



(11)

**EP 4 174 150 B1**

(12)

**EUROPEAN PATENT SPECIFICATION**

(45) Date of publication and mention  
of the grant of the patent:  
**25.09.2024 Bulletin 2024/39**

(51) International Patent Classification (IPC):  
**C10G 1/10** <sup>(2006.01)</sup> **C10G 1/00** <sup>(2006.01)</sup>  
**C10G 45/08** <sup>(2006.01)</sup> **C10G 65/02** <sup>(2006.01)</sup>  
**C10G 9/36** <sup>(2006.01)</sup>

(21) Application number: **21205587.5**

(52) Cooperative Patent Classification (CPC):  
**C10G 1/10; C10G 1/002; C10G 9/36; C10G 45/08;**  
**C10G 65/02; C10G 2300/202**

(22) Date of filing: **29.10.2021**

(54) **METHOD OF TREATING WASTE PLASTIC**

VERFAHREN ZUR BEHANDLUNG VON KUNSTSTOFFABFÄLLEN

PROCÉDÉ DE TRAITEMENT DE DÉCHETS DE PLASTIQUE

(84) Designated Contracting States:  
**AL AT BE BG CH CY CZ DE DK EE ES FI FR GB**  
**GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO**  
**PL PT RO RS SE SI SK SM TR**

(43) Date of publication of application:  
**03.05.2023 Bulletin 2023/18**

(73) Proprietor: **Neste Oyj**  
**02150 Espoo (FI)**

(72) Inventors:  
• **Kurkijärvi, Antti**  
**06101 Porvoo (FI)**  
• **Aho, Marjut**  
**06101 Porvoo (FI)**  
• **Kela, Jarmo**  
**06101 Porvoo (FI)**  
• **Paasikallio, Ville**  
**06101 Porvoo (FI)**

- **Sairanen, Emma**  
**06101 Porvoo (FI)**
- **Pérez Nebreda, Andrea**  
**06101 Porvoo (FI)**
- **Keyriläinen, Jukka**  
**06101 Porvoo (FI)**
- **Uotila, Perttu**  
**06101 Porvoo (FI)**
- **Kettunen, Mika**  
**06101 Porvoo (FI)**
- **Jamieson, John**  
**06101 Porvoo (FI)**

(74) Representative: **Kolster Oy Ab**  
**Salmisaarenaukio 1**  
**P.O. Box 204**  
**00181 Helsinki (FI)**

(56) References cited:  
**WO-A1-2021/105326 WO-A1-2021/204819**  
**FR-A1- 3 107 530**

Note: Within nine months of the publication of the mention of the grant of the European patent in the European Patent Bulletin, any person may give notice to the European Patent Office of opposition to that patent, in accordance with the Implementing Regulations. Notice of opposition shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

**Description****FIELD OF THE INVENTION**

**[0001]** The present invention relates to a method of treating waste plastic, especially liquified waste plastic treatment by hydrotreatment. The method includes removal of impurities and hydrogenation of the LWP. In detail, the method comprises two separate hydrotreatments of the LWP, where the second hydrotreatment is performed on a blend of hydrocarbons and already hydrotreated LWP.

**BACKGROUND OF THE INVENTION**

**[0002]** Environmental concerns and a wish to limit the use of fossil based feedstock leads to a need to develop possibilities to use waste plastic. Waste plastic is a growing environmental concern, since many of the polymers constituting the plastics are very stable and do not degrade in nature. Incineration of waste plastic increases greenhouse gases and also leads to other environmental concerns in the form of air and land pollution. Incineration of waste plastic is largely considered a waste of valuable raw material, even if the energy in form of heat is collected.

**[0003]** Plastics or polymers mainly constitute carbon, hydrogen and heteroatoms such as oxygen and/or nitrogen. However, waste plastics also contain many impurities, such as metal and chlorine impurities. There is a growing interest in making use of waste plastic for producing various hydrocarbon components. Fuels are mixtures of hydrocarbons, but production of liquid fuels from waste plastic is generally not considered useful. Direct incineration of waste plastic also produces energy, which can be captured and used for heating and/or production of electricity etc. Therefore, there is a need to upgrade waste plastic to high end hydrocarbon components, which can be utilized in the production of new plastics, chemicals or other materials.

**[0004]** Waste plastics have been treated by pyrolysis to produce liquefied waste plastic (LWP), but the LWP feed still contains large amounts of various impurities and contaminants. The LWP feed therefore needs to undergo various purification and pre-treatment steps before it can be used as feedstock for various upgrading processes.

**[0005]** Document WO2021/110395 describes a process for treating a feed comprising waste plastic pyrolysis oil, the process includes a hydrogenation step at a temperature of 100 °C to 250 °C, followed by a hydrotreatment step at a temperature of 250 °C to 430 °C. The product thus obtained is further separated into a gaseous effluent, an aqueous effluent and a hydrocarbon effluent.

**[0006]** WO2021/204819, FR3107530 and WO2021/105326 all disclose a method of processing LWP and the obtained product.

**[0007]** The current invention provides an improved process of treating and purifying LWP obtained e.g.

through pyrolysis of waste plastic.

**BRIEF DESCRIPTION OF THE INVENTION**

**[0008]** The present invention aims to provide an optimised solution for chemical recycling of waste plastics. The invention strives to make chemical recycling a viable and economical and thereby a complementary solution to recycled waste plastic streams that are not suitable for mechanical recycling. The chemical processes needed are devised in such a way that they can handle the complexities of chemical components in the waste products. Waste plastics are, on a general level, very heterogeneous materials. Depending on the polymer type and in what application it has been used, different plastic products will contain different types of additives such as pigments, fillers, flame retardants and so forth. When the waste plastic is converted into LWP via e.g. pyrolysis, the polymers and the various additives etc. will react/decompose in certain ways, and consequently a plurality of different compounds will be transferred into the product LWP. Conversion of LWP into higher quality value-added products entails the use of catalytic processes, and catalysts that are typically employed in such processes are sensitive to different impurities, i.e. the activity of the catalysts can be deactivated due to deposition of various catalyst poisons. It has been observed that LWP contains various impurities that are detrimental to catalysts, and consequently its further catalytic processing is technically more challenging e.g. when compared to conventional crude oil. This has led to the present invention, where these problems have been resolved by the process steps as claimed. Claimed process allows the processing of waste plastics to be made continuous and economical without having to worry about the damage and detrimental effects caused to the assets carrying out those processing.

**[0009]** The objects of the invention are achieved by a method characterized by what is stated in the independent claim. The preferred embodiments of the invention are disclosed in the dependent claims.

**BRIEF DESCRIPTION OF THE DRAWINGS**

**[0010]** In the following the invention will be described in greater detail by means of preferred embodiments with reference to the attached drawings, in which Figure 1 is a schematic view of a specific embodiment of the current invention. In figure 1 the dotted box= optional step; P1= Product 1; P2=Product 2; A1/A2= hydrotreatment step a); B= blending step b); C=hydrotreatment step c); CF= hydrocarbons stream.

**DETAILED DESCRIPTION OF THE INVENTION**

**[0011]** The current invention relates to a method of processing liquefied waste plastic, wherein the method comprises a first hydrotreatment of the LWP in mild con-

ditions followed by blending the hydrotreated LWP with a stream comprising hydrocarbons.

**[0012]** With the term "liquefied waste plastic" is hereby meant a liquid product produced from any waste plastic through a non-oxidative thermolysis process. Typically, liquefied waste plastic is produced by pyrolysis of waste plastic. Other processes to produce LWP include but are not limited to hydrothermal liquefaction processes. The LWP is a mixture of hydrocarbonaceous organic components with a wide range of carbon chain lengths. Provided the large variations of carbon chain lengths and chemical structures and the properties of the LWP varies depending on the types of plastics (polymers) used in the production of LWP, the type of liquefaction process and conditions of the liquefaction process. Typical waste plastic feedstock used in the liquefaction method includes mainly polyethylene with varying amounts of polypropylene, polystyrene and other minor components such as polyamides, polyethylene terephthalate and polyvinyl chloride.

**[0013]** The liquefied waste plastic can be obtained by pyrolyzing waste plastic and subsequently collecting a liquid fraction from the pyrolyzed waste plastic. In a typical pyrolysis process, the solid waste plastic is heated to a temperature of 400-600 °C under non-oxidative conditions. The polymers thermally decompose and consequently release vapours and gases that exit the reactor in the gas phase. This vapor/gas stream is subsequently cooled down to condense the LWP product and to separate the gases. The LWP typically has a boiling range of about 40 °C - 550 °C, which corresponds approximately to carbon chain lengths of C5 to C55. Depending on the conversion technology, the final boiling point of the LWP can go up to 750 °C.

**[0014]** LWP is a thermal cracking product of various polymers and is a complex mixture of mainly paraffins, olefins, naphthenes and aromatic hydrocarbons. The total amount of olefins is typically high, from 40 wt.% to 60 wt.%, whereas the amount of aromatic hydrocarbons is typically lower than 20 wt.%. LWP also contains heteroatoms, including oxygen, nitrogen, chlorine and sulphur, in the form of organic compounds with heteroatom substituents. The amounts of heteroatoms vary depending on the polymers used in production of LWP. Water is usually removed from the LWP product, but some dissolved water may still be present in the LWP.

**[0015]** The liquefied waste plastic can also undergo pre-treatment processes before the hydrotreatments according to the present invention. The LWP undergoes a pre-treatment step before hydrotreatment step a) and the pre-treatment step comprises reactive extraction, solvent extraction, adsorption, filtration, centrifugation, oxidation, reduction or any combination thereof.

**[0016]** All of the hydrotreatments stated herein are performed in the presence of at least one catalyst. The catalyst may, for example, comprise at least one component selected from IUPAC group 6, 8 or 10 of the Periodic Table of Elements. When employing a supported catalyst, the catalyst preferably contains Mo and at least one

further transition metal on a support. Examples of such a supported catalyst are a supported NiMo catalyst or a supported CoMo catalyst, or a mixture of both. In a supported catalyst, the support preferably comprises alumina and/or silica. These catalysts are usually employed as sulphided catalysts to ensure that the catalysts are in their active (sulphided) form. Turning the catalysts into their active (sulphided) form may be achieved by sulphiding them in advance (i.e. before starting the hydrotreatment reaction) and/or by adding a sulphur-containing feed (containing sulphur e.g. as an organic or inorganic sulphide). The feed may contain the sulphur from the start, or a sulphur additive may be admixed to the feed. In a preferable embodiment, the hydrotreating employs a catalyst and the catalyst is a supported NiMo catalyst and the support comprises alumina (NiMo/Al<sub>2</sub>O<sub>3</sub>) and/or the catalyst is a supported CoMo catalyst and the support comprises alumina (CoMo/Al<sub>2</sub>O<sub>3</sub>).

**[0017]** The catalyst of the hydrotreatment step a) is preferably supported NiMo, wherein the support preferably comprises alumina and/or silica.

**[0018]** In one embodiment of the current invention the hydrotreatment step a) is repeated before the subsequent blending step. The hydrotreatment step a) can be repeated to ensure sufficient hydrotreatment of LWP in the stream. The possible need for repeating the hydrotreatment step a) depends on among others, on the hydrotreatment conditions, the hydrotreatment catalyst and reactor design, such as number of reactors, type of catalyst beds and number of catalyst beds in the reactors and so forth.

**[0019]** In one embodiment of the current invention the stream of LWP consists only of LWP and the hydrotreatment in step a) is performed only on LWP. In this specific embodiment, the hydrotreatment a) in mild hydrotreatment conditions is performed solely on a stream containing only LWP and no other streams are directed to the first hydrotreatment step (step a) in claims). The hydrotreatment step a) in this embodiment is a step where only components of the stream of LWP originating from waste plastic are hydrotreated in the mild hydrotreatment conditions.

**[0020]** In one embodiment of the current invention the hydrotreatment step a) includes a step where a part of the formed stream of hydrotreated LWP from the hydrotreatment step a) is recycled back to the reactor carrying out the hydrotreatment step a). The amount of recycling, if present, depends among others on the hydrotreatment conditions, the hydrotreatment catalyst and reactor design, such as number of reactors, type of catalyst bed and number of catalyst beds in the reactors.

**[0021]** As a result of the hydrotreatment step a), a stream of first hydrotreated LWP is formed. The formed hydrotreated LWP stream contains lower amounts of impurities, contaminants and harmful components compared to the before hydrotreated LWP feed. With impurities, contaminants and harmful components is herein meant any substance, compound or composition which

have detrimental properties to any component, equipment or catalyst downstream of the hydrotreatment. Especially harmful components are compounds containing hetero atoms, metals and metalloids. Especially harmful hetero atoms include halogens such as chlorine. Especially harmful metals include but are not limited to mercury, lead, sodium, arsenic, vanadium, iron, zinc and aluminium. Compounds containing silicon, phosphorous, oxygen, nitrogen and sulphur can also be problematic downstream from the hydrotreatment, if not removed. Furthermore, the conjugated diolefins and olefins are considered agents causing coking or fouling which have to be minimised from the LWP in order for the treated LWP to be used downstream as a feedstock for steam cracking for example.

**[0022]** The purpose of hydrotreating a stream of liquified waste plastic (LWP) according to the invention is to reduce the risk of harmful and/or detrimental properties of any of the impurities, contaminants and harmful components, which might be present in the LWP. The hydrotreating step reduces the amount of these components and therefore reduces the risks and harms they would otherwise pose on any component, equipment or catalyst downstream of the hydrotreatment. After the hydrotreatment step a) in mild hydrotreatment conditions as specified, the conjugated diolefin content in the LWP is reduced to below 0.2 wt. %.

**[0023]** The method of the current invention further comprises blending the stream of hydrotreated LWP obtained from mild hydrotreatment step a), with a stream comprising hydrocarbons to form a mixed stream comprising hydrotreated LWP and hydrocarbons. The stream comprising hydrocarbons would have a different impurities profile than the LWP feed being subjected to the hydrotreatment step a), since said hydrocarbons is of any origins other than LWP thus "hydrocarbons" and "hydrocarbons of other origins" are to mean synonymously.

**[0024]** In one embodiment of the current invention hydrocarbons of other origins in the form of stream is selected from vacuum gas oil (VGO) fraction, gas oil (GO) fraction, heavy gas oil (HGO) fraction, kerosene fraction, light gas oil fraction, atmospheric residue (AR) fraction, vacuum residue (VR) fraction and deasphalted oil (DAO) fraction. The other suitable hydrocarbon streams to be used for blending include a crude oil-derived feedstock comprising at least one crude oil-fraction, or a bio-based fats or oils or fatty acids, or lignocellulosic based hydrocarbons, or Fischer Tropsch or other synthetic hydrocarbons.

**[0025]** In one embodiment the stream comprising hydrocarbons have one or more of the following properties:

- a boiling point range from 60 °C - 700 °C, most preferably from 100 °C - 600 °C, boiling point can be measured according to ASTM D2887, or EN15199-2 depending on the boiling point range;
- a molecular weight of 250 - 400 g/mol, most preferably 280 - 350 g/mol, as measured according to

ASTM D2887;

- aromatics content >10 wt.%, most preferably >35 wt.%, as measured according to ASTM D2549;
- density from 870-940 kg/m<sup>3</sup>, most preferably 890-920 kg/m<sup>3</sup>, as measured according to EN ISO 12185;
- a sulphur content of <5 wt.%, preferably <1.8 wt.%;
- bromine number <10 g Br/100g, preferably <4 g Br/100g according to ISO 3839M;
- asphaltene content of <300 mg/kg, preferably 250 mg/kg according to TOTAL 642; and
- a silicon content of <2.5 mg/kg, preferably <1 mg/kg according to ASTM D5185.

**[0026]** Keeping the mixed stream at an elevated temperature to ensure sufficient mixing of the two streams. Mixing at an elevated temperature also ensures no or minimal precipitation of impurities. The stream of hydrocarbons to be blended with the hydrotreated LWP will typically have a higher temperature compared to the stream of hydrotreated LWP.

**[0027]** According to one embodiment of the invention the mixed stream of hydrotreated LWP and hydrocarbons contains up to 70 wt.% LWP based on total weight of stream, preferably the content of LWP in said stream is from 5 wt.% to 70 wt.%, more preferably from 10 wt.% to 50 wt.% and even more preferably from 15 wt.% to 30 wt.%.

**[0028]** According to the current invention the method further comprises

c) hydrotreating said mixed stream of hydrotreated LWP and hydrocarbons in the presence of hydrogen and a catalyst in severe hydrotreatment conditions to provide a refined stream.

**[0029]** The hydrotreatment step c) is defined by its severe conditions which is carried out at a temperature of 355 °C to 400 °C, preferably 360 °C to 390 °C. In addition, hydrotreatment step c) is referred to as the hydrotreatment step subsequent to hydrotreatment step a) after the hydrotreated stream of step a) has been blended with a stream of hydrocarbons of other origins.

**[0030]** In one embodiment of the present invention, the catalyst of the hydrotreatment step a) and c) is a supported catalyst, and the catalyst preferably comprises at least one component selected from IUPAC group 6, 8 or 10 of the Periodic Table of Elements. Furthermore, the supported catalyst can contain Mo and at least one further transition metal on a support, such as a supported NiMo catalyst or a supported CoMo catalyst, wherein the support preferably comprises alumina and/or silica. In particular, the catalyst is a supported CoMo catalyst and the support comprises alumina (CoMo/Al<sub>2</sub>O<sub>3</sub>) and/or the catalyst is a supported NiMo catalyst and the support comprises alumina (NiMo/Al<sub>2</sub>O<sub>3</sub>).

**[0031]** The conditions of the hydrotreatment step c) are preferably selected from the following:

- a H<sub>2</sub> to oil ratio is 150 - 400 Nm<sup>3</sup>/stdm<sup>3</sup>, preferably

180 - 250 Nm<sup>3</sup>/stdm<sup>3</sup>;

- a LHSV of 0.5 - 2.0 h<sup>-1</sup>, preferably 1.1 - 1.5 h<sup>-1</sup>;
- a temperature of 355-400 °C, preferably 360-390 °C
- a pressure of 4000-6000 kPa(a), preferably 4800-5500 kPa(a).

**[0032]** In one embodiment, hydrotreatment steps a) and c) can be carried out respectively in a single reactor unit comprising at least one catalyst bed. In another embodiment, hydrotreatment step a) and c), can be carried out respectively in a reactor system comprising at least two reactor units, wherein each reactor unit contains at least one catalyst bed.

**[0033]** In one embodiment of the present invention, hydrogen is being mixed with the LWP before carrying out hydrotreatment step a) and/or step c).

**[0034]** In one embodiment of the invention, the LWP undergoes a pre-treatment step before hydrotreatment step a) and the pre-treatment step comprises reactive extraction, solvent extraction, adsorption, filtration, centrifugation, oxidation, reduction or any combination thereof.

**[0035]** In one embodiment the method further comprises a step of adding water to said process and/or removal of an aqueous phase from said process after said hydrotreatment step a) and/or after said hydrotreatment c). In one embodiment of the current invention, water is added to the process after any of the hydrotreatment steps in order to remove impurities. The impurities are or become water soluble in the hydrotreatment and can thus be removed by washing the hydrotreated LWP stream with water. The water soluble impurities are dissolved in the water stream and the aqueous phase containing the impurities is then decanted from the hydrotreated LWP stream.

**[0036]** In one embodiment of the invention, the method further comprises a step of subjecting the refined stream after the hydrotreatment step c), to one or more fractionation step(s) to form two or more product streams. Preferably the fractionated product streams include a naphtha fraction having a 5-95 wt.% boiling point range of 30-200 °C, preferably from about 30 °C to about 180 °C, more preferably from about 30 °C to about 110 °C, and a middle distillate fraction having a 5-95 wt.% having a boiling point from about 150 °C to about 400 °C, preferably from about 160 °C to about 360 °C, and more preferably from about 160 °C to about 330 °C, and a liquefied petroleum gas (LPG) fraction comprising one or more of ethane, propane or butane. The naphtha fraction can further be subjected to steam cracking, and/or the middle distillate can further be subjected to steam cracking, and/or the LPG fraction can further be subjected to steam cracking.

**[0037]** In one further embodiment of the current invention, hydrotreatment step a) and hydrotreatment step c) are carried out in a reactor system comprising one or more reactors, each reactor having one or more catalyst beds and at least one reactor with a direct hydrogen feed

to the reactor. The reactor designated for the hydrotreatment step a) and c) can also be carried out respectively in separate reactors, each having a plurality of independent catalyst beds and independent reaction temperatures, or any combination thereof.

**[0038]** In one embodiment of the present invention, it further relates to a LWP product, P1, obtainable by hydrotreating LWP according to hydrotreatment step a) and blending according to step b) and wherein the product comprises

- a reduced amount of silicon to be below 6 mg/kg, more preferably < 1 mg / kg, and/or phosphorous to be below 5 mg/kg, more preferably 1 mg/kg, as measured by ICP-MS/MS,
- a low ratio of diolefin to total olefin content to be below 0.01, more preferably below 0.001, measured by ASTM D8071
- a low ratio of conjugated diolefin to non-conjugated diolefin to be below 2, more preferably below 1, measured by ASTM D8071
- a halogen content to be under 5 mg/kg, preferably 1 mg/kg

**[0039]** Metals measurement by ICP-MS/MS is performed on a sample that is warmed to liquid if needed prior to weighing. It is digested with acids in the microwave oven to a clear water/acid matrix, diluted to a known amount and analysed against the acid based calibration using ICP-MS/MS. Low elemental results are determined as ppb (µg/kg).

**[0040]** In one embodiment of the invention, the method further comprises a step of subjecting the refined stream after the hydrotreatment step a), and blending step b), i.e., product P1, to one or more fractionation step(s) to form two or more product streams. Preferably the fractionated product streams include a naphtha fraction having a 5-95 wt.% boiling point range of 30-200 °C, preferably from about 30 °C to about 180 °C, more preferably from about 30 °C to about 110 °C, and a middle distillate fraction having a 5-95 wt.% having a boiling point from about 150 °C to about 400 °C, preferably from about 160 °C to about 360 °C, and more preferably from about 160 °C to about 330 °C, and a liquefied petroleum gas (LPG) fraction comprising one or more of ethane, propane or butane. The naphtha fraction can further be subjected to steam cracking, and/or the middle distillate can further be subjected to steam cracking, and/or the LPG fraction can further be subjected to steam cracking.

**[0041]** It will be obvious to a person skilled in the art that, as the technology advances, the inventive concept can be implemented in various ways. The invention and its embodiments are not limited to the examples described above but may vary within the scope of the claims.

## Claims

1. A method of processing liquefied waste plastic (LWP), wherein the method comprises:

step a) hydrotreating a stream of liquified waste plastic (LWP) in presence of hydrogen and a catalyst in a first hydrotreatment step in mild hydrotreatment conditions in a temperature from 170 °C to 350 °C, to form a stream of hydrotreated LWP, in a reactor system comprising at least one reactor each containing at least one catalyst bed,

step b) blending said stream of hydrotreated LWP with a stream comprising hydrocarbons to form a mixed stream of hydrotreated LWP and hydrocarbons, wherein said mixed stream comprising hydrotreated LWP and hydrocarbons is kept at a temperature of 140 °C to 350 °C before subjecting it to hydrotreatment step c), and

step c) hydrotreating said mixed stream of hydrotreated LWP and hydrocarbons in presence of hydrogen and a catalyst in severe hydrotreatment conditions in a temperature of from 355 °C to 400 °C to provide a refined stream.

2. The method according to claim 1, wherein the stream of LWP undergoes a pre-treatment step before hydrotreatment step a) and the pre-treatment step comprises reactive extraction, solvent extraction, adsorption, filtration, centrifugation, oxidation, reduction or any combination thereof.

3. The method according to any of the previous claims, wherein said stream comprising hydrocarbons is a crude oil-derived feedstock comprising at least one crude oil-fraction or a bio-based fats or oils or fatty acids, or lignocellulosic based hydrocarbons, or Fischer Tropsch hydrocarbons, wherein the crude oil fraction is selected from vacuum gas oil (VGO) fraction, gas oil (GO) fraction, heavy gas oil (HGO) fraction, kerosene fraction, light gas oil fraction, atmospheric residue (AR) fraction, vacuum residue (VR) fraction and deasphalted oil (DAO) fraction.

4. The method according to any of the previous claims, wherein said mixed stream of hydrotreated LWP and hydrocarbons contains up to 70 wt.% LWP based on total weight of stream, preferably the content of LWP in said stream is from 5 wt.% to 70 wt.%, more preferably from 10 wt.% to 50 wt.% and even more preferably from 15 wt.% to 30 wt.%.

5. The method according to any of the previous claims, wherein the catalyst in said hydrotreatment step a) is a supported catalyst, and the catalyst preferably comprises at least one component selected from IUPAC group 6, 8 or 10 of the Periodic Table of El-

ements.

6. The method according to claim 5, wherein the supported catalyst contains Mo and at least one further transition metal on a support, such as a supported NiMo catalyst or a supported CoMo catalyst, wherein the support preferably comprises alumina and/or silica.

7. The method according to claim 6, wherein the catalyst is a supported CoMo catalyst and the support comprises alumina ( $\text{CoMo/Al}_2\text{O}_3$ ) and/or the catalyst is a supported NiMo catalyst and the support comprises alumina ( $\text{NiMo/Al}_2\text{O}_3$ ).

8. The method according to any of the previous claims, wherein the method further includes a step of adding water to said process and/or removal of an aqueous phase from said process after said hydrotreatment step a) and/or after said hydrotreatment step c).

9. The method according to any of the previous claims, wherein said hydrotreatment step a) is repeated before the step of blending said stream of hydrotreated LWP with a stream comprising hydrocarbons to form a mixed stream of hydrotreated LWP and hydrocarbons.

10. The method according to any of the previous claims, wherein the stream of LWP consists only of LWP and the hydrotreatment step a) is performed only on LWP.

11. The method according to any of the previous claims, wherein said hydrotreatment step a) is performed in the following conditions

- a  $\text{H}_2$  to oil ratio is 200 - 450  $\text{Nm}^3/\text{stdm}^3$ , preferably 220 - 400  $\text{Nm}^3/\text{stdm}^3$ ;
- a LHSV of 0.1 - 2.0  $\text{h}^{-1}$ , preferably 0.2 - 0.5  $\text{h}^{-1}$ ;
- a temperature of 170-340 °C.

12. The method according to any of claims 1 - 11, wherein said hydrotreatment step c) is performed in the following conditions

- a  $\text{H}_2$  to oil ratio is 150 - 400  $\text{Nm}^3/\text{stdm}^3$ , preferably 180 - 250  $\text{Nm}^3/\text{stdm}^3$ ;
- a LHSV of 0.5 - 2.0  $\text{h}^{-1}$ , preferably 1.0 - 1.5  $\text{h}^{-1}$ ;
- a temperature of 355-400 °C, preferably 360-390 °C.

13. The method according to any of claims 1 - 12, wherein the method further comprises a step of subjecting said refined stream to one or more fractionation step(s) to form two or more product streams, preferably the product streams include a naphtha fraction having a 5-95 wt.% boiling point range of 30-200 °C,

preferably from about 30 °C to about 180 °C, more preferably from about 30 °C to about 110 °C, and a middle distillate fraction having a 5-95 wt.% having a boiling point from about 150 °C to about 400 °C, preferably from about 160 °C to about 360 °C, and more preferably from about 160 °C to about 330 °C.

14. The method according to claim 13, wherein the naphtha fraction is further subjected to steam cracking, and/or the middle distillate is further subjected to steam cracking and/or LPG fraction is further subjected to steam cracking.
15. The method according to any of claims 1 - 14, wherein hydrotreatment steps a) and c) is carried out respectively in a single reactor unit comprising at least one catalyst bed, or hydrotreatment step a) and c), are carried out respectively in a reactor system comprising at least two reactor units, wherein each reactor unit contains at least one catalyst bed, or any combination thereof.
16. The method according to any one of the preceding claims, wherein the at least one reactor has a direct hydrogen quench to the reactor.
17. The method according to any one of claims 1 - 16, wherein hydrogen is being mixed with the stream of LWP before carrying out hydrotreatment step a) and step c).
18. A purified hydrocarbon product, obtainable by hydrotreating LWP according to hydrotreatment step a) and blending according to step b) according to claim 1 and wherein the product comprises
  - a reduced amount of silicon to be below 6 mg/kg, more preferably < 1 mg/kg, and/or phosphorous to be below 5 mg/kg, more preferably 1 mg/kg, as measured by ICP-MS/MS,
  - a low ratio of diolefin to total olefin content to be below 0.01, more preferably below 0.001, measured by ASTM D8071
  - a low ratio of conjugated diolefin to non-conjugated diolefin to be below 2, more preferably below 1, measured by ASTM D8071
  - a halogen content to be under 5 mg/kg, preferably 1 mg/kg.

#### Patentansprüche

1. Verfahren zur Verarbeitung von verflüssigten Kunststoffabfällen (Liquefied Waste Plastic - LWP), wobei das Verfahren umfasst:

Schritt a) Wasserstoffbehandlung (Hydrotreating) eines Stroms von verflüssigten Kunststoff-

abfällen (LWP) bei Vorhandensein von Wasserstoff und eines Katalysators in einem ersten Wasserstoffbehandlungsschritt unter milden Wasserstoffbehandlungsbedingungen bei einer Temperatur von 170 °C bis 350 °C, um einen Strom von wasserstoffbehandelten LWP zu bilden, in einem Reaktorsystem, das mindestens einen Reaktor umfasst, der jeweils mindestens ein Katalysatorbett umfasst,  
 Schritt b) Mischen des Stroms von wasserstoffbehandelten LWP mit einem Strom, der Kohlenwasserstoffe umfasst, um einen gemischten Strom von wasserstoffbehandelten LWP und Kohlenwasserstoffen zu bilden, wobei der gemischte Strom, der wasserstoffbehandelte LWP und Kohlenwasserstoffe umfasst, auf einer Temperatur von 140 °C bis 350 °C gehalten wird, bevor er dem Wasserstoffbehandlungsschritt c) unterzogen wird, und  
 Schritt c) Wasserstoffbehandeln des gemischten Stroms von wasserstoffbehandelten LWP und Kohlenwasserstoffen bei Vorhandensein von Wasserstoff und eines Katalysators unter rauen Wasserstoffbehandlungsbedingungen bei einer Temperatur von 355 °C bis 400 °C, um einen raffinierten Strom bereitzustellen.

2. Verfahren nach Anspruch 1, wobei der Strom von LWP vor dem Wasserstoffbehandlungsschritt a) einem Vorbehandlungsschritt unterzogen wird und der Vorbehandlungsschritt Reaktivextraktion, Solventextraktion, Adsorption, Filtration, Zentrifugieren, Oxidation, Reduktion oder eine beliebige Kombination davon umfasst.
3. Verfahren nach einem der vorhergehenden Ansprüche, wobei der Strom, der Kohlenwasserstoffe umfasst, ein aus Rohöl gewonnener Einsatzstoff ist, der mindestens eine Rohölfraction oder biobasierte Fette oder Öle oder Fettsäuren oder Kohlenwasserstoffe auf Lignocellulosebasis oder Fischer-Tropsch-Kohlenwasserstoffe umfasst, wobei die Rohölfraction ausgewählt wird aus Vakuumgasöl(VGO)-Fraktion, Gasöl(GO)-Fraktion, schwerer Gasöl(HGO)-Fraktion, Kerosinfraktion, leichter Gasölfraktion, atmosphärischer Rückstand(AR)-Fraktion, Vakuumrückstand(VR)-Fraktion und entasphaltierter Öl(DAO)-Fraktion.
4. Verfahren nach einem der vorhergehenden Ansprüche, wobei der gemischte Strom von wasserstoffbehandelten LWP und Kohlenwasserstoffen bis zu 70 Gew.-% LWP, bezogen auf das Gesamtgewicht des Stroms, umfasst, wobei der Gehalt an LWP in dem Strom vorzugsweise zwischen 5 Gew.-% und 70 Gew.-%, mehr zu bevorzugen zwischen 10 Gew.-% und 50 Gew.-% und sogar noch mehr zu bevorzugen zwischen 15 Gew.-% und 30 Gew.-%, beträgt.

5. Verfahren nach einem der vorhergehenden Ansprüche, wobei der Katalysator in dem Wasserstoffbehandlungsschritt a) ein Trägerkatalysator ist und der Katalysator vorzugsweise mindestens eine Komponente umfasst, die ausgewählt ist aus der IUPAC-Gruppe 6, 8 oder 10 des Periodensystems der Elemente. 5
6. Verfahren nach Anspruch 5, wobei der Trägerkatalysator Mo und mindestens ein weiteres Übergangsmetall auf einem Träger umfasst, wie beispielsweise einen NiMo-Trägerkatalysator oder einen CoMo-Trägerkatalysator, wobei der Träger vorzugsweise Aluminiumoxid und/oder Siliziumdioxid umfasst. 10
7. Verfahren nach Anspruch 6, wobei der Katalysator ein CoMo-Trägerkatalysator ist und der Träger Aluminiumoxid ( $\text{CoMo/Al}_2\text{O}_3$ ) umfasst und/oder der Katalysator ein NiMo-Trägerkatalysator ist und der Träger Aluminiumoxid ( $\text{NiMo/Al}_2\text{O}_3$ ) umfasst. 15
8. Verfahren nach einem der vorhergehenden Ansprüche, wobei das Verfahren ferner nach dem Wasserstoffbehandlungsschritt a) und/oder nach dem Wasserstoffbehandlungsschritt c) einen Schritt des Beimengens von Wasser zu dem Prozess und/oder des Beseitigens einer wässrigen Phase von dem Prozess umfasst. 20
9. Verfahren nach einem der vorhergehenden Ansprüche, wobei der Wasserstoffbehandlungsschritt a) vor dem Schritt des Mischens des Stroms von wasserstoffbehandelten LWP mit einem Strom, der Kohlenwasserstoffe umfasst, wiederholt wird, um einen gemischten Strom von wasserstoffbehandelten LWP und Kohlenwasserstoffen zu erhalten. 25
10. Verfahren nach einem der vorhergehenden Ansprüche, wobei der Strom von LWP lediglich aus LWP besteht und der Wasserstoffbehandlungsschritt a) lediglich auf LWP durchgeführt wird. 30
11. Verfahren nach einem der vorhergehenden Ansprüche, wobei der Wasserstoffbehandlungsschritt a) unter den folgenden Bedingungen durchgeführt wird 35
- ein Verhältnis von  $\text{H}_2$  zu Öl beträgt 200 bis 450  $\text{Nm}^3/\text{stdm}^3$ , vorzugsweise 220 bis 400  $\text{Nm}^3/\text{stdm}^3$ ;
  - einer LHSV von 0,1 bis 2,0  $\text{h}^{-1}$ , vorzugsweise 0,2 bis 0,5  $\text{h}^{-1}$ ;
  - einer Temperatur von 170 bis 340 °C.
12. Verfahren nach einem der Ansprüche 1 bis 11, wobei der Wasserstoffbehandlungsschritt c) unter den folgenden Bedingungen durchgeführt wird 40
- ein Verhältnis von  $\text{H}_2$  zu Öl beträgt 150 bis 400  $\text{Nm}^3/\text{stdm}^3$ , vorzugsweise 180 bis 250  $\text{Nm}^3/\text{stdm}^3$ ;
  - einer LHSV von 0,5 bis 2,0  $\text{h}^{-1}$ , vorzugsweise 1,0 bis 1,5  $\text{h}^{-1}$ ;
  - einer Temperatur von 355 bis 400 °C, vorzugsweise 360 bis 390 °C.
13. Verfahren nach einem der Ansprüche 1 bis 12, wobei das Verfahren ferner einen Schritt des Aussetzens des raffinierten Stroms gegenüber einem oder mehreren Fraktionierungsschritt/en umfasst, um zwei oder mehr Produktströme zu bilden, wobei die Produktströme vorzugsweise eine Naphtha-Fraktion, die einen 5 bis 95 Gew.-% Siedepunktbereich von 30 bis 200 °C, vorzugsweise von etwa 30 °C bis etwa 180 °C, mehr zu bevorzugen von etwa 30 °C bis etwa 110 °C, aufweist, und eine Mitteldestillatfraktion, die einen 5 bis 95 Gew.-% Siedepunkt von etwa 150 °C bis etwa 400 °C, vorzugsweise von etwa 160 °C bis etwa 360 °C, und mehr zu bevorzugen von etwa 160 °C bis etwa 330 °C, aufweist, umfassen. 45
14. Verfahren nach Anspruch 13, wobei die Naphtha-Fraktion ferner Steamcracking unterzogen wird und/oder das Mitteldestillat ferner Steamcracking unterzogen wird und/oder die LPG-Fraktion ferner Steamcracking unterzogen wird. 50
15. Verfahren nach einem der Ansprüche 1 bis 14, wobei die Wasserstoffbehandlungsschritte a) und c) jeweils in einer Einzelreaktoreinheit durchgeführt werden, die mindestens ein Katalysatorbett umfasst, oder die Wasserstoffbehandlungsschritte a) und c) jeweils in einem Reaktorsystem, das mindestens zwei Reaktoreinheiten umfasst, wobei jede Reaktoreinheit mindestens ein Katalysatorbett umfasst, oder einer beliebigen Kombination davon durchgeführt werden. 55
16. Verfahren nach einem der vorhergehenden Ansprüche, wobei der mindestens eine Reaktor eine direkte Wasserstoffabschreckung zum Reaktor aufweist.
17. Verfahren nach einem der Ansprüche 1 bis 16, wobei vor dem Durchführen des Wasserstoffbehandlungsschritts a) und Schritts c) Wasserstoff mit dem Strom von LWP gemischt wird.
18. Gereinigtes Kohlenwasserstoffprodukt, das durch Wasserstoffbehandeln von LWP gemäß dem Wasserstoffbehandlungsschritt a) und Mischen gemäß dem Schritt b) nach Anspruch 1 erhältlich ist, wobei das Produkt umfasst
- eine verringerte Menge an Silizium, um, gemessen durch ICP-MS/MS, unter 6 mg/kg, mehr zu bevorzugen < 1 mg/kg, zu betragen, und/oder Phosphor, um unter 5 mg/kg, vorzugsweise 1



mg/kg, zu betragen,

- ein niedriges Verhältnis von Diolefin zum Gesamtolfingehalt, um, gemessen durch ASTM D8071, unter 0,01, mehr zu bevorzugen unter 0,001, zu betragen,

- ein niedriges Verhältnis von konjugiertem Diolefin zu nicht konjugiertem Diolefin, um, gemessen durch ASTM D8071, unter 2, mehr zu bevorzugen unter 1, zu betragen

- einen Halogengehalt von unter 5 mg/kg, vorzugsweise 1 mg/kg.

## Revendications

1. Procédé de traitement de déchets plastiques liquéfiés (LWP), lequel procédé comprend :

une étape a) d'hydrotraitement d'un courant de déchets plastiques liquéfiés (LWP) en présence d'hydrogène et d'un catalyseur dans une première étape d'hydrotraitement dans des conditions d'hydrotraitement douces à une température de 170°C à 350°C, pour former un courant de LWP hydrotraités, dans un système de réacteurs comprenant au moins un réacteur contenant chacun au moins un lit de catalyseur, une étape b) de mélange dudit courant de LWP hydrotraités avec un courant comprenant des hydrocarbures pour former un courant mixte de LWP hydrotraités et d'hydrocarbures, dans laquelle ledit courant mixte comprenant des LWP hydrotraités et des hydrocarbures est maintenu à une température de 140°C à 350°C avant d'être soumis à l'étape c) d'hydrotraitement, et une étape c) d'hydrotraitement dudit courant mixte de LWP hydrotraités et d'hydrocarbures en présence d'hydrogène et d'un catalyseur dans des conditions d'hydrotraitement dures à une température de 355°C à 400°C pour former un courant raffiné.

2. Procédé selon la revendication 1, dans lequel le courant de LWP subit une étape de prétraitement avant l'étape a) d'hydrotraitement, et l'étape de prétraitement comprend une extraction réactive, une extraction au solvant, une adsorption, une filtration, une centrifugation, une oxydation, une réduction ou l'une quelconque de leurs combinaisons.

3. Procédé selon l'une quelconque des revendications précédentes, dans lequel ledit courant comprenant des hydrocarbures est une charge dérivée de pétrole brut comprenant au moins une fraction de pétrole brut ou des acides gras ou huiles ou graisses d'origine biologique, ou des hydrocarbures d'origine lignocellulosique, ou des hydrocarbures issus d'une réaction de Fischer Tropsch, dans lequel la fraction

de pétrole brut est choisie parmi une fraction de gazole sous vide (VGO), une fraction de gazole (GO), une fraction de gazole lourd (HGO), une fraction de kérosène, une fraction de gazole léger, une fraction de résidus atmosphériques (AR), une fraction de résidus sous vide (VR), et une fraction de pétrole désasphalté (DAO).

4. Procédé selon l'une quelconque des revendications précédentes, dans lequel ledit courant mixte de LWP hydrotraités et d'hydrocarbures contient jusqu'à 70 % en poids de LWP par rapport au poids total du courant, de préférence la teneur en LWP dans ledit courant est de 5 % en poids à 70 % en poids, mieux encore de 10 % en poids à 50 % en poids et plus particulièrement de 15 % en poids à 30 % en poids.

5. Procédé selon l'une quelconque des revendications précédentes, dans lequel le catalyseur dans ladite étape a) d'hydrotraitement est un catalyseur supporté, et le catalyseur comprend de préférence au moins un composant choisi parmi les Groupes 6, 8 et 10 du Tableau Périodique des Éléments IUPAC.

6. Procédé selon la revendication 5, dans lequel le catalyseur supporté contient du Mo et au moins un autre métal de transition sur un support, tel qu'un catalyseur au NiMo supporté ou un catalyseur au CoMo supporté, dans lequel le support comprend de préférence de l'alumine et/ou de la silice.

7. Procédé selon la revendication 6, dans lequel le catalyseur est un catalyseur au CoMo supporté et le support comprend de l'alumine ( $\text{CoMo}/\text{Al}_2\text{O}_3$ ) et/ou le catalyseur est un catalyseur au NiMo supporté et le support comprend de l'alumine ( $\text{NiMo}/\text{Al}_2\text{O}_3$ ).

8. Procédé selon l'une quelconque des revendications précédentes, lequel procédé comprend en outre une étape d'addition d'eau audit procédé et/ou d'élimination de la phase aqueuse hors dudit procédé après ladite étape a) d'hydrotraitement et/ou après ladite étape c) d'hydrotraitement.

9. Procédé selon l'une quelconque des revendications précédentes, dans lequel ladite étape a) d'hydrotraitement est répétée avant l'étape de mélange dudit courant de LWP hydrotraités avec un courant comprenant des hydrocarbures pour former un mélange mixte de LWP hydrotraités et d'hydrocarbures.

10. Procédé selon l'une quelconque des revendications précédentes, dans lequel le courant de LWP consiste uniquement en LWP et l'étape a) d'hydrotraitement est effectuée uniquement sur des LWP.

11. Procédé selon l'une quelconque des revendications précédentes, dans lequel ladite étape a) d'hydrotraitement

tement est effectuée dans les conditions suivantes :

- un rapport du  $H_2$  au pétrole de 200 à 450  $Nm^3/normo-m^3$ , de préférence de 220 à 400  $Nm^3/normo-m^3$  ;
- une VHSL de 0,1 à 2,0  $h^{-1}$ , de préférence de 0,2 à 0,5  $h^{-1}$  ;
- une température de 170 à 340°C.

12. Procédé selon l'une quelconque des revendications 1 à 11, dans lequel ladite étape c) d'hydrotraitement est effectuée dans les conditions suivantes :

- un rapport du  $H_2$  au pétrole de 150 à 400  $Nm^3/normo-m^3$ , de préférence de 180 à 250  $Nm^3/normo-m^3$  ;
- une VHSL de 0,5 à 2,0  $h^{-1}$ , de préférence de 1,0 à 1,5  $h^{-1}$  ;
- une température de 355 à 400°C, de préférence de 360 à 390°C.

13. Procédé selon l'une quelconque des revendications 1 à 12, lequel procédé comprend en outre une étape de soumission dudit courant raffiné à une ou plusieurs étapes de fractionnement pour former deux ou plus de deux courants de produits, de préférence lesquels courants de produits comprennent une fraction de naphta dont 5 à 95 % en poids ont une plage de points d'ébullition de 30 à 200°C, de préférence d'environ 30°C à environ 180°C, mieux encore d'environ 30°C à environ 110°C, et une fraction de distillat moyen dont 5 à 95 % en poids ont une plage de points d'ébullition d'environ 150°C à environ 400°C, de préférence d'environ 160°C à environ 360°C, et mieux encore d'environ 160°C à environ 330°C.

14. Procédé selon la revendication 13, dans lequel la fraction de naphta est en outre soumise à un vapocraquage, et/ou le distillat moyen est en outre soumis à un vapocraquage et/ou une fraction de GPL est en outre soumise à un vapocraquage.

15. Procédé selon l'une quelconque des revendications 1 à 14, dans lequel les étapes a) et c) d'hydrotraitement sont effectuées respectivement dans une seule unité de réacteur comprenant au moins un lit de catalyseur, ou les étapes a) et c) d'hydrotraitement sont effectuées respectivement dans un système de réacteurs comprenant au moins deux unités de réacteurs, dans lequel chaque unité de réacteur contient au moins un lit de catalyseur, ou l'une quelconque de leurs combinaisons.

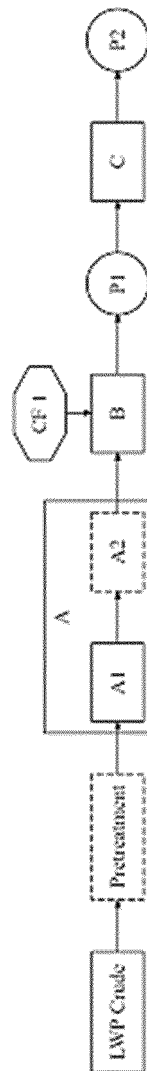
16. Procédé selon l'une quelconque des revendications précédentes, dans lequel l'au moins un réacteur a un refroidissement à l'hydrogène direct vers le réacteur.

17. Procédé selon l'une quelconque des revendications 1 à 16, dans lequel l'hydrogène est mélangé avec le courant de LWP avant la mise en œuvre de l'étape a) et de l'étape c) d'hydrotraitement.

18. Produit hydrocarboné purifié, pouvant être obtenu par hydrotraitement de LWP conformément à l'étape a) d'hydrotraitement et mélange conformément à l'étape b) selon la revendication 1, lequel produit comprend

- une quantité de silicium réduite de façon à être inférieure à 6 mg/kg, mieux encore < 1 mg/kg, et/ou de phosphore réduite de façon à être inférieure à 5 mg/kg, mieux encore 1 mg/kg, telle que mesurée par ICP-MS/MS,
- un rapport des dioléfines à la teneur totale en oléfines réduit de façon à être inférieur à 0,01, mieux encore inférieur à 0,001, tel que mesuré conformément à la norme ASTM D8071,
- un rapport des dioléfines conjuguées aux dioléfines non conjuguées réduit de façon à être inférieur à 2, mieux encore inférieur à 1, mesuré conformément à la norme ASTM D8071,
- une teneur en halogènes qui va être inférieure à 5 mg/kg, de préférence 1 mg/kg.

Figure 1



**REFERENCES CITED IN THE DESCRIPTION**

*This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.*

**Patent documents cited in the description**

- WO 2021110395 A [0005]
- WO 2021204819 A [0006]
- FR 3107530 [0006]
- WO 2021105326 A [0006]