

REMOVAL OF ARSENIC IN RENEWABLE FUEL PRODUCTION

TECHNICAL FIELD

The present invention relates to the removal of arsenic in the processing of renewable feedstocks.

5 BACKGROUND

A particular problem, but hitherto unrealized problem, with certain renewable feedstocks and especially those that are produced from residual and waste products is that they may, contrary to what is common for first generation plant oil based renewable feedstocks, contain heteroatom contaminants such as arsenic (As). Arsenic is known to be a severe catalyst
10 poison and efficient hydrotreating process requires completely removal of As prior to the hydrotreating process. Arsenic is further due to its high degree of toxicity unwanted in bio-fuel product streams. Thus, arsenic must be removed when processing renewable feedstocks, in particular sewage sludge.

On the other hand, arsenic removal is not such an issue in fossil fuel-based refining
15 processes, as the arsenic content of the feed in fossil fuels is typically significantly lower.

Commercial plants processing fossil based feedstocks or first generation renewable feedstocks conventionally remove arsenic together with other possible heteroatom s such as phosphorus (P), silicon (Si), iron (Fe), nickel (Ni), vanadium (V), halides or combinations thereof, as the first step prior to the hydrotreating processes. This is necessary in
20 conventional processes because such heteroatoms quickly deactivate conventional catalysts for hydrotreating and cycle length is reduced dramatically. Refiners processing fossil feedstocks containing arsenic need to remove arsenic even if it is present in ppb levels as it is a severe catalyst poison. Because of this deactivation, refiners processing renewable feedstocks are forced to load more material for guarding the hydrotreating catalyst. For
25 processing renewable feedstocks said hydrotreating processes comprise both the initial stabilization processes of the liquid oil feed as well as the subsequent catalytic hydroprocessing.

SUMMARY

It has been found by the present inventor(s) that arsenic may be effectively removed after a liquid oil feed has been through a stabilization process step which provides a stabilized liquid oil feed and before a process step comprising catalytic hydroprocessing. The arsenic is
5 captured using a guard material. In this way, removal of arsenic may take place between the initial stabilization and the catalyst hydroprocessing. For processing renewable feedstocks with a high content of arsenic it is surprisingly not necessary to remove the arsenic prior to the hydrotreating process as for the conventional process. Some conversion of organically bound arsenic may occur in the stabilization reactor, which is why the stabilization reactor
10 may beneficially have a top layer suited for capture of solid heteratom products, e.g. by having an open structure.

So, in a first aspect the present invention relates to a process for removal of arsenic in the processing of renewable feedstocks. Said process comprises using a system comprising:

- a liquid oil feed derived from a renewable feedstock;
- 15 - a stabilization reactor;
- a guard material;
- at least a first hydroprocessing reactor;

wherein said process comprises the steps of:

- 20 - feeding the liquid oil feed to said stabilization reactor and providing a stabilized liquid oil feed;
- feeding at least a portion of the stabilized liquid oil feed to said guard material, and capturing the arsenic in the guard material, so to provide an arsenic-poor liquid oil
25 feed,
- feeding said arsenic-poor liquid oil feed to said hydroprocessing reactor, and subjecting it to catalytic hydroprocessing, to provide one or more hydroprocessed product stream(s).

Additional aspects of the invention are presented in the following description text, figures and
30 claims.

LEGENDS TO THE FIGURE

The technology is illustrated by means of the following schematic illustrations, in which:

Figure 1 shows a simple layout of one aspect of the system of the invention.

Figure 2 shows one embodiment the system of the invention.

Figure 3 shows another embodiment the system of the invention.

Figure 4 shows a third embodiment of the system of the invention. Embodiments combining
5 features of Figure 2-4 are also included in the invention.

Figure 5 shows the content of sulfur (S) in ppm in the product stream as a function of time given in normalised run hours, in the example.

DETAILED DISCLOSURE

10 A "unit" performs a change in the chemical composition of a feed, and may additionally comprise elements such as e.g. heat exchanger, mixer or compressor, which do not change the chemical composition of a feed or stream.

In a first aspect, a process for removal of arsenic in the processing of renewable feedstocks is provided. Said process comprises using a system comprising:

- 15 - a liquid oil feed derived from a renewable feedstock;
- a stabilization reactor;
- a guard material;
- at least a first hydroprocessing reactor.

Process aspects

20 In one specific aspect feeding the liquid oil feed to said stabilization reactor may involve contact a stabilization hydrotreatment catalyst, which comprises less than 10 wt% Ni, such as less than 8 wt% Ni, less than 5 wt% Ni or in which Ni is absent, with the associated benefit of such a material catalyzing stabilization reactions, without capture or deactivation by arsenic.

25 In another specific aspect, said guard material comprises more than 10 wt% Ni, such as more than 12 wt% Ni. This has the benefit of high concentrations of Ni being beneficial for capture of arsenic as guard.

Renewable feedstock

In a first aspect, the process comprises a liquid oil feed derived from a renewable feedstock.

In one aspect, said renewable feedstock comprises:

- 5 - a lignocellulosic biomass such as wood products, algae, grass, forestry waste and/or agricultural residue;
 - municipal waste, in particular the organic portion thereof, where the municipal waste is defined as a feedstock containing materials of items discarded by the public, such as mixed municipal waste given in EU Directive 2018/2001 (RED II), Annex IX, part A
 - nitrogen-rich renewable feedstock such as manure or sewage sludge.
- 10 In an embodiment, the portion of the renewable feedstock originating from a renewable source is 5-60 wt%, such as 10 or 50 wt%. In another embodiment, the portion of the feedstock originating from a renewable source is higher than 60 wt%, for instance 70-90 wt%. When the renewable source is recycled waste, this may be characterized by the content of biological matter, since a part of the waste may be of non-biological origin, such as waste
- 15 plastic. Objectively the amount of biological matter may be judged by the C-isotope content, since the ¹⁴C-isotope is practically absent in fossil material. Therefore renewable feedstock rich in biological material can be defined as feedstock where in at least 20 % of the carbon is ¹⁴C. One source of waste is municipal waste rich in biological material containing materials of items discarded by the public, such as mixed municipal waste given in EU Directive
- 20 2018/2001 (RED II), Annex IX, part A. *Deriving the liquid oil feed*

Said renewable feedstock may need to be decomposed to produce said liquid oil feed.

Therefore, in one aspect, said process further comprises a step of thermal decomposition of the renewable feedstock to produce said liquid oil feed where said thermal decomposition comprises a pyrolysis step and/or a hydrothermal liquefaction step.

- 25 The pyrolysis step may include the use of a pyrolysis unit such as fluidized bed, transported bed, or circulating fluid bed, as is well known in the art. For instance, the pyrolysis step may comprise the use of a pyrolysis unit (also referred herein as pyrolysis reactor), cyclone(s) to remove particulate solids such as char, and a cooling unit for thereby producing an off-gas stream (i.e., pyrolysis off-gas) and said liquid oil stream, i.e. condensed pyrolysis oil. The off-
- 30 gas stream comprises light hydrocarbons e.g., C1-C4 hydrocarbons, CO and CO₂. The liquid oil stream is also referred to as pyrolysis oil or bio-oil and is a liquid substance rich in blends of molecules usually consisting of more than two hundred different compounds including aldehydes, ketones and/or other compounds such as furfural having a carbonyl group,

resulting from the depolymerisation of products treated in pyrolysis. In this way, the liquid oil feed derived from a renewable feedstock may be pyrolysis oil or bio-oil.

In an embodiment, the pyrolysis step comprises fast pyrolysis, also referred to in the art as flash pyrolysis. Fast pyrolysis means the thermal decomposition of a solid renewable feedstock in the absence of oxygen, at temperatures in the range 350-650°C e.g. about 500°C and reaction times of 10 seconds or less, e.g. below 10 seconds, such as 5 seconds or less, e.g. about 2 seconds; i.e. the vapor residence time is 10 seconds or below, such as 2 seconds or less e.g. about 2 seconds. In this way, the reaction is provided with sufficient heat to at least partly decompose larger organic compounds such as polymers present in the renewable feedstock. The elevated temperature will not cause the renewable feedstock to combust because the reaction occurs under oxygen-poor conditions.

Traditionally, fast pyrolysis may for instance also be conducted by autothermal operation e.g., in a fluidized bed reactor. The latter is also referred as autothermal pyrolysis and is characterized by employing air, optionally with an inert gas or recycle gas, as the fluidizing gas, or by using a mixture of air and inert gas or recycle gas. Thereby, the partial oxidation of pyrolysis compounds being produced in the pyrolysis reactor (autothermal reactor) provides the energy for pyrolysis while at the same time improving heat transfer. For details about autothermal pyrolysis, reference is given to e.g. "Heterodoxy in Fast Pyrolysis of Biomass" by Robert Brown: <https://dx.doi.org/10.1021/acs.energyfuels.0c03512>. In an embodiment, the pyrolysis step comprises autothermal pyrolysis.

In embodiments, the pyrolysis step comprises catalytic fast pyrolysis (CFP). Such a catalytic fast pyrolysis step comprises using a catalyst e.g. an acid catalyst, such as a zeolite catalyst. Catalytic fast pyrolysis can both be operated in an in-situ mode, where the catalyst is located inside a pyrolysis unit, and in an ex-situ mode, where the catalyst is placed in a separate reactor.

The pyrolysis step may comprise in-situ catalytic fast pyrolysis. In one embodiment, the catalyst is located inside the pyrolysis unit and deoxygenation (DO) (through e.g. decarbonylation, decarboxylation by an acid-based catalyst such as a zeolite catalyst) takes place inside the pyrolysis reactor immediately after the pyrolysis vapours are formed. Suitable catalysts for CFP include alumina and all the types of zeolite catalysts that are normally used for hydrocracking (HCR) and cracking in refinery processes, such as HZSM-5. Alternatively, in one embodiment, a hydrotreating catalyst such as a hydrodeoxygenating catalyst is located in the pyrolysis unit, and the pyrolysis vapors are hydrodeoxygenated immediately in the pyrolysis reactor after they are formed. Said process is referred to as in-situ HDO (also called reactive catalytic fast pyrolysis, RCFP). Suitably catalysts for HDO are

metal-based catalysts, including reduced Ni, Mo, Co, Pt, Pd, Re, Ru, Fe, such as CoMo or NiMo catalysts, suitably also in sulfide form: CoMoS, NiS, NiMoS, NiWS, RuS. The catalyst supports may be the same in conventional HDO in refinery processes, typically a refractory support such as alumina, silica or titania, or combinations thereof.

- 5 The liquid product of pyrolysis oil renewable feedstock has not been known to contain arsenic of significance, such as levels of arsenic above 1 ppb-wt, 5 ppb-wt, 50 ppb-wt, 500 ppb-wt or 5 ppm-wt, and no specific advice on the processes for arsenic pyrolysis oil is found. The content of arsenic has been observed to be higher in pyrolysis oil of biological origin, than e.g. pyrolysis oil from recycled plastics, so while the process presented believed to be
10 relevant for pyrolysis oil in general, it is believed to be especially relevant for biological pyrolysis oil.

- The use of a catalyst in the pyrolysis reactor significantly reduces the required temperature for conducting the pyrolysis. In addition, increased selectivity towards desired pyrolysis oil compounds may be achieved. When catalytic fast pyrolysis is operated with feeds containing
15 arsenic, it is preferred that the catalyst for the pyrolysis section is not a Ni containing catalyst, such as Mo, CoMo or an acid catalyst, since these catalysts are less poisoned by the arsenic than Ni-based catalysts, also in this position.

- In an embodiment the pyrolysis step is fast pyrolysis, in which the vapor residence time is 10 seconds or less, e.g. below 10 seconds, such as 5 seconds or less, e.g. about 2 seconds, or 1
20 second, or in the range 1-5 seconds, and which is selected from: simple fast pyrolysis; in-situ catalytic fast pyrolysis (in-situ CFP); ex-situ catalytic fast pyrolysis (ex-situ CFP); reactive catalytic fast pyrolysis (RCFP); hydrolysis (HP); catalytic fast hydrolysis (CHP).

As an alternative to fast pyrolysis, intermediate and/or slow pyrolysis may also be used, and may – in some instances – be preferred.

- 25 In an embodiment, the pyrolysis step is intermediate pyrolysis, in which the vapor residence time is in the range of 10 seconds – 5 minutes, such as 11 seconds – 3 minutes. As for fast pyrolysis, the temperature is also in the range 350-650°C e.g. about 500°C. Often this pyrolysis is conducted in pyrolysis reactors handling different types of waste, where the vapor is burned after the pyrolysis reactor. Typical reactors are: Herreshoff furnace, rotary drums,
30 amaron, CHOREN paddle pyrolysis kiln, auger reactor, and vacuum pyrolysis reactor.

In another embodiment, the pyrolysis step is slow pyrolysis, in which the solid residence time is in the range of 5 minutes – 2 hours, such as 10 min – 1 hour. The temperature is suitably about 300°C. This pyrolysis gives a high char yield and the char can be used as a fertilizer or

as char coal; the pyrolysis still produces some gas and biocrude and if the carbon is used a fertilizer the final bio-oil can have a GHG above 100 %, thus being carbon negative. Typical reactors are auger reactor - yet with a different residence time than for intermediate pyrolysis -, fixed bed reactor, kiln, lambiotte SIFIC/CISR retort, Lurgi process, wagon reactor, and carbo twin resort.

Accordingly, said liquid oil feed comprises compounds formed under moderately elevated temperatures (>80 °C) but below the temperatures resulting in substantially complete hydrotreatment. Said liquid oil feed may comprise i) a feed rich in conjugated diolefins or styrene and its homologs resulting from thermochemical decomposition of plastic waste, municipal solid waste, refuse derived fuel and solid recovered fuel, ii) a feed rich in carbonyls and sugars resulting from thermochemical decomposition of lignocellulosic biomass and/or iii) a feed rich in nitrogen resulting from thermochemical decomposition of nitrogen-rich renewable feedstock, such as manure and sewage sludge, and/or similar compositions from other sources. In embodiments, said liquid oil feed may comprise larger compounds as the compounds resulting from thermochemical decomposition (e.g. compounds of i)-iii)) may subsequently react i.e. reactive functional groups may react with either the same functional group (e.g. diolefin with diolefin) or across functional groups (e.g. aldehyde with phenol) to provide larger compounds. Said larger compounds may potentially result in full or partial blockage of reactors, tubes, heaters, heat exchangers and catalysts comprised in later process steps.

Stabilization of the liquid oil feed

In a first aspect, the process comprises the use of a system comprising a stabilization reactor and said process comprises feeding the liquid oil feed to said stabilization reactor and providing a stabilized liquid oil feed.

The purpose of said process step is to provide a stabilized liquid oil feed, which may be characterised as a feed comprising a lower content of reactive compounds than the liquid oil feed. This may be achieved by modification of the chemical composition of the liquid oil and/or by removal of destabilization components from the liquid oil. Said stabilized liquid oil feed may have a lower vapor pressure than the liquid oil feed. In this way, said process step provides a less reactive liquid oil e.g. said stabilized liquid oil which may be fed as a feed in subsequent process steps.

In one aspect, said process comprises reacting said liquid oil feed with hydrogen within the stabilization reactor in the presence of a catalyst where said catalyst comprises at least one metal selected from Ni, Co, Mo, W, Cu, Pt, Pd, Ru such as said catalyst comprises nickel-

molybdenum molybdenum (Ni-Mo), cobalt-molybdenum (Co-Mo), nickel-tungsten (NiW), nickel-copper (NiCu), Pt, Pd, or Ru to provide at least one stabilized liquid oil feed.

5 In one aspect, said process comprises operating the stabilization reactor at a temperature of 100-230°C and at a pressure of 20-200 barg. Said temperature encompasses the inlet temperature of the liquid oil stream and the outlet temperature of stabilized liquid oil stream. The unit barg denotes pressure above atmospheric (atmospheric pressure is about 1 bar), where said pressure may also be referred to as "hydrogen pressure". Said process may be conducted at a hydrogen to liquid oil ratio of 500- 10000 NL/L, such as 2000-5000 NL/L, for 10 instance 2500, 3000, 3500, 4000 or 4500 NL/L. As used herein, the term "hydrogen to liquid oil ratio" or "H₂/oil ratio" means the volume ratio of hydrogen to the flow of the liquid oil stream. It would be understood, that the unit NL means "normal" liter, i.e. the amount of gas taken up this volume at 0°C and 1 atmosphere. The volume of liquid is taken as standard volume at 15°C and 1 atmosphere.

15 In this way, said process step may result in the modification of the liquid oil feed composition through hydrogenation to remove destabilizing components from the liquid oil feed, thus said process convert reactive compounds present in the liquid oil feed to less reactive compounds under low temperature conditions. In one aspect, the liquid oil feed comprises at least 0.5 20 wt% oxygen (O), such as at least 4 wt% O, such as at least 20 wt% O, such as at least 30 wt% O, or at least 45 wt% O. Pyrolysis oil from recycled plastic typically contains 0.5-4 wt% O, while pyrolysis oil from biological materials typically contains 5-50 wt% O. The oxygen may be present as reactive compounds such as furfural, furans, aldehydes, ketones and acids, which may be converted into alcohols, for instance by efficiently converting carbonyls 25 into alcohols. Conversion of carbonyls into alcohols occurs at a temperature of approx. 200°C (temperature within the reactor). The alcohols can further be converted to saturated organic compounds during the stabilization, and/or in a subsequent hydroprocessing process step such as hydrodeoxygenation (HDO).

30 In one specific embodiment, said process step comprises hydrotreating a liquid oil stream by, in a continuous operation in a fixed bed reactor, reacting the liquid oil stream with hydrogen in the presence of a nickel-molybdenum (Ni-Mo) based catalyst at a temperature, e.g. inlet temperature, of 100-230°C, a pressure of 100-200 barg, a liquid hourly space velocity (LHSV) of 0.1 -1.1 h⁻¹, and a hydrogen to liquid oil ratio, defined as the volume ratio of 35 hydrogen to the flow of the liquid oil stream, of 500-10000 NL/L, such as 2000-5000 NL/L, thereby forming a stabilized liquid oil stream.

The combination of features i.e. low temperatures, high pressure, low LHSV and high H₂-to liquid oil ratio, as recited above, enables stabilization of the liquid oil by i.e. converting

carbonyls to alcohols and thereby increase operation time before plugging issues - if any - arise, while at the same time suppressing coking of the catalyst and attendant catalyst deactivation, as well as avoiding hydrogen starvation.

- 5 The temperature range 100-230°C encompasses the inlet temperature of the liquid oil stream and the outlet temperature of stabilized liquid oil stream. For instance, the inlet temperature can be 100, 110, 120 or 130°C. The higher the inlet temperature e.g. 130°C, the easier the ignition of the process to initiate the exotherm. The outlet temperature can for instance be 200 or 215 or 230°C. More generally, the temperature in a given step or reactor (unit)
- 10 thereof, means the inlet temperature in an adiabatic step, or the reaction temperature in an isothermal step. Accordingly, suitably said temperature of 100-230°C means inlet temperature. The term continuous operation, as is well known in the art, means that the incoming stream of liquid oil during a given production cycle is constant, as also is the stabilized liquid oil stream being withdrawn as the outcoming product. This contrasts a batch
- 15 operation i.e. discontinuous operation, as is also well known in the art, in which the total amount of liquid oil and catalyst is introduced at the beginning of the process, and the outcoming product is withdrawn after a certain period of time.
- Hence, low temperature (100-230°C) operation result in stabilization of a liquid oil and avoids plugging problems, but also allows for stabilization without deactivating the catalyst and
- 20 without risk of hydrogen starvation. Surprisingly, it has been found that arsenic does not in any significant manner interact/react with any material present within the stabilization reactor such as with a catalyst under the low temperature conditions, thus does not deactivate the catalyst. In this way, arsenic may be removed from the stabilized liquid oil feed in a subsequent process step using a guard material.

25

Capturing the arsenic and optionally additional heteroatom(s)

- In a first aspect, a process for removal of arsenic in the processing of renewable feedstocks is provided, wherein said process comprises feeding at least a portion of the stabilized liquid oil feed to said guard material, and capturing the arsenic in the guard material, so to provide an
- 30 arsenic-poor liquid oil feed. Arsenic-poor may be considered on an absolute scale, such as less than 1 ppb-wt, 5 ppb-wt or 50 ppb-wt, or on a relative scale, such as less than 10 % or less than 1 % of the arsenic content of the feedstock.

- The liquid oil feed may comprise 5 ppb-wt – 50 wt ppm-wt arsenic (As). The content of arsenic may vary significantly depending on the feedstock. For instance, the As content
- 35 maybe 5ppb or greater. The ppm units are provided on weight basis. i.e. ppm-wt. In one aspect, the process further comprises capturing one or more additional heteroatom(s) in the

guard material where said heteroatom(s) is/are selected from one or more of phosphorus (P), silicon (Si), iron (Fe), nickel (Ni), vanadium (V), halides or combinations thereof. Said heteroatoms may be advantageously captured as they can solidify as sulfides or other solid compounds in said guard material.

5

The guard material capturing the arsenic may be a metal guard bed. A metal guard bed means a bed i.e. a fixed bed which comprises a material active in hydrometallation (HDM) and/or hydrodeoxygenation (HDO). The process of hydrodemetallation (HDM) is meant to
10 cover a pre-treatment, by which free metals are generated and then converted into metal sulfides. Hydrodemetallation hereby differ from e.g. hydrodesulfurization (HDS) as, the heteroatom (S) in HDS is removed in gas form. In addition to removing arsenic and additional heteroatoms such as P, Si, Fe, Ni, V, halides and combinations thereof, the guard material may also be provided with deoxygenation activity.

15

A suitable guard bed may be a porous material comprising alumina, the alumina comprising alpha-alumina. The alumina may further comprise theta-alumina such as 0-50 wt% and optionally smaller amounts gamma-alumina such as 0-10 wt% as determined by XRD. Said porous material may have a BET-surface area of 1-110 m²/g measured according to ASTM
20 D4567-19 (i.e. single-point determination of surface area by the BET equation), suitably also having a total pore volume of 0.50-0.80 ml/g, as measured by mercury intrusion porosimetry according to ASTM D4284. The pore size distribution (PSD) of said porous material may be of at least 30 vol% of the total pore volume being in pores with a radius > 400 Å, suitably pores with a radius > 500 Å, such as pores with a radius up to 5000 Å; as for instance disclosed in
25 Applicant's co-pending patent application PCT/EP2021/068656. The porous material may further comprise one or more metals selected from Co, Mo, Ni, W and combinations thereof, preferably Ni. Combinations of Ni with at least one other metal are possible. The content of the one or more metals is 0.25-20 wt%, such as 0.25-15 wt%, 0.25-10 wt%, or 0.25-5 wt%. In one embodiment, at least one metal is in the form of oxides or sulfides.

30

In one embodiment, a suitable guard bed is a catalyst comprising molybdenum supported on alumina, i.e. a Mo/Al₂O₃ catalyst. In yet another embodiment, a suitable catalyst is a catalyst having demetallization activity and moderate hydrodesulfurization activity, such as a commercial NiMo/Al₂O₃ catalyst. In this way, in one aspect, said process comprises capturing
35 the arsenic in the guard material where said guard material is a metal guard bed such as Mo/Al₂O₃ and/or Ni/Al₂O₃.

Guards for the purpose of capture arsenic preferably contain high amounts of Ni, such as 10-20 wt%. In addition low amounts of Mo are beneficial, such as less than 1 wt% Mo, less than 0.5 wt% Mo or absence of Mo.

5 Use of a porous material with pores above 400 Å allows for better penetration of the stabilized liquid oil feed, and thereby penetration of arsenic comprising molecules. The porous material may for instance show a broad peak as a unimodal pore system or show a bimodal or even trimodal pore system, in which particularly the smaller pores add the possibility for providing the hydrotreating activity to the porous material.

10 It is advantageous that the guard material has some hydrotreating activity such as deoxygenation activity to avoid coking and high exothermicity when contacting the feed with the main downstream catalyst bed for hydrotreating. The most reactive molecules in the feed are converted, thereby reducing the risk of excessive temperature rise which can lead to gumming. Said hydrotreating activity may be achieved by the presence of one or more metals selected from Co, Mo, Ni, W and combinations thereof, preferably Ni, when present in
15 the porous material in the content of 0.25-20 wt%, such as 0.25-15 wt%, 0.25-10 wt%, or 0.25-5 wt%. Furthermore, some preheating of said arsenic-poor liquid oil feed is achieved prior to said feed being fed to said hydroprocessing reactor, and subjecting it to catalytic hydroprocessing. Said preheating is an advantage as the hydroprocessing reactor may be operated at elevated temperatures compared to temperatures used for operating the
20 stabilization reactor. In one aspect, said process comprises operating the guard material optionally as guard material unit(s) at a temperature above 250°C, such as at 250-360 °C. Said temperature enables optimised capture of arsenic within said guard material through the process of hydrodemetalation.

25 Said guard material may be arranged in a variety of ways. In one aspect, at least a portion of said guard material is located within said first catalytic hydroprocessing reactor, upstream the hydroprocessing catalyst. This may be an advantage as said first catalytic hydroprocessing reactor is heated to elevated temperatures such as above 250°C, wherefore the guard material without further arrangements is operated at a temperature above 250°C.

30 In aspects, said guard material is arranged in units and said process comprises using one or more guard material units. In aspects where more than one guard material units are used, said process may comprise using more than one guard material units arranged in parallel. Alternatively, or additionally, said process may comprise using more than one guard material units arranged in series. Using more than one guard material unit allows for said unit e.g.
35 reactor to be exchanged without any other additional changes in the system, preferably without pausing said process during the exchange.

Some conversion of organically bound arsenic and/or other heteroatoms may occur in the stabilization reactor. In this way, it may be beneficial to additionally capture heteroatoms such as solid heteroatom products at the inlet of the stabilization reactor, such as in a guard material. Accordingly, in one aspect, said process may further comprise that the stabilization reactor additionally comprises a top layer suited for capture of solid heteroatom products, e.g. by having an open structure.

In aspects, the arsenic-poor liquid oil provided by the capturing the arsenic process step is subsequently feed as a feed to said hydroprocessing reactor, and subjecting it to catalytic hydroprocessing.

15 *Catalytic hydroprocessing*

In a first aspect, the process comprises using a system comprising at least a first hydroprocessing reactor and feeding said arsenic-poor liquid oil feed to said hydroprocessing reactor, and subjecting it to catalytic hydroprocessing, to provide one or more hydroprocessed product stream(s). In this way, the process encompasses at least one catalytic hydroprocessing step.

In one aspect, said process comprises one or more catalytic hydroprocessing steps selected from hydrodeoxygenation (HDO), hydrotreating, hydrodenitrogenation (HDN), hydrodesulfurization (HDS), saturation of aromatic rings (HDA), hydrocracking and/or isomerisation, performed within one or more hydroprocessing reactors. Hydrodeoxygenation (HDO) refers to the process where oxygen is removed from the liquid oil feed mainly as H₂O.

The material catalytically active in hydrotreating, e.g. HDO, typically comprises an active metal (sulfided base metals such as nickel, cobalt, tungsten and/or molybdenum, but possibly also either elemental noble metals such as platinum and/or palladium) and a refractory support (such as alumina, silica or titania, or combinations thereof). Hydrotreating e.g. HDO conditions involve a temperature in the interval 250-400°C, a pressure in the interval 30-200 bar, and a liquid hourly space velocity (LHSV) in the interval 0.1-2, optionally together with intermediate cooling by quenching with cold hydrogen, feed or product.

Hydrodearomatization (HDA) refers to a hydrotreating process in which hydrogen is used in the presence of heat, pressure, and catalysts to saturate aromatic hydrocarbons to produce low-aromatic hydrocarbon content in the product stream. The material catalytically active in

hydrodearomatization typically comprises an active metal (typically elemental noble metals such as platinum and/or palladium but possibly also sulfided base metals such as nickel, cobalt, tungsten and/or molybdenum) and a refractory support (such as amorphous silica-alumina, alumina, silica or titania, or combinations thereof). Hydrodearomatization conditions involve a temperature in the interval 200-350°C, a pressure in the interval 20-200 bar, and a liquid hourly space velocity (LHSV) in the interval 0.5-8.0.

Hydrocracking refers to a bi-functional catalytic process combining catalytic cracking and hydrogenation, thus wherein the liquid oil feed undergo cracking in the presence of hydrogen. The material catalytically active in hydrocracking is of similar nature to the material catalytically active in isomerization, and it typically comprises an active metal (either elemental noble metals such as platinum and/or palladium or sulfided base metals such as nickel, cobalt, tungsten and/or molybdenum), an acidic support (typically a molecular sieve showing high cracking activity, and having a topology such as MFI, BEA and FAU) and a refractory support (such as alumina, silica or titania, or combinations thereof). The difference to material catalytically active isomerization is typically the nature of the acidic support, which may be of a different structure (even amorphous silica-alumina) or have a different acidity e.g. due to silica:alumina ratio. Hydrocracking conditions involve a temperature in the interval 250-400°C, a pressure in the interval 30-200 bar, and a liquid hourly space velocity (LHSV) in the interval 0.5-8.0, optionally together with intermediate cooling by quenching with cold hydrogen, feed or product.

Isomerization process (including hydrodewaxing) is intended to improve flow indexes of the liquid oil feed. The material catalytically active in isomerization typically comprises an active metal (either elemental noble metals such as platinum and/or palladium or sulfided base metals such as nickel, cobalt, tungsten and/or molybdenum), an acidic support (typically a molecular sieve showing high shape selectivity, and having a topology such as MOR, FER, MRE, MWW, AEL, TON and MTT) and a refractory support (such as alumina, silica or titania, or combinations thereof). Isomerization conditions involve a temperature in the interval 250-400°C, a pressure in the interval 20-200 bar, and a liquid hourly space velocity (LHSV) in the interval 0.5-8.0.

30 *Specific embodiments of the invention*

Figure 1 shows a schematic process for removal of heteroatoms according to the invention. Liquid oil feed (1) is fed to stabilization reactor (10) and provides a stabilized liquid oil feed (11). The stabilized liquid oil feed (11) is fed to the guard material (20), and the heteroatoms are captured in the guard material, so to provide an heteroatom-poor liquid oil feed (21). The

heteroatom-poor liquid oil feed (21) is fed to hydroprocessing reactor (30) which may contain one or more catalyst of similar or different nature, and subjected to catalytic hydroprocessing, to provide hydroprocessed product stream(s) (31).

Figure 2 shows a similar layout to that of Figure 1, in which two or more guard material units (20a,b,c) are arranged in parallel. Figure 3 shows a similar layout to that of Figure 1, in which two or more guard material units (20a,b,c) are arranged in series. Figure 4 shows a similar layout to that of Figure 1, in which guard material (20) is located within the first catalytic hydroprocessing reactor (30), upstream the hydroprocessing catalyst.

EXAMPLES

10 The uptake of arsenic was tested with and without the use of guard material in two tests.

A liquid oil feed derived from different batches of sewage sludge containing about 6 wt ppm arsenic and with a sulfur content of about 1 wt% and an oxygen content of about 6 wt% was processed in a pilot plant unit equipped with two reactors in series followed by a gas liquid separation section. In test 1 115 ml of a commercially available Ni-Mo based catalyst was loaded in the first reactor for stabilization and 115 ml of a commercially available high activity Ni-Mo based catalyst was loaded in the second reactor for hydroprocessing. In test 2 the first reactor was loaded as in test 1 and the second reactor was loaded with 57.5 ml guard catalyst on top of 115 ml of the same hydroprocessing catalysts as loaded in test 1. The guard catalyst was a Ni based alumina catalyst.

20 Test 1 and 2 were conducted with a feed flow of 57.5 ml/h using a hydrogen to liquid oil ratio of 4000 NI/I at a pressure of 70 barg. The reactor temperature in the first reactor was for both tests kept constant at 220°C. In test 1 the second reactor was operated at the following reactor temperatures: 330°C, 340°C, 360°C, and 380°C. In test 2 the following reactor temperatures were used in the second reactor: 330°C, 340°C, 360°C, 380°C, and 400°C.

25 The amount of sulfur in the liquid product sampled after the reactor system was measured by the ASTM method D-7039. The product sulfur in ppm in the liquid product is shown in Fig. 5 as a function of time (hours). The reactor temperature used in the second reactor is shown in the legend. Test 1 without guard material resulted in a significantly higher sulfur content in the product stream as compared to the sulfur content found in test 2 with guard catalyst at comparable temperatures of the second reaction. The tested showed a fast deactivation of the hydroprocessing catalyst when no guard material was present. No deactivation is observed for the hydroprocessing catalyst in the tests comprising guard material.

The present invention has been described with reference to a number of embodiments and examples. The skilled person may combine these embodiments and examples within the scope of the invention, which is defined by the claims. All references cited here are incorporated by reference.

CLAIMS

1. A process for removal of arsenic in the processing of renewable feedstocks using a system comprising:

- 5
- a liquid oil feed (1) derived from a renewable feedstock;
 - a stabilization reactor (10);
 - a guard material (20);
 - at least a first hydroprocessing reactor (30);

wherein said process comprises the steps of:

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- feeding the liquid oil feed (1) to said stabilization reactor (10) to contact a stabilization hydrotreatment catalyst and providing a stabilized liquid oil feed (11);
 - feeding at least a portion of the stabilized liquid oil feed (11) to said guard material (20), and capturing the arsenic in the guard material, so to provide an arsenic-poor liquid oil feed (21),
 - 15 - feeding said arsenic-poor liquid oil feed (21) to said hydroprocessing reactor (30), and subjecting it to catalytic hydroprocessing, to provide one or more hydroprocessed product stream(s) (31),
 - wherein said stabilization hydrotreatment catalyst comprises less than 10 wt% Ni, such as less than 8 wt% Ni, less than 5 wt% Ni or in which Ni is absent,
 - 20 - and wherein said guard material comprises more than 10 wt% Ni, such as more than 12 wt% Ni.

2. The process according to claim 1, wherein the renewable feedstock contains :

- 25
- a lignocellulosic biomass such as wood products, algae, grass, forestry waste and/or agricultural residue;
 - municipal waste, in particular the organic portion thereof,
 - nitrogen-rich renewable feedstock such as manure or sewage sludge.

3. The process according to any one of the preceding claims, wherein said process further comprises a step of thermal decomposition of the renewable feedstock to produce said liquid oil feed where said thermal decomposition comprises a pyrolysis step and/or a hydrothermal liquefaction step.

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4. The process according to any one of the preceding claims, wherein the liquid oil feed comprises at least 1 wt % oxygen (O), such as at least 20 wt% O, such as at least 30 wt% O, or at least 45 wt% O.

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5. The process according to any one of the preceding claims, wherein said process comprises operating the stabilization reactor (10) at a temperature of 100-230°C and at a pressure of 20-200 barg.
6. The process according to any one of the preceding claims, wherein said process comprises reacting said liquid oil feed (1) with hydrogen within the stabilization reactor (10) in the presence of a stabilization hydrotreatment catalyst where said catalyst comprises at least one metal selected from Ni, Co, Mo, W, Cu, Pt, Pd, Ru such as said catalyst comprises nickel-molybdenum molybdenum (Ni-Mo), cobalt-molybdenum (Co-Mo), nickel-tungsten (NiW), nickel-copper (NiCu), Pt, Pd, or Ru to provide at least one stabilized liquid oil feed (11).
7. The process according to any one of the preceding claims, wherein the stabilization reactor additionally comprises a top layer suited for capture of solid heteroatom products, e.g. by having an open structure.
8. The process according to any one of the preceding claims, wherein said guard material (20) is arranged in units and wherein said process comprises using one or more guard material units (20a,b,c).
9. The process according to claim 7, wherein said process comprises using two or more guard material units (20a,b,c) arranged in parallel.
10. The process according to claim 7, wherein said process comprises using two or more guard material units (20a,b,c) arranged in series.
11. The process according to any one of the preceding claims, wherein at least a portion of said guard material (20) is located within said first catalytic hydroprocessing reactor (30), upstream the hydroprocessing catalyst.
12. The process according to any one of the preceding claims, wherein said process comprises capturing the arsenic in the guard material (20) where said guard material (20) is a metal guard bed such Ni/Al₂O₃.
13. The process according to any one of the preceding claims, wherein said process comprises operating the guard material (20) at a temperature above 250°C, such as at 250-420°C.

14. The process according to any one of the preceding claims, wherein said process comprises capturing one or more additional heteroatom(s) in the guard material (20) where said heteroatom(s) is/are selected from one or more of phosphorus (P), silicon (Si), iron (Fe),
5 nickel (Ni), vanadium (V), halides or combinations thereof.

15. The process according to any one of the preceding claims, wherein said one or more catalytic hydroprocessing steps are selected from hydrodeoxygenation (HDO), hydrotreating, hydrodenitrogenation (HDN), hydrodesulfurization (HDS), saturation of aromatic rings (HDA)
10 hydrocracking and/or isomerisation.