a particularly high yield of ethylene. In the present invention, the ratio is

defined on a weight basis, i.e. content by weight of i-paraffins divided by content by weight of n-paraffins.

Preferably, the renewable stabilized naphtha-range hydrocarbon feed has a
5 content ratio of i-paraffins to n-paraffins in the range of 2.0 or more, preferably 2.2 or more.

An i-paraffins (iP) to n-paraffins (nP) ratio within the above limits provides a particularly high yield of propylene. In other words, by appropriately
10 adjusting the i-paraffins to n-paraffins ratio, it is possible to adjust the product distribution towards desired products, thus providing higher flexibility of the product range.

An intermediate range within 1.7 to 2.0 may be employed as well, though
15 being not preferred because it is not optimal for ethylene production and not optimal for propylene production.

In addition, such a high iP/nP ratio lowers viscosity and improves mixing characteristics and blendability, which is particularly (but not exclusively)
20 beneficial when employing a co-feed in the cracking step.

Preferably, the renewable stabilized naphtha-range hydrocarbon feed is obtainable by a method as disclosed for the above-described step (a) of providing the renewable stabilized naphtha-range hydrocarbon feed in the
25 method of the present invention.

Specifically, the renewable stabilized naphtha-range hydrocarbon feed is preferably obtainable by a method comprising hydrotreatment of an oxygenate bio-renewable feed and optionally isomerisation. The method
30 preferably comprises the isomerisation.

It is to be noted that the renewable stabilized naphtha-range hydrocarbon feed employed in the method is preferably the renewable stabilized naphtha-

range hydrocarbon feed disclosed herein, i.e. having the characteristics mentioned herein.

In an embodiment, the renewable stabilized naphtha-range hydrocarbon feed
5 may be obtainable or obtained by a method comprising subjecting an
oxygenate bio-renewable feed to hydrotreatment comprising at least
hydrodeoxygenation to provide a hydrotreatment effluent, subjecting at least
part of the hydrotreatment effluent to gas-liquid separation to provide a
gaseous stream and a first liquid hydrocarbon stream, providing the first
10 liquid hydrocarbon stream as a liquid hydrocarbon stream or subjecting at
least part of the first liquid hydrocarbon stream to a further hydrotreatment
comprising at least hydroisomerisation, followed by optional further gas-liquid
separation, to provide at least a second liquid hydrocarbon stream as the
liquid hydrocarbon stream, and feeding at least part of the liquid
15 hydrocarbon stream to a first distillation column, preferably a first
stabilisation column, to obtain a first overhead fraction and a stabilised heavy
liquid hydrocarbon fraction, optionally using at least part of the stabilised
heavy liquid hydrocarbon fraction in diesel fuel and/or recovering from at
least part of the stabilised heavy liquid hydrocarbon fraction at least an
20 aviation fuel range fraction and a bottoms fraction, separating from the first
overhead fraction at least a fuel gas fraction and a naphtha range fraction,
refluxing a portion, preferably at least 50 wt.-%, more preferably at least 70
wt.-%, even more preferably at least 85 wt.-% of the naphtha range fraction
back to the first distillation column, feeding at least a portion of the naphtha
25 range fraction to a second distillation column, preferably a second
stabilisation column, to obtain a second overhead fraction, preferably
comprising at least part of components boiling below 20°C, and a stabilised
naphtha range fraction, separating from the second overhead fraction at least
a further fuel gas fraction and light liquid hydrocarbons, and refluxing at least
30 a portion, preferably at least 50 wt.-%, more preferably at least 70 wt.-%,
even more preferably at least 85 wt.-% of the light liquid hydrocarbons back
to the second distillation column, and recovering at least a portion of the
stabilised naphtha range fraction as the renewable stabilized naphtha-range

hydrocarbon feed.

Cracking effluent

The present invention further relates to a renewable thermal cracking effluent
5 having a benzene content of 6.0 wt.-% or less, a total content of ethylene
and propylene of 45.0 wt.-% or more and a carbon monoxide content of 0.25
wt.-% or less. The benzene content may be 0.01 wt.-% to 6.0 wt.-%, such
as 0.1 wt.-% to 4.0 wt.-%, 0.1 wt.-% to 3.6 wt.-%, 0.1 wt.-% to 3.4 wt.-%,
0.1 wt.-% to 3.2 wt.-%, 0.1 wt.-% to 3.0 wt.-%, 0.1 wt.-% to 2.8 wt.-%,
10 0.1 wt.-% to 2.6 wt.-%, 0.2 wt.-% to 2.4 wt.-%, 0.3 wt.-% to 2.2 wt.-%, or
0.5 wt.-% to 2.0 wt.-% or less.

Preferably, the renewable thermal cracking effluent has a total content of
ethylene and propylene of 45 wt.-% to 65 wt.-%, preferably 46.0 wt.-% to
15 65.0 wt.-%, 47.0 wt.-% to 65.0 wt.-%, 48.0 wt.-% to 65.0 wt.-%, 49.0 wt.-%
to 65.0 wt.-%, 50.0 wt.-% to 65.0 wt.-%, 50.0 wt.-% to 60.0 wt.-%, or
50.0 wt.-% to 55.0 wt.-%.

Preferably, the renewable thermal cracking effluent has a total content of
20 ethylene and propylene and total C4 olefins of 45 wt.-% to 80 wt.-%,
preferably 50 wt.-% to 75 wt.-%, 50 wt.-% to 70 wt.-%, 50 wt.-% to 65 wt.-%
%, or 55 wt.-% to 65 wt.-%.

Preferably, the renewable thermal cracking effluent has a total content of C4
25 olefins of at least 5.0 wt.-%, such as 5.0 wt.-% to 20.0 wt.-%, preferably 8.0
wt.-% to 20.0 wt.-%, 10.0 wt.-% to 20.0 wt.-%, 12.0 wt.-% to 20.0 wt.-%,
12.6 wt.-% to 20.0 wt.-%, 13.0 wt.-% to 20.0 wt.-%, or 13.5 wt.-% to 20.0
wt.-%.

30 The total C4 olefins refer to 1-butene, 2-butene (including cis-2-butene and
trans-2-butene), 1,3-butadiene, and isobutene. The total content of ethylene
and propylene and total C4 olefins may also be referred to as total content of
valuable light olefins.

The renewable thermal cracking effluent is preferably the effluent of the thermal cracking furnace of step (b) of the method of the present invention. Similarly, step (b) of the method preferably provides an effluent of the thermal cracking furnace having the properties of the renewable thermal cracking effluent mentioned herein.

Preferably, the renewable thermal cracking effluent has a carbon monoxide content of 0.23 wt.-% or less, preferably 0.21 wt.-% or less, 0.20 wt.-% or less, 0.19 wt.-% or less, 0.18 wt.-% or less, 0.17 wt.-% or less, 0.16 wt.-% or less, 0.15 wt.-% or less, 0.14 wt.-% or less, 0.13 wt.-% or less, 0.12 wt.-% or less, 0.11 wt.-% or less, 0.10 wt.-% or less, or 0.09 wt.-% or less.

Carbon monoxide acts as a catalyst poison for polymerisation catalysts. It is thus favourable to minimize its content in an early stage, thus reducing the efforts required to remove it. The present invention provides means to achieve very low CO contents even without the need for CO removal.

Preferably, the renewable thermal cracking effluent has a C4 monoolefin content of 6.0 wt.-% or more, preferably 6.5 wt.-% or more, 6.8 wt.-% or more, 7.0 wt.-% or more, 7.2 wt.-% or more, or 7.4 wt.-% or more. The upper limit may for example be 15.0 wt.-%, such as 13.0 wt.-%. In other words, the renewable thermal cracking effluent may for example have a C4 monoolefin content in the range of 6.0 wt.-% to 15.0 wt.-%, such as 6.5 wt.-% to 13.0 wt.-%.

Preferably, the renewable thermal cracking effluent has an isobutene content of at least 2.0 wt.-%, preferably at least 2.4 wt.-%, more preferably at least 3.0 wt.-%, even more preferably at least 3.2 wt.-%. The upper limit may for example be 10.0 wt.-%, such as 9.0 wt.-% or 8.0 wt.-%. In other words, the renewable thermal cracking effluent may for example have an isobutene content in the range of 2.0 wt.-% to 10.0 wt.-%, such as 2.5 wt.-% to 9.0 wt.-% or 3.0 wt.-% to 8.0 wt.-%.

- Among C4 olefins, isobutene is highly attractive molecule as it can be easily converted by reacting with methanol or ethanol to obtain methyl tert-butyl ether (MTBE) or ethyl tert-butyl ether (ETBE), respectively, and transported, whereafter the MTBE/ETBE can be reversed in a similar manner to isobutene and the corresponding alcohol. MTBE and ETBE are also highly valuable gasoline components. Furthermore, the derivatives of isobutene are more valuable than derivatives of linear C4 olefins, including butyl rubber, polyisobutene, methylmethacrylate, gasoline alkylate, just to name a few.
- Additionally separating isobutene from other C4 olefins is relatively simple, for example by reacting methanol or ethanol with an isobutene containing C4 olefins fraction to obtain MTBE or ETBE, respectively, followed by separating the formed ethers from the remaining C4 olefins mixture.
- Preferably, the renewable thermal cracking effluent has a total content of n-C4 monoolefins of 3.0 wt.-% or more, preferably 3.5 wt.-% or more, such as 4.0 wt.-% or more. The upper limit may for example be 15.0 wt.-%, such as 12.0 wt.-%, or 10.0 wt.-%.
- Preferably, the renewable thermal cracking effluent has a 1,3-butadiene content of at least 5.0 wt.-%, preferably at least 5.5 wt.-%, more preferably at least 6.0 wt.-%, or at least 6.2 wt.-%. The upper limit may for example be 15.0 wt.-%, such as 13.0 wt.-% or 11.0 wt.-%. In other words, the renewable thermal cracking effluent may for example have a 1,3 butadiene content in the range of 5.0 wt.-% to 15.0 wt.-%, such as 5.5 wt.-% to 13.0 wt.-% or 5.5 wt.-% to 11.0 wt.-%.
- Specifically, the renewable stabilized naphtha-range hydrocarbon feed of the present invention is particularly suitable for achieving high butadiene content.
- In other words, this feed is similarly suitable as a fossil naphtha and thus may be co-fed with fossil naphtha in broad blending ratios without a drop in the butadiene content.

Preferably, the renewable thermal cracking effluent has a toluene content in the range of from 0.2 wt.-% to 1.8 wt.-%, preferably 0.2 wt.-% to 1.6 wt.-%, 0.2 wt.-% to 1.4 wt.-%, 0.2 wt.-% to 1.2 wt.-%, 0.2 wt.-% to 1.0 wt.-%, 0.2 wt.-% to 0.9 wt.-%, 0.2 wt.-% to 0.8 wt.-%, 0.2 wt.-% to 0.7 wt.-%, or 0.3 wt.-% to 0.6 wt.-%.

A thermal cracking effluent of the present invention is particularly suitable for further upgrading into monomer(s) for polymerisation.

10 Examples

The present invention is further illustrated by way of Examples. It is to be understood that the Examples shall in no way limit the present invention.

Thermal cracking of five feed compositions (C1, C2, C3, E1 and E2) was evaluated. A fossil feed composition (C1) corresponds to a conventional fossil light naphtha. The remaining four feeds correspond to hydrotreated and isomerised bio-renewable fat/oil having varying degrees of isomerisation and boiling point range. Of these, feed composition C2 is a broad-cut naphtha composition, feed composition C3 is a highly isomerized diesel range composition, feed composition E1 is a stabilized naphtha range composition and feed composition E2 is a stabilized and highly isomerised naphtha range composition.

PIONA data and oxygen content of these composition are shown in the following Table 1

Table 1:

Component	C1	C2	C3	E1	E2
n-paraffins (nP)	34.0%	33.1%	8.4%	41.4%	<40%
i-paraffins (iP)	39.9%	59.5%	91.5%	53.9%	>60%
olefins (O)	0%	0.3%	0%	0%	0%
naphthenes (N)	25.4%	6.3%	0%	4.3%	1.9%
aromatics (A)	0.7%	0.8%	0.1%	0.4%	0%
oxygen	n.a.	n.a.	<3 ppm	10 ppm	4 ppm

*n.a. means not available / not measured

The following Table 2 shows boiling properties (according to EN ISO 3405-2019) and carbon number analysis based on PIONA data correlating carbon number (assumed to be a float number by linear interpolation) vs. content range (by weight) of the total composition and calculated IQR, IDR and IVR values.

Table 2:

	C1	C2	C3	E1	E2
IBP (0 vol%)	n.a.	n.a.	187°C	47°C	46°C
5 vol% Temp. (T5)	n.a.	n.a.	246°C	61°C	62°C
95 vol% Temp. (T95)	n.a.	n.a.	295°C	137°C	122°C
FBP	n.a.	n.a.	309°C	170°C	137°C
C_min (measured)	4	3	5	5	5
C_max (measured)	7	18	20	13	10
c_05	4.1	4.3	12.2	4.4	4.4
c_10	4.4	4.8	14.2	4.7	4.9
c_25	5.0	5.7	15.2	5.4	5.5
c_50	5.3	6.9	16.1	6.2	6.3
c_75	5.7	8.4	17.2	7.0	7.0
c_90	5.9	9.6	17.7	7.9	7.7
c_95	5.9	10.7	17.9	8.5	8.0
IQR	0.7	2.6	2.0	1.6	1.5
IDR	1.5	4.8	3.5	3.1	2.9
IVR	1.8	6.5	5.6	4.2	3.5
carbon range	3	15	15	8	5

*IBP= initial boiling point, FBP=final boiling point, c_05= Fractional carbon number corresponding to 5% of the mass when sorted by ascending carbon number (c_10 and others similarly, as explained above)

Comparative Examples 1, 2, 3 and Example 1 and 2

The five compositions were subjected to steam cracking at two distinct coil outlet temperatures (COT) of 820°C and 850°C at a dilution (water/oil ratio) of 0.5 and a coil outlet pressure (COP) of 1.7 bar (absolute).

The resulting yield of relevant products are shown in Table 3 below.

Table 3:

	CEx.1	CEx.2	CEx.3	Ex.1	Ex.2
	C1	C2	C3	E1	E2
COT 820°C					
ethylene	21.3	27.3	29.6	29.2	27.9
propylene	16.0	19.5	18.7	20.1	21.9
ethylene+propylene	37.3	46.8	48.3	49.3	49.8
butadiene	4.4	5.8	6.7	6.6	5.9
n-C4 monoolefins	3.9	4.6	4.3	5.1	6.1
isobutene	2.8	3.9	3.0	4.0	4.9
C4 monoolefins	6.7	8.5	7.3	9.1	11.0
C2-C4 paraffins	4.0	-*	4.4	5.5	4.7
benzene	4.5	3.2	6.7	1.4	1.1
toluene	0.6	1.6	2.7	0.6	0.4
PFO (C10 and heavier)	0.3	-**	1.2	0.2	0.2
carbon monoxide	0.00	0.32	0.05	0.04	0.08
COT 850°C					
ethylene	29.0	30.9	n.a.	32.5	30.8
propylene	17.5	17.6		17.8	19.1
ethylene+propylene	46.5	48.5		50.3	49.9
butadiene	5.0	5.4		6.6	6.3
n-C4 monoolefins	3.1	2.8		3.6	3.7
isobutene	2.7	3.1		2.4	3.5
C4 monoolefins	5.8	5.9		6.0	7.2
C2-C4 paraffins	4.4	-		5.2	4.4
benzene	5.8	5.6		3.8	3.2
toluene	1.1	2.1		1.3	1.1
PFO (C10 and heavier)	3.1	-		0.8	0.7
carbon monoxide	0.04	0.23		0.08	0.16

* no propane/butane ; ** no heavy components

As can be seen from the above data, the steam cracker feed compositions E1
5 and E2 according to the present invention provide low aromatics and high
light olefins yield, especially at relatively low COT. In particular in comparison
to conventional (fossil) naphtha, low COT may be employed while still
achieving high yield. Furthermore, low coke formation was observed for the
inventive compositions and for fossil naphtha composition C1. Further, the
10 cracking effluent produced from fossil naphtha shows high benzene content.

It is assumed that this is because benzene is contained in the fossil naphtha cracker feed in relatively high amounts (and does not convert in the cracking process) and because fossil naphtha contains high amounts of naphthenes which are converted to aromatics, such as benzene as well.

5

The low-to-moderately isomerized composition E1 particularly provides improved yield of ethylene and butadiene and the highly-isomerized composition E2 provides particularly good yield of propylene and C4 monoolefins.

10

The above data show that by using the renewable stabilized naphtha-range hydrocarbon compositions of the present invention, such as compositions E1 and E2, as steam cracker feed, it is possible to obtain very high combined yield of ethylene and propylene and high yield of total C4 olefins, particularly 1,3-butadiene. At the same time only very little coke, minimal aromatics, particularly benzene, and minimal heavies are formed even at elevated COT:s. Conveniently, these benefits are seen already at low COT:s, where also C4 monoolefins formation is favoured.

15

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In accordance with the present invention, the combined yield of ethylene and propylene may be further increased by separating and recycling formed C2-C4 paraffins. Further, the product slate can be easily adjusted to a desired direction depending e.g. on market demand, product price, further purification or post-processing capacity, etc: for example by selecting a renewable stabilized naphtha-range hydrocarbon feed having a lower content ratio of i-paraffins to n-paraffins and/or using a higher COT in the thermal cracking, it is possible to increase the weight ratios of ethylene to propylene and 1,3-butadiene to C4 monoolefins in the cracking effluent.

25

Claims

1. A method comprising
 - (a) a step of providing a renewable stabilized naphtha-range hydrocarbon feed,
5 feed,
 - (b) a step of thermally cracking the renewable stabilized naphtha-range hydrocarbon feed in a thermal cracking furnace, optionally together with co-feed(s) and/or additive(s), and
 - (c) a step of subjecting the effluent of the thermal cracking furnace of step
10 (b) to a separation treatment to provide at least a light olefin(s) fraction.
2. The method according to claim 1, wherein the thermal cracking step (b) is a steam cracking step.
15
3. The method according to any one of the preceding claims, wherein the thermal cracking step (b) is conducted at a coil outlet temperature (COT) selected from the range from 780°C to 880°C, preferably from 800°C to 860°C, more preferably from 820°C to 850°C.
20
4. The method according to any one of the preceding claims, wherein the content of the renewable stabilized naphtha-range hydrocarbon feed in the total cracker feed is in the range of from 10 wt.-% to 100 wt.-%, preferably 20 wt.-% to 100 wt.-%, 30 wt.-% to 100 wt.-%, 40 wt.-% to 100 wt.-%, 50
25 wt.-% to 100 wt.-%, 60 wt.-% to 100 wt.-%, 70 wt.-% to 100 wt.-%, 80 wt.-% to 100 wt.-%, or 90 wt.-% to 100 wt.-%, and the thermal cracking in step (b) is preferably carried out in the presence of co-feed(s), wherein the total cracker feed refers to the renewable stabilized naphtha-range hydrocarbon feed plus optional co-feed(s) and optional additive(s).
30
5. The method according to any one of the preceding claims, wherein the separation treatment in step (c) further provides a fraction comprising one or more of C2 to C4 paraffins, and the method comprises recycling at least part

of said fraction as a co-feed to step (b) and/or recovering at least part of said fraction as an NGL (natural gas liquids) composition.

6. The method according to any one of the preceding claims, further comprising
- an optional step comprising derivatisation of at least part of the light olefin(s) to obtain one or more derivate(s) of the light olefin(s) as bio-monomer(s), and
- (d) a step of (co)polymerizing at least one of the light olefin(s) separated in step (c) and/or at least one of bio-monomer(s), optionally together with other (co)monomer(s) and/or after optional further purification, to produce a biopolymer composition.
7. A biopolymer composition obtainable by the method according to claim 6.
8. A renewable stabilized naphtha-range hydrocarbon feed for thermal cracking.
9. The renewable stabilized naphtha-range hydrocarbon feed according to claim 8, wherein the renewable stabilized naphtha-range hydrocarbon feed has a content of C4 and lower carbon number compounds of 5.0 wt.-% or less, preferably 2.5 wt.-% or less, more preferably 2.0 wt.-% or less, even more preferably 1.5 wt.-% or less.
10. The renewable stabilized naphtha-range hydrocarbon feed according to claim 8 or 9, wherein the renewable stabilized naphtha-range hydrocarbon feed has a content of naphthenes in the range of from 0.1 wt.-% to 10.0 wt.-%, preferably 0.2-10.0 wt.-%, such as 0.5-8.0 wt.-%, 0.5-6.0 wt.-%, 0.6 to 5.8 wt.-%, 0.8 to 5.8 wt.-%, 1.0 to 5.6 wt.-% or 1.2 to 5.6 wt.-%, based on the total weight of the renewable stabilized naphtha-range hydrocarbon feed, and/or wherein the renewable stabilized naphtha-range hydrocarbon feed has a content of olefins of 0.50 wt.-% or less, preferably 0.40 wt.-% or less, 0.30

wt.-% or less, 0.25 wt.-% or less, 0.20 wt.-% or less, 0.15 wt.-% or less, 0.12 wt.-% or less, 0.10 wt.-% or less, 0.07 wt.-% or less, or 0.05 wt.-% or less.

5 11. The renewable stabilized naphtha-range hydrocarbon feed according to any one of claims 8 to 10, wherein the renewable stabilized naphtha-range hydrocarbon feed has a content of aromatics of 0.80 wt.-% or less, preferably 0.70 wt.-% or less, 0.60 wt.-% or less, 0.50 wt.-% or less, 0.40 wt.-% or less, 0.35 wt.-% or less, 0.30 wt.-% or less, 0.25 wt.-% or less, 0.20 wt.-% or less, or 0.15 wt.-% or less.

12. The renewable stabilized naphtha-range hydrocarbon feed according to any one of claims 8 to 11, wherein the renewable stabilized naphtha-range hydrocarbon feed has a carbon range of 10 or less, preferably 8 or less, 7 or less, 6 or less, or 5 or less.

13. The renewable stabilized naphtha-range hydrocarbon feed according to any one of claims 8 to 12, wherein the renewable stabilized naphtha-range hydrocarbon feed has an interquartile carbon number range (IQR) of 2.5 or less, preferably 2.0 or less, 1.8 or less, or 1.5 or less, and/or the renewable stabilized naphtha-range hydrocarbon feed has an interventile carbon number range (IVR) of 6.5 or less, preferably 5.0 or less, 4.5 or less, 4.0 or less or 3.8 or less, and/or the renewable stabilized naphtha-range hydrocarbon feed has an interdecile carbon number range (IDR) of 4.5 or less, preferably 4.0 or less, 3.5 or less, or 3.0 or less.

14. The renewable stabilized naphtha-range hydrocarbon feed according to any one of claims 8 to 13, wherein the renewable stabilized naphtha-range hydrocarbon feed has a content of C11 and higher carbon number components of less than 5.0 wt.-%, preferably 4.5 wt.-% or less, 4.0 wt.-% or less, 3.5 wt.-% or less, 3.0 wt.-% or less, 2.5 wt.-% or less or 2.0 wt.-% or less.

15. The renewable stabilized naphtha-range hydrocarbon feed according to any one of claims 8 to 14, wherein the renewable stabilized naphtha-range hydrocarbon feed has a content of C17 and higher carbon number compounds of 1.0 wt.-% or less, such as 0.0 to 0.9 wt.-%, preferably 0.0 to 0.8 wt.-%, more preferably 0.0 to 0.5 wt.-% or 0.0 to 0.2 wt.-%.

16. The renewable stabilized naphtha-range hydrocarbon feed according to any one of claims 8 to 15, wherein the renewable stabilized naphtha-range hydrocarbon feed has a total paraffins content of 90 wt.-% or more, preferably 92 wt.-% or more, 93 wt.-% or more, 94 wt.-% or more or 95 wt.-% or more.

17. The renewable stabilized naphtha-range hydrocarbon feed according to any one of claims 8 to 16, wherein the renewable stabilized naphtha-range hydrocarbon feed has a content ratio of i-paraffins to n-paraffins in the range of 1.7 or less, preferably 1.5 or less, such as 0.5 to 1.7, or 0.7 to 1.5.

18. The renewable stabilized naphtha-range hydrocarbon feed according to any one of claims 8 to 16, wherein the renewable stabilized naphtha-range hydrocarbon feed has a content ratio of i-paraffins to n-paraffins in the range of 2.0 or more, preferably 2.2 or more.

19. The method according to any one of claims 1 to 6, wherein the renewable stabilized naphtha-range hydrocarbon feed is according to any one of claims 8 to 18.

20. A renewable thermal cracking effluent having a benzene content of 6.0 wt.-% or less, a total content of ethylene and propylene of 45.0 wt.-% or more and a carbon monoxide content of 0.25 wt.-% or less.

30

21. The renewable thermal cracking effluent according to claim 20, having a benzene content of 0.01 wt.-% to 6.0 wt.-%, such as 0.1 wt.-% to 4.0 wt.-%, 0.1 wt.-% to 3.6 wt.-%, 0.1 wt.-% to 3.4 wt.-%, 0.1 wt.-% to 3.2 wt.-%

%, 0.1 wt.-% to 3.0 wt.-%, 0.1 wt.-% to 2.8 wt.-%, 0.1 wt.-% to 2.6 wt.-%, 0.2 wt.-% to 2.4 wt.-%, 0.3 wt.-% to 2.2 wt.-%, or 0.5 wt.-% to 2.0 wt.-% or less.

5 22. The renewable thermal cracking effluent according to claim 20 or 21,
wherein the renewable thermal cracking effluent has a total content of
ethylene and propylene of 45 wt.-% to 65 wt.-%, preferably 46.0 wt.-% to
65.0 wt.-%, 47.0 wt.-% to 65.0 wt.-%, 48.0 wt.-% to 65.0 wt.-%, 49.0 wt.-%
to 65.0 wt.-%, 50.0 wt.-% to 65.0 wt.-%, 50.0 wt.-% to 60.0 wt.-%, or
10 50.0 wt.-% to 55.0 wt.-%.

23. The renewable thermal cracking effluent according to any one of claims
20 to 22, which is obtainable by the method according to any one of claims 1
to 6 and 19.

15

24. The renewable thermal cracking effluent according to any one of claims
20 to 23, wherein the renewable thermal cracking effluent has a carbon
monoxide content of 0.23 wt.-% or less, preferably 0.21 wt.-% or less, 0.20
wt.-% or less, 0.19 wt.-% or less, 0.18 wt.-% or less, 0.17 wt.-% or less,
20 0.16 wt.-% or less, 0.15 wt.-% or less, 0.14 wt.-% or less, 0.13 wt.-% or
less, 0.12 wt.-% or less, 0.11 wt.-% or less, 0.10 wt.-% or less, or 0.09 wt.-%
or less.

25. The renewable thermal cracking effluent according to any one of claims
25 20 to 24, wherein the renewable thermal cracking effluent has

 a total content of C4 olefins of at least 8.0 wt.-%, at least 10.0 wt.-%,
at least 11.0 wt.-%, or at least 12.0 wt.-%; and/or

 a content of 1,3-butadiene of at least 5.0 wt.-%, at least 5.5 wt.-%,
or at least 6.0 wt.-%, and/or at most 15.0 wt.-%, at most 13.0 wt.-%, or at
30 most 11.0 wt.-%; and/or

 a C4 monoolefin content of 6.0 wt.-% or more, preferably 6.5 wt.-%
or more, 6.8 wt.-% or more, 7.0 wt.-% or more, 7.2 wt.-% or more, or 7.4
wt.-% or more, and/or at most 15.0 wt.-% or at most 13.0 wt.-%; and/or

an isobutene content of least 2.0 wt.-%, at least 2.4 wt.-%, or at least 3.0 wt.-%, and/or at most 10.0 wt.-%, at most 9.0 wt.-%, or at most 8.0 wt.-%; and/or

5 a content of n-C4 monoolefins of 3.0 wt.-% or more, 3.5 wt.-% or more, or 4.0 wt.-% or more, and/or at most 15.0 wt.-%, at most 12.0 wt.-%, or at most 10.0 wt.-%.

26. The renewable thermal cracking effluent according to any one of claims 20 to 25, wherein the renewable thermal cracking effluent has

10 a total content of C2-C4 paraffins of more than 4.0 wt.-%, preferably 4.2 wt.-% or more, more preferably 4.3 wt.-% or more and/or at most 15.0 wt.-%, at most 12.0 wt.-% or at most 10.0 wt.-%; and/or

a content of pyrolysis fuel oil (C10 and heavier compounds) of less than 1.5 wt.-%, preferably less than 1.2 wt.-%, more preferably less than
15 1.0 wt.-%.