

PROCESS FOR PRODUCING HTL OILS WITH IMPROVED THERMAL STABILITY AND LOW INORGANIC CONTENT

FIELD OF THE INVENTION

- 5 The present invention relates to a process for producing low oxygen containing HTL oil with improved thermal stability and low inorganic content so that it could be used directly as a blendable marine fuel. The present invention also relates to the HTL oil with improved thermal stability and low inorganic content, and to the use of the HTL oil with improved thermal stability and low inorganic content as
- 10 marine fuel, co-processing feedstock in commercial refineries, or in stand-alone upgrading facilities.

BACKGROUND

- 15 Biofuel refers to any fuel that is derived from biomass. Biofuel is produced over a short period of time, in contrast to the very slow natural processes by which fossil fuels, such as oil, are formed. Biofuel can be produced from plants or from agricultural, domestic or industrial bio waste. Biofuels are mostly used for transportation, but can also be used for heating and electricity.
- 20 First-generation biofuels, also denoted "conventional biofuels" are made from food crops grown on arable land. The crop's carbonaceous material, i.e. sugar, starch and oil content, is typically converted into biodiesel or ethanol using transesterification or yeast fermentation.
- 25 Second-generation biofuels, also referred to as "advanced biofuels" or "sustainable biofuels", are made from waste products, thereby avoiding a "food versus fuel" dilemma. The second-generation fuels are derived from agriculture and forestry activities. The feedstocks used to make the fuels either grow on arable land but are by-products of the main crop, or they are grown on marginal
- 30 land. Second-generation fuels are typically produced by biochemical or thermochemical pathways, such as pyrolysis and hydrothermal liquefaction.

Hydrothermal liquefaction (HTL) is one known method to produce second-generation fuels. HTL biocrude may be produced from various organic wastes and residues, such as biomass left in the forests after forestry operations (forestry residues). One promising application of this HTL pathway has been developed by
5 Steeper Energy and is described in WO 2020/228990A1. This HTL process produces a high-dense biocrude, rich in diesel boiling point range hydrocarbons, with a High Heating Value (HHV) of about 38 MJ/kg with a high mass and carbon yield. Up to 45 wt% of the incoming biomass is captured in the HTL biocrude. This biocrude has a low oxygen content of about 10 wt%, low level of heteroatoms,
10 about 0.25 wt% of nitrogen, about 150 ppm sulphur and lower water content (< 1 wt%) compared to other biocrudes.

HTL biocrude is a promising drop-in fuel that can be mixed with marine fuel. Although biocrude resembles its fossil counterparts in many properties, it has
15 physicochemical properties that differ from conventional marine fuel, limiting its blendability due to the heteroatoms and polar compounds present in HTL biocrude. Furthermore, the HTL biocrude is typically not fully thermally stable, especially at temperatures above 80°C, due to its content of reactive residual oxygenates. This means that improvements are required to ensure that the
20 biocrude remains fit for purpose during storage, handling and blending.

It is known that as HTL biocrude ages, dehydration, polymerization, aldol condensation, oligomerization and acid formation reactions occur, which increases the biocrude's viscosity, water content and corrosivity and thus affecting oil
25 handling, including pumping, injection and atomization in engines. The effect of temperature is critical in the aging process as the aging reactions are enhanced by temperature increases.

A biocrude must meet six properties in order to be acceptable for use as a marine
30 fuel. These properties relate to ash content, metal content (in particular sodium, vanadium, aluminum + silicon), acidity, as well as the flash point and thermal stability at the temperature required to reach the viscosity specified for atomization of the fuel of around 10 cSt while ensure that the temperature required to reach this viscosity is not higher than the maximum allowed in the
35 engines ($\leq 130^{\circ}\text{C}$). In addition, compatibility with petroleum fuels is required, as the biocrude must be able to be mixed with the petroleum fuel.

Upgrading HTL biocrudes are typically required to become acceptable for use as a marine fuel. Mild hydrotreating is a common way of upgrading HTL biocrudes to produce marine fuels. A mild hydrotreated HTL oil has less oxygen content, total acid number (TAN), viscosity and density compared to HTL biocrude, which improves the compatibility with petroleum-derived marine fuels. However, this hydrotreating process requires a source of hydrogen and commercial catalysts as well as hydrotreating reactors and gas handling equipment to recycle the non-reacted hydrogen and remove gas impurities such as ammonia and hydrogen sulphide.

Other approaches to improve the HTL biocrude quality and slow the aging process include emulsification, solvent extraction and vacuum distillation. However, these methods do not improve oil thermal stability at higher temperatures required for combustion, and they would only allow a very minimum quantity of HTL biocrude that can be used for marine applications leaving about 40 wt% of the biocrude with no market. Furthermore, high concentrations of solvents and emulsifying agents would also be required leading to higher costs of HTL biocrude.

Solvent addition is yet another option for enhancing biocrude stability and compatibility with petroleum fuels. Several solvents have been evaluated including ethyl acetate, methyl ethyl ketone, acetone, ethanol and methanol. The most promising solvent additive is methanol at concentrations between 5 to 20 wt%. Adding methanol would drastically reduce the biocrude viscosity and retard the polymerization reactions, thereby reducing the oil's aging rate; it however, negatively impacts critical properties for marine fuel infrastructure, such as flash point, reducing it to below the minimum limit of 60°C. This would worsen the handling and storage operations and lower the fuel's heating value, possibly resulting in ignition delays.

Azeotropic distillation with at least one alcohol followed by alcoholysis is another known method for converting crude bio-oil into an upgraded bio-oil for use as marine fuel. Such method is disclosed for example in US 2014/0256965 A1. Yet another method is disclosed in WO 2024/051909 A1. In this method, HTL biocrude is mixed with at least one alcohol and then the mixture is subjected to a processing temperature to form a viscosity reduced biocrude and to separate an

evaporated water fraction. These methods, however, are not focused on reducing the mineral content in the final upgraded bio-oil.

5 The inventors of the present invention has developed a new method to improve HTL biocrude, in particular thermal stability and acidity of the HTL biocrude, making it possible to use the obtained HTL oil as marine fuel, co-processing feedstock in commercial refineries, or in stand-alone upgrading facilities.

10 SUMMARY OF THE INVENTION

10 The inventors of the present invention have found that thermally stable HTL oil can be produced by heating HTL biocrude at 80 to 200°C for 1 to 200 hours in the presence of an additive. The thermally stable HTL biocrude can be subjected to an additional washing phase, resulting in a thermally stable HTL oil with a lower
15 inorganic content that can be used directly, for example, as a marine fuel, co-processing feedstock in commercial refineries, or in stand-alone upgrading facilities where a high inorganic content could significantly reduce hydrotreating catalyst life. In addition, the lower total acid number of the stable HTL oil reduces the corrosion effect in the metallurgic of the existing marine engines or refineries.

20 BRIEF DESCRIPTION OF THE FIGURES

Figure 1 shows a schematic overview of a continuous high pressure process for transforming the carbonaceous materials into HTL biocrude described in Example 1.

25 Figure 2 shows a schematic overview of the continuous process for producing HTL oils with improved thermal stability.

30 Figure 3 shows a schematic overview of the continuous process for producing HTL oils with improved thermal stability and low inorganic content.

Figure 4 shows a schematic overview of the continuous process for producing HTL oils with improved thermal stability performed in two stages.

Figure 5 shows corrosion effect on carbon steel pieces A) before accelerated ageing tests; B) after accelerated ageing test using fresh HTL biocrude; C) after accelerated ageing test with chemically treated HTL biocrude at 160°C for 140 hours.

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Figure 6 shows chemical family distribution determined by FTIR of fresh HTL biocrude and chemically treated HTL oil compared to a petroleum-derived marine fuel.

10 Figure 7 shows of spot test for evaluation of compatibility between chemically treated HTL oil and commercial marine fuel described in Example 4.

DETAILED DESCRIPTION OF THE INVENTION

The results of the experimental work presented in this patent application provide
15 valuable insights into the scalability of the chemical treatment process and its potential for commercial application. Moreover, the chemical treatment according to the present invention offers a sustainable and efficient solution to address the surging energy demands of the marine sector, which is a critical component of global transportation infrastructure. The utilization of chemically treated HTL oil as
20 a fuel source has significant potential to reduce the shipping industry's carbon footprint and contribute to the transition to a more sustainable energy system.

In a first aspect, the present invention relates to a process for producing Hydrothermal Liquefaction (HTL) oil with improved thermal stability and low
25 inorganic content. The process is shown in Figures 2-4. The process comprises the steps of:

a. Providing a low oxygen containing HTL biocrude having:

- an oxygen content in the range of 3.0 to 15 wt%,
- a water content of less than 1.5 wt%,
- 30 - a total acid number in the range of 20 to 80 mg KOH/g,
- an oil fraction having a boiling point below 350°C of less than 70 wt%,
- a residue fraction having a boiling point of more than 450°C of at least 10 wt%; and
- an ash content below 0.1 wt%;

- b. Heating the low oxygen containing HTL biocrude of step a to a temperature in the range of 25 to 80°C;
- c. Adding and mixing an additive comprising at least one alcohol to the heated low oxygen containing HTL biocrude of step b;
- 5 d. Further heating the mixture of step c to a temperature in the range of 80 to 200°C in a reaction zone;
- e. Maintaining the heated mixture of step d in the reaction zone for a conversion time of 1 to 200 hours;
- f. Cooling the converted mixture of step e to a temperature in the range of 20 to 180°C; and
- 10 g. Separating the cooled converted feed mixture of step f into a chemically treated HTL oil, a light boiling point fraction, water and un-consumed additive.

By the term "HTL biocrude" as used herein is meant a biocrude which has been produced by hydrothermal liquefaction. For example, the HTL biocrude is produced using the process which has been developed by Steeper Energy and which is described in WO 2020/228990A1. This method is shown in Figure 1. Preferably, the HTL biocrude is produced by subjecting carbonaceous material to a hydrothermal liquefaction treatment, which operates at supercritical water conditions at 390-420°C and 300-350 bar.

By the term "low inorganic content" as used herein means a content below 400 ppm, preferably below 200 ppm. By the term "inorganic" as used herein is meant the metal content determined by ICP-digest analysis and ash determination in accordance with ASTM D482. Some of the metals determined by ICP are Aluminum - Al, Arsenic - As, Calcium - Ca, Chromium - Cr, Copper - Cu, Iron - Fe, Nickel - Ni, Phosphorous - P, Potassium - K, Silicon - Si, Sodium - Na, Tin - Sn, Titanium - Ti, Vanadium - V, Zinc - Zn.

In step a, HTL biocrude is provided. This HTL biocrude has a low oxygen content in the range of 3.0 to 15 wt%, a water content of less than 1.5 wt%, a total acid number in the range of 20 to 80 mg KOH/g, an oil fraction having a boiling point below 350°C of less than 70 wt%, a residue fraction having a boiling point of more than 450°C of at least 10 wt%, and an ash content below 0.1 wt%.

In step b, the low oxygen containing HTL biocrude of step a is heated to a temperature in the range of 25 to 80°C to reduce viscosity and improve miscibility with the additive.

- 5 In step c, an additive is added and mixed with the heated low oxygen containing HTL biocrude of step b. The additive comprises at least one alcohol. During this step, esterification and acetalization reactions occur, accelerating the conversion of reactive molecules of the HTL biocrude, such as organic acids and aldehydes to esters, acetals and water. While the process occurs, polymerization and
- 10 agglomeration reactions also arise, affecting the blend's homogeneity and viscosity, i.e. the viscosity is increased. This increase in viscosity is an unfortunate unavoidable result of the process according to the invention, and can only be accepted as long as the resulting viscosity of the final chemical treated HTL oil meets the requirements of ISO 8217 for conventional marine fuel. Positively, as
- 15 carboxylic acids are consumed during the process, a reduction in TAN is observed, which can be advantageous to improve the HTL biocrude's thermal stability.

- The additive comprises at least one alcohol. The at least one alcohol includes short-chain alcohol(s) and/or long-chain alcohol(s). The at least one alcohol is
- 20 added in a proportion up to 50 wt% of the additive mixture. Preferably, the concentration of alcohol in the additive is 1 to 70 wt% based on total weight of additive mixture, more preferred in the range of 3 to 50 wt%, most preferred in the range of 5 to 40 wt%. Suitable examples of alcohols include methanol, ethanol, propanol, isopropanol, butanol, isobutanol, pentanol, isopentanol,
- 25 hexanol, isohexanol, octanol, nonanol, decanol, undecanol, dodecanol, tridecanol, tetradecanol, pentadecanol, hexadecanol, heptadecanol. Preferred examples of alcohols include methanol, ethanol, isopropanol, n-butanol, isobutanol and n-pentanol, and even more preferred examples of alcohols include methanol, ethanol and isopropanol. Preferred alcohols are those produced from renewable
- 30 sources such as organic waste.

- In step d, the mixture of low oxygen HTL biocrude and additive is further heated to a temperature in the range of 80 to 200°C in a reaction zone. More preferred the mixture is heated to a temperature in the range of 110 to 180°C, even more
- 35 preferred in the range of 130 to 170°C.

In step e, the heated mixture of step d is maintained at the specified temperature in the reaction zone for a period of time in order for the conversion to occur. More particular, the further heated mixture is maintained at the temperature for a conversion time of 1 to 200 hours, more preferred from 3 to 180 hours, even
5 more preferred from 10 to 160 hours.

In a preferred embodiment, the heated mixture of step d reaches a pressure in the reaction zone of between 3 to 200 bar, more preferred from 5 to 150 bar, even more preferred from 7 to 110 bar.

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In a preferred embodiment, the mixture is subjected to agitation during the conversion time in order to enhance the rate of reaction. In cases where the mixture is agitated, the conversion time can be reduced to between 1 to 70 hours.

15 It is important to note that substantially no water or other compounds are removed during the heat treatment steps b-f. This is a significant difference compared to other methods, such as the azeotropic distillation processes mentioned in US 2014/0256965 and WO 2024/052909, where water and alcohol is evaporated and thereby removed during the heat treatment step(s), which
20 results in different reaction products being formed as compared to the process of the present invention. This is evident from the fact that the viscosity increases during heat treatment in the process according to the present invention, whereas a reduction in viscosity is observed during the azeotropic distillation process.

25 In step f, the converted mixture from step e is cooled to a temperature in the range of 20 to 180°C, more preferred from 40 to 150°C even more preferred from 50 to 130°C.

In step g, the cooled and converted mixture of step f is separated into a
30 chemically treated HTL oil, a light boiling point fraction, water and un-consumed additive. Un-consumed additive is preferably recycled to step c.

A particular preferred embodiment is shown in Figure 3. In this embodiment, the process further comprises a step of reducing the level of inorganic content to
35 below 200 ppm, preferably below 100 ppm, by mixing the cooled and converted mixture of step f with a liquid containing at least 70 wt% of demineralized water,

prior to separating said mixture into the fractions mentioned in step g. In a preferred embodiment, this step of mixing with water is performed at 5 to 80°C and pressures below 20 bar. When the mixture is mixed with water, at least some of the inorganic content, will be transferred to the water phase, which provides a chemically treated HTL oil with reduced inorganic content. The excess of water is removed by gravity. Then, by removing the formed water and reducing the concentration of light hydrocarbons, a thermal stable HTL oil is produced with a flash point and viscosity within the allowed ranges for marine fuel.

Another particular preferred embodiment is shown in Figure 4, in which the process is focused on reducing the total acid number (TAN). In this embodiment, step e is performed in two stages: the first stage (first sub-reaction zone) targets a reduction of total acid number of at least 50% reduction compared to the low oxygen containing HTL biocrude and the second stage (second sub-reaction zone) is a polishing step to reduce further the total acid number of at least 20% reduction. In the first sub-reaction zone, the heated mixture of low oxygen containing HTL biocrude and additive of step c is maintained at a temperature of 80 to 200°C for 10 to 170 hours. In the second sub-reaction zone, the reaction mixture of the first sub-reaction zone is mixed with additional additive to obtain a concentration in the range of 5 to 30 wt% of additive and the temperature in the second sub-reaction zone is maintained at between 100 to 170°C for 10 to 170 hours, preferable 15 to 140 hours.

Preferably, the total TAN reduction of the low oxygen containing HTL oil is at least 70%, preferable at least 75%, more preferable at least 80% as compared to the low oxygen containing HTL biocrude. Accordingly, the chemically treated HTL oil obtained in step g has a total acid number of at most 24 mg KOH/g, more preferred of at most 6 mg KOH/g, even more preferred at most 5 mg KOH/g.

As mentioned above, the viscosity of the chemically treated HTL oil is typically higher than the viscosity of the low oxygen containing HTL biocrude. In an embodiment the kinematic viscosity at 50°C of the low oxygen containing HTL biocrude of step a is in the range of 150-200 cSt, whereas the kinematic viscosity at 50°C of the chemically treated HTL oil of step g is in the range of 230-280 cSt.

In a preferred embodiment, the low oxygen containing HTL biocrude in step a is provided by a process, which comprises the steps of:

- Providing a carbonaceous material in the form of biomass contained in one or more feedstocks;
 - 5 - Providing a feed mixture by slurring the carbonaceous material in one or more fluids, at least one of which comprises water;
 - Pressurizing the feed mixture to a pressure in the range 150 to 400 bar;
 - Heating the pressurized feed mixture to a temperature in the range of 300°C to about 450°C;
 - 10 - Maintaining the pressurized and heated feed mixture in a reaction zone for a conversion time in the range 3 to 30 minutes; and thereby causing the carbonaceous material to be converted;
 - Cooling the converted feed mixture to a temperature in the range from 25°C to 200°C; and
 - 15 - Expanding the converted feed mixture to a pressure in the range 1-120 bar, and separating the converted feed mixture into at least a low oxygen containing HTL biocrude, a gas phase and a water phase comprising water-soluble organics and dissolved salts;
- thereby providing the low oxygen containing HTL biocrude having an oxygen
- 20 content in the range from 3.0 wt% to 15 wt%, a water content of less than 1.5 wt%, a total acid number in the range from 20 to 80 mg KOH/g, an oil fraction having a boiling point below 350°C of less 70 wt%, a residue fraction having a boiling point of more than 450 °C of at least 10 wt%, and an ash content below 0.1 wt%.

- 25 In a second aspect, the present invention relates to a chemically treated HTL oil with improved thermal stability and low inorganic content, which preferably has been obtained using the process according to the present invention. This HTL oil is characterized by having an oxygen content of at most 10 wt%, a water content of
- 30 less than 0.1 wt%, a total acid number of at most 6 mg KOH/g, an ash content of less than 400 ppm, a flash point of at least 60°C, an oil fraction having a boiling point below 150°C of at most 0.1 wt%, an oil fraction having a boiling point below 350°C of 30-40 wt% and a residue fraction having a boiling point of at least 550 °C of at least 20 wt%.

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In a particular preferred embodiment, the ash content of the HTL oil is less than 100 ppm.

In a third aspect, the present invention relates to the use of the chemically treated HTL oil with improved thermal stability and low inorganic content as marine fuel, co-processing feedstock in commercial refineries, or in stand-alone upgrading facilities. A skilled person would know that the above list of suitable uses are not limited to those mentioned in the list.

10 **EXAMPLES**

Example 1: Preparation and characterization of the HTL biocrude produced by hydrothermal liquefaction

15 The low oxygen containing HTL biocrude was produced from a 50/50 mixture of spruce and pine using the process in Figure 1. This mixture was subjected to a hydrothermal liquefaction treatment, which operates at supercritical water conditions at 390-420°C and 300-350 bar. The analysis of the wood chips as received is shown in Table 1 below.

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Table 1. Composition of carbonaceous material on a dry ash free basis.

Element	Spruce	Pine	50/50 mixture
	wt%, dry	wt%, dry	
C, wt%	50.4	50.2	50.3
H, wt%	6.1	6.2	6.15
O, wt%	43.1	43.4	43.25
S, wt%	0	0	0
N, wt%	0.2	0.1	0.15
Cl, wt%	0.008	0.007	0.0074
HHV, MJ/kg	20.2	20.1	20.15

Feed preparation

25 The wood chips were size reduced to wood flour in a hammer mill system and mixed with recycled water (inclusive dissolved salts and water soluble organics), recycled oil, catalysts to produce a homogeneous and pumpable feed mixture.

Potassium carbonate was used as catalyst and sodium hydroxide was used for pH adjustment. It was attempted to keep the potassium concentration constant during the runs i.e. the potassium concentration in the water phase was measured and the required make-up catalyst concentration was determined on this basis.

- 5 Sodium hydroxide was added in amounts sufficient to maintain the outlet pH of the separated water phase in the range 8.0-8.5. Further CMC (Carboxy Methyl Cellulose, Mw = 30000) in a concentration of 0.8 wt% was added to the feed slurry as a texturing agent to avoid sedimentation in the feed barrel and improve pumpability.

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As neither water nor oil phases was available for the first cycle (batch), crude tall oil was used as start up oil and 5.0 wt% ethanol and pure water (Reversed Osmosis water, RO water) was used to emulate the water phase in the first cycle.

- 15 Multiple cycles (batches) are required before the process can be considered in steady state and representative oil and water phases are produced. Approximately 6 cycles are required to produce oil with less than 10% concentration of the start up oil. Hence, 6 cycles were carried out, where the oil and water phase produced from the previous cycle was added to the feed mixture for the subsequent cycle. The feed composition for the 6th cycle run is shown in Table 2 below:

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Table 2. Feed mixture composition for 6th cycle run.

Pine	11.1 wt% dry
Spruce	11.1 wt% dry
CMC	0.8 wt% dry
Recirc. oil from 5th cycle	18.2 wt% dry
Water contained in wood and recycled oil	9.8 wt%
Recirc. water phase from 5th cycle	45.2 wt%
K	2.3 wt%
NaOH	1.5 wt%
Total	100.0 wt%

- 25 The feed mixture in Table 2 were processed at a pressure of about 320 bar and a temperature around 400°C. The de-gassed product was collected as separate mass balance samples (MB) in barrels from the start of each test, and numbered MB1, MB2, MB3, etc. The collected products were weighed, and the oil and water

phases were gravimetrically separated and weighed. Data was logged both electronically and manually for each batch.

Total Mass Balance

5 The Total mass balance (MBTot) is the ratio between the total mass leaving the unit and the total mass entering the unit during a specific time. The total mass balance may also be seen as a quality parameter of the data generated. The average MBTot closure was 100.8%.

10 HTL biocrude Yield from Biomass

The Oil Yield from Biomass expresses the fraction of incoming dry biomass that is converted to dry ash free oil. It is defined as the mass of dry ash free Oil produced from dry biomass during a specific time divided by the mass of dry biomass entering the unit during the same time. The recirculated oil is not included in the balance, it is subtracted from the total amount of oil recovered when calculating the oil yield from biomass. The average oil yield was found to be 45.3 wt% with a standard deviation of 4.1 wt% i.e. 45.3% of the mass of dry biomass (wood+CMC) in the feed is converted to dry ash free Oil.

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Detailed HTL biocrude analysis

Data measured for the HTL biocrude are presented in Table 3.

Table 3. Physico-chemical properties of the low oxygen containing HTL biocrude

Test	Low oxygen containing HTL biocrude
Water content [wt%]	0.18
Ash [wt%]	0.09
MCR [wt%]	17.08
TAN [mg KOH/g]	33.19
SAN [mg KOH/g]	<0.01
HHV daf [MJ/kg]	38.14
Density @ 15°C [kg(m3]	1043
Kinematic Viscosity @ 50°C [cSt]	177
Inorganic analysis	
Aluminum- Al [mg/kg]	<4.4
Arsenic - As [mg/kg]	<1.5
Calcium - Ca [mg/kg]	16

Chromium - Cr [mg/kg]	<0.4
Copper - Cu [mg/kg]	<1.5
Iron - Fe [mg/kg]	76.9
Nickel - Ni [mg/kg]	<6.0
Phosphorous - P [mg/kg]	<2.7
Potassium - K [mg/kg]	237
Silicon - Si [mg/kg]	<6.2
Sodium - Na [mg/kg]	297
Tin - Sn [mg/kg]	<3.2
Titanium - Ti [mg/kg]	12
Vanadium - V [mg/kg]	<2.0
Zinc [mg/kg]	6.2
Al+Silicon [mg/kg]	<10.6

Elemental analysis (daf)

Carbon [wt%]	80.89
Hydrogen [wt%]	9.15
Nitrogen [wt%]	0.25
Sulphur [wt%]	146
Oxygen [wt%]	9.69
H/C molar ratio	1.35

SAP by TLC-FID

Saturates [wt%]	8.2
Aromatics [wt%]	26.4
Polars [wt%]	65.4
Pour point [°C]	6
Flash point [°C]	74

Simdist

Naphtha (IBP-150°C) [wt%]	1.93
Middle distillates (150-343°C) [wt%]	38.68
Heavy gas oils (343-550°C) [wt%]	39.87
Residue (550+°C) [wt%]	19.51

Daf: dry ash free

Energy Recovery in the produced HTL biocrude

- 5 The Energy Recovery (ERoil) expresses how much of the chemical energy in the fed wood that are recovered in the oil. It does not take into account the energy required for heating nor the electrical energy supplied to the unit. For the calculations of recoveries, a High Heating Value (HHV) for the oil of 38.6 MJ/kg were used together with the HHV for the wood mixture given in Table 1. The resulting energy recovery for the 6th cycle oil was 85.6% with a standard

deviation of 7.7 i.e. 85.6% of the (chemical) energy in wood fed to the plant is recovered in the produced oil.

Gas production and gas analyses

5 Gas is produced in the process of converting biomass into oil. The yield of gas produced from dry wood in the feed is 41.2 wt%. The gas is composed of mainly CO₂, CH₄ and other short hydrocarbons (C₂-C₄), H₂ and some lower alcohols. Gas was sampled and analyzed by Sveriges Tekniska Forskningsinstitut (SP) in Sweden. The analysis of 6th cycle gas is shown in Table 4 along with heating values of the gas estimated from the gas composition. Since a HTL process runs at reductive conditions, it is assumed that the gas is oxygen (O₂) free and the detected oxygen in the gas origin from air leaking into the sample bags when filled with gas sample. The gas composition is corrected for the oxygen (and nitrogen). The calculated elemental composition of the gas is shown in Table 4.

Table 4. Gas composition for the gas produced in the process.

Component	vol%, a.r	vol%, air free*	wt%, air free	HHV, MJ/kg	LHV, MJ/kg
H ₂	24.00	25.79	1.69	2.40	2.02
O ₂ *	0.40	0.0	0.0	0.0	0.0
N ₂	1.50	0.02	0.01	0.00	0.00
CO ₂	56.90	61.14	87.27	0.00	0.00
CO	0.30	0.32	0.29	0.03	0.03
CH ₄	6.70	7.20	3.75	2.08	1.87
Ethene	0.16	0.17	0.16	0.08	0.07
Ethane	2.20	2.36	2.31	1.20	1.10
Propene	0.27	0.29	0.40	0.19	0.18
Propane	0.95	1.02	1.46	0.74	0.68
Sum C ₄	0.63	0.68	1.25	0.62	0.57
Methanol	0.41	0.44	0.46	0.10	0.09
Ethanol	0.27	0.29	0.43	0.13	0.12
Acetone	0.26	0.28	0.53	0.17	0.15
Total	94.95	100	100	7.73	6.89

* Oxygen (O₂) in the as received gas (a.r) is assumed to origin from air contamination of the gas when filling the sample bag. The produced gas composition is assumed air (Oxygen) free.

Table 5. Elemental gas composition.

Element	wt%
C	32.0
H	3.8
N	0.0
O	64.1
Total	100

5 **Example 2: Determination of HTL biocrude suitability for direct use as marine fuel**

10 The potential use of HTL biocrude as a marine fuel is being evaluated according to various criteria, including biocrude characterization, stability in a rig test where biocrude is heated and sprayed through a pressure nozzle which will be followed by combustion and engine trials. While the marine industry is flexible regarding some of the ISO 8217 properties, some must be met to ensure safe operation, engine longevity, and reduction of emissions. Metals, especially sodium, vanadium, and silicon+aluminum, and properties such as flash point, thermal
15 stability, compatibility with conventional marine fuels, ash content, and heteroatom (S and N) composition are all important factors to consider. HTL biocrude, marine fuel, and ISO 8217 properties are included in Table 6.

20 The results in Table 6 reveal that HTL biocrude has a higher oxygen content (9-10 wt%) than marine fuel (0.03 wt%), but it has lower sulphur (146 ppm) and nitrogen content (0.25 wt%), than marine fuel (S: 4591 ppm and N: 0.28 wt%). SAP's hydrocarbon analysis shows that 51.9 wt% of the marine fuel components are aromatics, 36.9 wt% are saturates, and 11.2 wt% are polars. In contrast, HTL biocrude has a significantly higher concentration of polars (65.4 wt%), a slightly
25 lower concentration of aromatics (26.37 wt%), and a much lower concentration of saturates (8.23 wt%). These differences in functional group distribution cause limited compatibility allowing blending ratios up to 2 wt%. Regarding distillation, the HTL biocrude extends over the entire boiling range of crude oils (i.e., from naphtha to vacuum residue), while marine fuel is made up primarily of the heavy
30 gas oil distillation cut and contains no components with boiling points in the naphtha range.

- The ash content in the HTL biocrude is on the maximum limit indicated in the ISO 8217 (<0.1 wt%); however, a closer look at the type of metals suggests high content of potassium (237 ppm) and sodium (297 ppm), almost three times
- 5 higher than what is suggested by ISO 8217. Levels of vanadium, silicon and aluminum are within the allowed levels ($V < 450$ ppm and $Si+Al < 60$ ppm). The flash point is also above the minimum critical value of 60°C.

10 **Table 6.** Properties of HTL biocrude compared to conventional marine fuel and ISO 8217

Test	HTL biocrude	Conventional Marine fuel	ISO 8217
Water Content [wt.%]	0.18	<0.1	max: 0.50
Ash [wt.%]	0.09	0.014	max: 0.10
MCR [wt.%]	17.08	6.25	max: 20
TAN [mg KOH/g]	33.19	0.13	max: 2.50
SAN [mg KOH/g]	BDL	<0.1	BDL
HHV daf [MJ/kg]	38.14	42.82	
Density @ 15°C [kg/m ³]	1043	952.53	max: 991
Kinematic Viscosity @ 50°C [cSt]	177	55.90	max: 380
Temp. to reach 10 cSt [°C]	103	83.45	130*
<i>Metal analysis</i>			
Aluminum – Al [mg/kg]	< 4.4	9	
Arsenic – As [mg/kg]	<1.5		
Calcium – Ca [mg/kg]	16	<3	max: 30
Chromium – Cr [mg/kg]	< 0.4		
Copper – Cu [mg/kg]	< 1.5		
Iron – Fe [mg/kg]	76.9		
Nickel – Ni [mg/kg]	< 6.0	15	
Phosphorus – P [mg/kg]	< 2.7	<1	max: 15
Potassium – K [mg/kg]	237		
Silicon – Si [mg/kg]	< 6.2	12	
Sodium – Na [mg/kg]	297	8	max: 100
Tin – Sn [mg/kg]	< 3.2		
Titanium – Ti [mg/kg]	12		
Vanadium – V [mg/kg]	< 2.0	21	max: 450
Zinc – Zn [mg/kg]	6.2	<1	max: 15
Al+Silicon [mg/kg]	<10.6	21	max: 60

<i>Elemental analysis (daf)</i>			
Carbon [wt.%]	80.89	88.60	
Hydrogen [wt.%]	9.15	10.63	
Nitrogen [wt.%]	0.25	0.28	
Sulphur [mg/kg]	146	4591	max: 0.1 wt.% or 0.5% wt.%
Oxygen [wt.%]	9.69	0.03	
H/C Molar Ratio	1.35	1.43	
SAP by TLC-FID			
Saturates [wt.%]	8.2	36.9	
Aromatics [wt.%]	26.4	51.9	
Polars [wt.%]	65.4	11.2	
Pour point [°C]	6	-9	max:30
Flash Point [°C]	74	106	minimum: 60
SimDist			
Naphtha (IBP-150°C) [wt.%]	1.93	0	
Middle distillates (150-343°C) [wt.%]	38.68	23.61	
Heavy gas oils (343-550°C) [wt.%]	39.87	55.74	
Residue (550+°C) [wt.%]	19.51	20.65	

Daf: dry ash free

Despite the HTL biocrude's apparent suitability for use as marine fuel, the thermal stability and ageing test indicated otherwise. According to a thermal gravimetric study (TGA), HTL biocrude becomes thermally unstable at temperatures above 80°C. Because of this, heating or storing the HTL biocrude for an extended period at temperatures above 80°C will significantly affect the biocrude's properties such as water content, TAN and viscosity. In addition, for certain engines, HTL biocrude preheating to 103°C is necessary to achieve the desired viscosity for adequate fuel spray at the engine nozzle (10 cSt), which could have a negative effect on the engine's metallurgy as indicated by the accelerated ageing test at 160°C for 140 hours where two pieces of carbon steel were used for qualitative corrosion analysis. Figure 5, shows the visible corrosion observed in the carbon steel pieces after accelerated ageing tests.

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The results in Table 7 shows that higher temperatures accelerate the ageing reactions, leading to greater water production and a reduction in TAN. Dehydration, polymerization, aldol condensation, oligomerization, and acid generation are all reactions that happen as the HTL biocrude ages. These reactions are intrinsically linked to water content and acidity. It is worth noting

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that the water content, TAN and viscosity remain almost constant for over 8 months when the oil is kept at atmospheric conditions (25°C and atmospheric pressure) confirming that HTL biocrude stored at room temperature degrades slower than the HTL biocrude stored at temperatures between 80 and 160°C.

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Table 7. Results from accelerated aging studies

Accelerate ageing test conditions	Water content [wt%]	TAN [mg KOH/g]
25°C, > 8 months	Water ↑ 6%; 0.18 → 0.19	TAN ↓ 3%; 33 → 32
110°C, > 140 h	Water ↑ 39%; 0.18 → 0.25	TAN ↓ 7%; 33 → 31
130°C, > 140 h	Water ↑ 106%; 0.18 → 0.37	TAN ↓ 14%; 33 → 29
160°C, 140 h	Water ↑ 289%; 0.18 → 0.70	TAN ↓ 49%; 33 → 17

The HTL biocrude contains a wide variety of chemical compounds. FTIR analysis allowed for the overall determination of families of compounds in the whole biocrude, GC-MS analysis allowed the distribution determination of the oil light fraction (boiling point below 350°C), while SAP analyzed the heavy fraction (boiling point above 300°C +). FTIR analysis for the HTL biocrude indicated the distribution of the main components families, including alkanes, aromatics, ketones, esters, ethers, phenols free and bonded, and carbonyl components (free and bonded).

GC-MS analysis indicated that 34% of the HTL biocrude light fraction (IBP-350°C) comprises polar heteroatoms containing mainly oxygenated compounds with a small contribution of nitrogen and sulphur-containing compounds. The oxygenated components are mostly carboxylic acids, ketones, and phenols, with a small contribution of esters and aldehydes. Those oxygenated compounds contained in the HTL biocrude are most likely from products of the hydrothermal liquefaction conversion of lignocellulosic components. In addition, 58% are aromatics and polycyclic compounds, including phenanthrene, alkylbenzenes, and naphthalenes. The remaining 8% corresponds to saturated compounds. A similar distribution is observed for the heavy fraction (boiling point above 300°C), where the SAP tests indicated that most of the components are polars>aromatics>saturates. Additionally, a significant increase in viscosity (70%) was observed.

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Example 3: Quality improvements from chemically treated HTL oil

HTL biocrude produced from the 50/50 mixture of spruce and pine as described in example 1 was subject to a chemical treatment as shown in Figures 2 and 3.

- 5 First the low oxygen content HTL biocrude was preheated to 35°C, then 5 to 10 wt% of alcohol additive was added (as indicated in Table 8). The mixture of low oxygen containing HTL biocrude and additive was then heated to 160°C and kept in a closed system for 140 hours. After completion of residence time, the products were atmospherically distilled to separate the unreacted additive, water and light
- 10 fraction (IBP-180°C) from the chemically treated HTL oil.

Various chemical treatment tests were performed with different types of alcohols, concentrations, and temperatures (see Table 8).

- 15 The results in Table 8 indicate that esterification and acetalization reactions could be accelerated by heat and alcohol concentration. Considerable reduction of TAN is observed at 160°C (70% reduction) compared to 130°C (46% reduction) when the ageing test is performed using a blend of HTL biocrude and IPA (90:10). This indicates that higher temperatures favor the chemical treatment process.
- 20 However, it was observed that temperatures above 200°C are not beneficial to the process; instead, agglomeration and coke formation was observed at this temperature.

- Similar to the temperature observation, the higher the alcohol concentration, the
- 25 faster TAN reduces, and this also correlates with the specific type of alcohol used. For example, the results in table 8 show that higher TAN reduction (89%) was achieved when using 10 wt% methanol, compared to 84% reduction by using 10% ethanol and 77% reduction when using 10% IPA. This is most likely related to the amount of OH⁻ ions available in the mixture, as more OH⁻ ions are available
- 30 in 100 g of methanol (3.1) compared to 2.2 with ethanol and 1.7 with IPA.

Table 8. Water content and TAN changes in the chemical treated tests performed on HTL biocrude using various additives at 160°C for 140 hours

Additive	Water content blend [wt%]	TAN blend [mg KOH/g]
IPA 10 wt. %	Water ↑ 150%; 0.16 → 0.4	TAN ↓ 77%; 30 → 7
Ethanol 5 wt. %	Water ↑ 168%; 0.15 → 0.4	TAN ↓ 74%; 34 → 9
Ethanol 10 wt. %	Water ↑ 197%; 0.15 → 0.41	TAN ↓ 84%; 32 → 5
Methanol 5 wt. %	Water ↑ 259%; 0.15 → 0.54	TAN ↓ 87%; 32 → 4
Methanol 10 wt. %	Water ↑ 208%; 0.15 → 0.46	TAN ↓ 89%; 30 → 3

140 hours of residency time were required to reach a steady state at 160°C and with the different concentrations of alcohol tested. Agitation can considerably reduce the residence time reaching process stability by half of the time (70 hours) using 10 wt % of methanol.

The thermal stability of the chemically treated HTL biocrude was demonstrated by accelerated aging experiments at 160°C for 140 hours. Carbon steel pieces were added to the test for visual determination of corrosion. The results are shown in Table 9 and Figure 5.

The results shown in Table 9 indicates that minimum changes in water content and TAN and no signs of corrosion were observed in the carbon steel pieces as shown in Figure 5. Notably, the tested temperature is higher than the temperature needed to achieve the viscosity of 10 cSt (128°C) required for appropriate nozzle spray in a marine engine. Consequently, validating the thermal stability of the HTL oil under test conditions.

Table 9. Water content and TAN changes in the accelerated ageing test of chemically treated HTL oil (Accelerate ageing tests performed at 160°C for 140 hours)

Sample	Water content blend [wt%]	TAN blend [mg KOH/g]	Viscosity [cSt at 25°C]
Chemically treated HTL oil	Water ≈ 0.24 → 0.20	TAN ≈ 4.5 → 4.6	≈ 3691 → 4121

Compared to the HTL biocrude, the chemically treated HTL oil has 86% less TAN, and slightly less oxygen content. Further, saturates, aromatics and polars distribution changes slightly towards an increase of saturates and aromatics as confirmed by SAP (Tables 6 & 10). In the FTIR analysis (Figure 6), slight changes are observed in the aromatic area (100-1500 cm⁻¹), while considerable shifting of

carboxylic bonded groups (1705 cm^{-1}) towards carbonyl free groups (1742 cm^{-1})
i.e. 47% reduction of carbonyl bonded and 98% increase in carbonyl free bands
are observed after chemical treatment of the HTL oil.

5 **Table 10.** Properties of low oxygen containing HTL biocrude and chemically treated HTL oil

Test	HTL biocrude	Chemically treated HTL oil
Water Content [wt%]	0.18	0.24
Ash [wt%]	0.09	0.09
MCR [wt%]	17.08	15.64
TAN [mg KOH/g]	33.19	4.48
SAN [mg KOH/g]	BDL	BDL
HHV daf [MJ/kg]	38.14	39.37
Density @ 15 °C [kg/m ³]	1043	1044
Kinematic Viscosity @ 50°C [cSt]	177	256
Temp. to reach 10 cSt [°C]	103	128
<i>Metal analysis</i>		
Aluminum + Silicon [mg/kg]	<10.6	<5
Sodium – Na [mg/kg]	297	158
Vanadium – V [mg/kg]	<2.0	<1.5
<i>Elemental analysis (daf)</i>		
Carbon [wt.%]	80.89	83.22
Hydrogen [wt%]	9.15	9.52
Nitrogen [wt%]	0.25	0.21
Sulphur [mg/kg]	146	227
Oxygen [wt%]	9.69	7.04
H/C Molar Ratio	1.35	1.36
<i>SAP by TLC-FID</i>		
Saturates [wt%]	8.2	10.90
Aromatics [wt%]	26.4	28.80
Polars [wt%]	65.4	60.30
Pour point [°C]	6	-4
Flash Point [°C]	74	82
<i>SimDist</i>		
Naphtha (IBP-150°C) [wt%]	1.93	0
Middle distillates (150–343°C) [wt%]	38.68	33.49
Heavy gas oils (343-550°C) [w.%]	39.87	38.94
Residue (550+°C) [wt%]	19.51	27.57

Further sodium content reduction in the chemically treated HTL oil (from 158 to 90 ppm) was accomplished by combining the cooled converted mixture of step f as depicted in Figure 3 with demineralized water in a ratio of 1:1. The water and cooled converted mixture was then separated by gravity, and the products after separation were atmospherically distilled to separate the unreacted additive, remaining water, and light fraction (IBP-180°C) from the chemically treated HTL oil.

10 **Example 4: Compatibility of chemically treated HTL oil with conventional marine fuel**

Compatibility of the chemically treated HTL oil produced as described in example 3 with conventional marine fuel was tested.

15 All of the properties improvement indicated in example 3 increase slightly the HHV and improves the compatibility of the chemically treated HTL oil with petroleum-derived marine fuels, up to 50% blend, as confirmed by spot tests and microscope shown in Figure 7.

20 The chemical treatment process according to the present invention has shown to have remarkable potential for the thermal stabilization of HTL biocrude. The process effectively increases thermal stability while reducing the acidity of the biocrude, eliminating the need for hydrotreating the HTL biocrude.

25 The comparative analysis of the chemical properties of the chemically treated HTL oil and marine fuel provides evidence for the potential of the former to serve as a viable option for marine fuel utilization. The chemically treated HTL oil exhibits superior properties to conventional marine fuels, such as a lower sulphur content, which is an essential factor in reducing GHG emissions from shipping.

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CLAIMS

1. A process for producing low oxygen containing Hydrothermal Liquefaction (HTL) oil with improved thermal stability and low inorganic content comprising
- 5 the steps:
- a. Providing a low oxygen containing HTL biocrude having:
- an oxygen content in the range of 3.0 to 15 wt%,
 - a water content of less than 1.5 wt%,
 - a total acid number in the range of 20 to 80 mg KOH/g,
 - 10 - an oil fraction having a boiling point below 350°C of less than 70 wt%,
 - a residue fraction having a boiling point of more than 450°C of at least 10 wt%; and
 - an ash content below 0.1 wt%;
- b. Heating the low oxygen containing HTL biocrude of step a to a temperature
- 15 in the range of 25 to 80°C;
- c. Adding and mixing an additive comprising at least one alcohol to the heated low oxygen containing HTL biocrude of step b;
- d. Further heating the mixture of step c to a temperature in the range of 80 to 200°C in a reaction zone;
- 20 e. Maintaining the heated mixture of step d in the reaction zone for a conversion time of 1 to 200 hours;
- f. Cooling the converted mixture of step e to a temperature in the range of 20 to 180°C; and
- 25 g. Separating the cooled converted feed mixture of step f into a chemically treated HTL oil, a light boiling point fraction, water and un-consumed additive.
2. The process according to claim 1, where the additive in step c comprises at least one alcohol in the concentration of 1 to 70 wt%, preferably 3 to 50 wt%, more preferably between 5 to 40 wt%.
- 30 3. The process according to any one of claims 1 and 2, where the mixture of low oxygen containing HTL biocrude and additive are heated in step d to a temperature in the range of 100 to 180°C, preferably in the range of 130 to 170°C.
- 35

4. The process according to any one of claims 1 to 3, where the heated mixture of low oxygen containing HTL biocrude and additive is maintained in the reaction zone in step e for a conversion time between 3 to 180 hours, preferably between 10 to 160 hours.
- 5
5. The process according to any one of the claims 1 to 4, where the heated mixture of step e reaches a pressure in the reaction zone of between 3 to 200 bar, more preferred from 5 to 150 bar, even more preferred from 7 to 110 bar.
- 10
6. The process according to any one of claims 1 to 5, where the chemically treated HTL oil obtained in step g has a total acid number of at least 6 to 24 mg KOH/g.
- 15
7. The process according to any one of claims 1 to 6, where the process comprises a further step of reducing the level of inorganic content to below 200 ppm, preferably below 100 ppm, by mixing the cooled converted mixture of step f with a liquid containing at least 70wt% of demineralized water.
- 20
8. The process according to claim 1, where the heated mixture of low oxygen containing HTL biocrude and additive is maintained in the reaction zone in step e under constant agitation thereby reducing the conversion time to between 1 to 70 hours.
- 25
9. The process according to any one of claims 1 to 8, where the reaction zone in step d comprises a first sub-reaction zone and a second sub-reaction zone, and where the mixture of low oxygen containing HTL biocrude and additive of step c is maintained in the first sub-reaction zone for 10 to 170 hours to obtain a TAN reduction of at least 50% and thereafter the reacted mixture product of the first sub-reaction zone is further mixed with additive to obtain a
- 30
- concentration of additive in the range of 5 to 30 wt%, and the mixture is maintained in the second sub-reaction zone for 10 to 110 hours to obtain a further TAN reduction of at least 20%.
- 10.
- 35
10. The process according to claim 9, where the temperature is adjusted to 100 to 170°C after mixing the reacted mixture product of the first sub-reaction zone with additive.

11. The process according to any one of claims 1 to 10, where the kinematic viscosity at 50°C of the low oxygen containing HTL biocrude provided in step a is in the range of 150-200 cSt and the kinematic viscosity at 50°C of the chemically treated HTL oil obtained in step g is in the range of 230-280 cSt.

12. The process according to any one of claims 1 to 11, where the low oxygen containing HTL biocrude in step a is provided by a process comprising:

- Providing a carbonaceous material in the form of biomass contained in one or more feedstocks;
- Providing a feed mixture by slurring the carbonaceous material in one or more fluids, at least one of which comprises water;
- Pressurizing the feed mixture to a pressure in the range 150 to 400 bar;
- Heating the pressurized feed mixture to a temperature in the range of 300°C to about 450°C;
- Maintaining the pressurized and heated feed mixture for a conversion time in the range 3 to 30 minutes; and thereby causing the carbonaceous material to be converted;
- Cooling the converted feed mixture to a temperature in the range from 25°C to 200°C; and
- Expanding the converted feed mixture to a pressure in the range 1-120 bar, and separating the converted feed mixture into at least a low oxygen containing HTL biocrude, a gas phase and a water phase comprising water-soluble organics and dissolved salts;

thereby providing the low oxygen containing HTL biocrude having an oxygen content in the range from 3.0 wt% to 15 wt%, a water content of less than 1.5 wt%, a total acid number in the range from 20 to 80 mg KOH/g, an oil fraction having a boiling point below 350°C of less 70 wt%, a residue fraction having a boiling point of more than 450 °C of at least 10 wt%, and an ash content below 0.1 wt%.

13. A HTL oil with improved thermal stability and low inorganic content, preferably obtainable by the process according to any one of claims 1 to 12, wherein said HTL oil comprises:

- an oxygen content of at most 10 wt%,
- a water content of less than 0.1 wt%,

- a total acid number of at most 6 mg KOH/g,
- an ash content of less than 400 ppm,
- a flash point of at least 60°C,
- an oil fraction having a boiling point below 150°C of at most 0.1 wt%,
- 5 - an oil fraction having a boiling point below 350°C of 30-40 wt%, and
- a residue fraction having boiling point of at least 550°C of at least 20 wt%.

14. The HTL oil according to claim 13, wherein the ash content is less than 100 ppm.

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15. Use of the chemically treated HTL oil with improved thermal stability and low inorganic content of any one of claims 13 and 14, preferably obtainable by the process according to any one of claims 1 to 11 as marine fuel, co-processing feedstock in commercial refineries, or in stand-alone upgrading facilities.