

METHOD FOR PROCESSING LIQUEFIED WASTE POLYMERS

FIELD

The present invention relates to methods for processing liquefied waste polymers,
5 in particular to methods comprising selective hydrogenation of diolefins present therein.

BACKGROUND

Processing of liquefied waste polymers (LWP), such as waste plastic pyrolysis oils (WPPO) and hydrothermally liquefied waste plastic oils using oil distillation units is
10 not straightforward. LWPs foul easily and comprise different components of very wide boiling point. In crude oil distillation units, the distillation would be feasible, but products from the crude oil distillation units are typically directed to units that are not designed for olefinic feeds. For example, diolefins present in LWPs may cause problems in hydrogenation processes designed for crude oil derived naphtha
15 fractions which do not include these components.

LWPs contain also different elemental impurities dependent mostly on the source of the polymer waste that is liquefied, but also on the liquefaction technology employed. For example, in post-consumer waste plastics (recycled consumer plastics), that has been identified as a potential large-scale source for polymer
20 waste, the most relevant impurities are nitrogen, oxygen, sulphur and chlorine, but also other halogens such as bromine and fluorine may be present. Bromine-containing impurities may be contained mainly in industry-derived polymer waste (e.g. originating from flame retardants). Furthermore, metals and other impurities, such as metalloids originating from additives and contaminations can also be
25 detected in LWPs. These impurities have a detrimental effect on the direct utilization of the LWPs. LWPs that are produced by a pyrolysis process or hydrothermal liquefaction usually contain significant amounts of olefins and aromatics, each of which may lead to problems in some downstream processes, such as polymerization (or coking) at elevated temperatures.

30 US5849964 discloses a method for processing used or waste plastic materials to recover chemical raw materials and liquid fuel components by depolymerization of the used materials, which are transformed into a pumpable and into a volatile phase.

The pumpable phase remaining once the volatile phase is separated is subjected to liquid phase hydrogenation, gasification, low temperature carbonization or to a combination of said processes.

WO2016142808 discloses an integrated process for conversion of waste plastics to
5 final petrochemical products. The process allows for operating with a hydroprocessing reaction which provides simultaneous hydrogenation, and dechlorination of components of a hydrocarbon stream to specifications which meet steam cracker requirements.

However, there is still a need for further methods for processing waste polymers.

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SUMMARY

The following presents a simplified summary in order to provide a basic understanding of some aspects of various embodiments of the invention. The summary is not an extensive overview of the invention. It is neither intended to identify key nor critical elements of the invention, nor to delineate the scope of the
15 invention. The following summary merely presents some concepts of the invention in a simplified form as a prelude to a more detailed description of exemplifying embodiments of the invention.

It was observed that when LWPs are hydrotreated prior to fractionating, their fouling tendency is significantly reduced. Furthermore, hydroprocessing of the resulting
20 naphtha fraction is easier, and the lifetime of the hydroprocessing catalyst used is longer, as there is less polymerization and other reactions which would result in blocking of the catalysis bed.

In accordance with the invention, there is provided a new method for processing liquefied waste polymers (LWP), wherein the method comprises following steps:

- 25 a) providing an LWP stream comprising diolefins and naphtha,
 b) subjecting the LWP stream to hydrotreatment reaction conditions in the presence of hydrogen and one or more hydrotreatment catalyst to produce diolefin depleted LWP stream, and

- c) distilling the diolefin depleted LWP stream to obtain one or more distillates comprising at least a naphtha fraction boiling below 180 °C at atmospheric pressure and a distillation bottom.

In accordance with the invention, there is also provided a new use of hydrogenated naphtha as steam cracker feed wherein the hydrogenated naphtha is produced by
5 a method comprising:

- a) providing an LWP stream comprising diolefins and naphtha,
b) subjecting the LWP stream to hydrotreatment reaction conditions in the presence of hydrogen and one or more hydrotreatment catalysts to produce
10 diolefin depleted LWP stream,
c) distilling the diolefin depleted LWP stream to obtain one or more distillates comprising at least a naphtha fraction boiling below 180 °C at atmospheric pressure and a distillation bottom and
d) subjecting the naphtha fraction to hydroprocessing reaction conditions in the
15 presence of hydrogen and one or more hydroprocessing catalysts.

In accordance with the invention there is also provided a new use of a mixture of crude oil and the distillation bottom of step c) as a crude oil refinery feed.

A number of exemplifying and non-limiting embodiments of the invention are described in accompanied dependent claims.

20 Various exemplifying and non-limiting embodiments of the invention and to methods of operation, together with additional objects and advantages thereof, are best understood from the following description of specific exemplifying embodiments when read in connection with the accompanying figures.

The verbs “to comprise” and “to include” are used in this document as open
25 limitations that neither exclude nor require the existence of also unrecited features. The features recited in depending claims are mutually freely combinable unless otherwise explicitly stated. Furthermore, it is to be understood that the use of “a” or “an”, i.e., a singular form, throughout this document does not exclude a plurality.

As definer herein, the “hydroprocessing” refers to a range of catalytic chemical
30 engineer processes, including hydrotreating and hydrocracking, in which the

reaction of hydrogen is used to remove impurities, such as oxygen, sulphur, nitrogen, phosphorous, silicon and metals, to saturate carbon-carbon bonds, to break carbon-carbon bonds, to reduce average molecular weight, to rearrange the molecular structure of the feed or any combination thereof.

- 5 As defined herein, the term "hydrotreating" refers to a chemical engineer process in which the reaction of hydrogen is used to remove impurities, such as oxygen, sulphur, nitrogen, phosphorous, silicon and metals, and/or to saturate carbon-carbon bonds, especially as part of oil refining.

Hydrotreating can be performed in one or several steps in one or more reactor units
10 or catalyst beds.

BRIEF DESCRIPTION OF FIGURES

The exemplifying and non-limiting embodiments of the invention and their advantages are explained in greater detail below with reference to the accompanying figure, which shows an exemplary non-limiting flow chart for
15 processing liquefied waste polymers 10 comprising diolefins.

DESCRIPTION

The present invention concerns a method for processing liquefied waste polymers (LWP). The principle of the method is shown in figure 1. Accordingly, an LWP stream 10 comprising diolefins and naphtha is fed to a hydrotreatment unit **A** to produce
20 diolefin depleted LWP stream 20. When the hydrotreatment reaction is performed in mild, preferably in liquid phase conditions, in the presence of hydrogen and one or more hydrotreatment catalysts known in the art, predominantly only the diolefins present in the LWP are reduced. Exemplary hydrotreatment reaction conditions for selective reduction of diolefins comprise temperature 120-210 °C and pressure 1-
25 50 barg. An exemplary pressure is 28.5 barg. Liquid hourly space velocity (LHSV) is typically 1-5 h⁻¹, preferably 4-4.5 h⁻¹. An exemplary hydrogen/hydrocarbon ratio is 15 N m³/m³. Exemplary hydrotreatment catalysts include NiMo and CoMo, preferably on a support. An exemplary hydrotreatment catalyst is NiMo/Al₂O₃. Another exemplary hydrotreatment catalyst is CoMo/Al₂O₃.

30 The diolefin depleted LWP stream is fed to a distillation unit **B**, wherein one or more distillates 30, 40 and a distillation bottom 50 are separated. According to one

embodiment the distillate comprises a naphtha fraction 30 boiling below 180 °C at atmospheric pressure. According to this embodiment the distillation bottom 50 comprises material boiling above 180 °C at atmospheric pressure.

According another embodiment the distillation produces two distillates namely a
5 naphtha fraction 30 boiling below 180 °C at atmospheric pressure, and a middle distillate 40 boiling between 180 °C and 360 °C at atmospheric pressure. According to this embodiment the distillation bottom 50 comprises material boiling above 360 °C at atmospheric pressure.

According to one embodiment the distillation is performed at atmospheric pressure.
10 According to another embodiment the distillation is performed at reduced pressure. According to still another embodiment the distillation is performed at excess pressure.

According to a preferable embodiment the naphtha fraction 30 is fed to a hydroprocessing unit **C**. The hydroprocessing is performed preferably with NiMo-
15 and CoMo-type catalysts which remove heteroatoms such as chlorine, oxygen, sulphur and nitrogen in the naphtha fraction and simultaneously carries out hydrogenation of olefins and aromatics present therein. The hydroprocessing of naphtha is performed typically in gas phase in elevated temperature and pressure in the presence of hydrogen. Exemplary hydroprocessing reaction conditions
20 comprise temperature 280–350°C and pressure 20–100 barg preferably 20–50 barg. LHSV is typically 1–5 h⁻¹, and hydrogen/hydrocarbon ratio 100–900 Nm³/m³ such as 360 Nm³/m³. Exemplary non-limiting hydroprocessing catalysts are CoMo/Al₂O₃ and NiMo/Al₂O₃. The product is a hydrogenated naphtha fraction 60.

It is known that steam crackers have specifications for olefinic, aromatic and
25 heteroatom content of the feed. Accordingly, the hydrogenated naphtha fraction 60 is suitable as a feed of steam cracker **D**.

LWPs can be co-processed with crude oil in an oil refinery. However, as the products from crude oil distillation units are typically directed to units that are not designed for olefinic feeds, the absence of olefinic components, and in particular diolefins,
30 would be beneficial. The aforementioned limitation is particularly relevant in the context of naphtha hydroprocessing units which are designed for the processing of

straight run naphtha. Such units typically operate in gas phase, and the overall exotherm, i.e. temperature increase which occurs inside the reactor due to heat released by the chemical reactions, is limited. Adding an olefinic feed to such a reactor can result in a substantial increase in the overall exotherm, which may in turn shorten the lifetime of the hydroprocessing catalyst. Thus, removing the naphtha fraction from LWP prior to co-processing at the refinery is beneficial also from the refinery perspective. Co-processing of the heavier LWP fractions at the refinery is less problematic compared to the naphtha fraction, as hydroprocessing units which designed for middle distillates and e.g., heavy gas oil or vacuum gas oil are otherwise also used for processing thermally cracked feeds from e.g., visbreaking or delayed coking units.

According to a particular embodiment the bottom fraction 50 is admixed with crude oil 70 e.g., in a mixing unit **E** to form an admixture 80 which is then fed to a crude oil distillation unit **F** where the admixture is separated to one or more streams 90, 100.

According to another embodiment the middle fraction 40 is admixed with crude oil 70 e.g., in a mixing unit **G** to form an admixture 110 which is then fed to a crude oil distillation unit **H** where the admixture is separated to one or more streams 120, 130.

According to another embodiment the present invention concerns use of hydrogenated naphtha produced from LWP comprising diolefins as a steam cracker feed. The steam cracker feed is produced by a method comprising the following steps:

- a) providing an LWP stream comprising diolefins and naphtha,
- b) subjecting the LWP stream to hydrogenation reaction conditions to produce diolefin depleted LWP stream,
- c) distilling the diolefin depleted LWP stream to obtain at least one naphtha fraction boiling below 180 °C at atmospheric pressure and a distillation bottom, and
- d) subjecting the naphtha fraction to hydrogenation reaction conditions to produce hydrogenated naphtha.

The method of the present invention is suitable for processing different type of liquefied waste polymers and their mixtures such as waste plastic pyrolysis oils (WPPO) and hydrothermally liquefied waste plastic oils. According to one embodiment the liquefied waste polymers comprises WPPO. According to another
5 embodiment the liquefied waste polymers comprises hydrothermally liquefied waste plastic oils.

The specific examples provided in the description given above should not be construed as limiting the scope and/or the applicability of the appended claims.

What is claimed is

1. A method for processing liquefied waste polymers (LWP), the method comprising the following steps:
 - a) providing an LWP stream comprising diolefins and naphtha,
 - 5 b) subjecting the LWP stream to hydrotreatment reaction conditions in the presence of hydrogen and one or more hydrotreatment catalysts to produce diolefin depleted LWP stream and
 - c) distilling the diolefin depleted LWP stream to obtain one or more distillates comprising at least a naphtha fraction boiling below 180 °C at atmospheric
10 pressure and a distillation bottom.
2. The method according to claim 1 comprising
 - d) subjecting the naphtha fraction of step c) to hydroprocessing reaction conditions in the presence of hydrogen and one or more hydroprocessing catalysts to produce hydrogenated naphtha.
- 15 3. The method according to claim 1 or 2, wherein the hydrotreatment reaction conditions of step b) comprise temperature 120-210 °C and pressure 1-50 barg.
4. The method according to claim 3 wherein the hydrotreatment reaction conditions comprise LHSV 1-5 h⁻¹, preferably 4-4.5 h⁻¹.
5. The method according to any one of claims 1-4 wherein the one or more
20 hydrotreatment catalysts are selected from CoMo and NiMo.
6. The method according to any one of claims 2-5, wherein the hydroprocessing reaction conditions of step d) comprise temperature 280-350 °C and pressure 20-100 barg, preferably 20-50 barg,
7. The method according to claim 6 wherein the hydroprocessing reaction
25 conditions comprise LHSV 1-5 h⁻¹, and hydrogen/hydrocarbon ratio 100-900 Nm³/m³.
8. The method according to any one of claims 2-7 wherein the one or more hydroprocessing catalysts are selected from CoMo and NiMo.

9. The method according to any one of claims 2-8 comprising feeding the hydrogenated naphtha to a steam cracker.
10. The method according to any one of claims 1-9 comprising admixing the distillation bottom and crude oil to form an admixture.
- 5 11. The method according to claim 10 comprising feeding the admixture to a crude oil distillation unit.
12. The method according to any of claims 1-11 wherein the one or more distillates comprise a middle fraction boiling between 180 °C and 360 °C at atmospheric pressure.
- 10 13. The method according to claim 12 comprising feeding the middle fraction to a crude oil distillation unit.
14. The method according to any one of claims 1-13 wherein the LWP is selected from waste plastic pyrolysis oil and hydrothermally liquefied waste plastic oil or mixtures thereof.
- 15 15. The method according to any one of claims 1-14 wherein the LWP comprises waste plastic pyrolysis oil.
16. Use of the hydrogenated naphtha produced according to any one of claims 2-8 as a steam cracker feed.
17. Use of a mixture of crude oil and the distillation bottom of step c) as a crude oil
20 refinery feed.
18. Use of a mixture of crude oil and the middle fraction of claim 12 as a crude oil refinery feed.