By the present invention, the liquid oil, e.g. pyrolysis oil is stabilized at low temperatures by the conversion of at least the most reactive compounds in the pyrolysis oil, such as furfural, furans, aldehydes, ketones and acids, into alcohols, for instance by efficiently converting carbonyls into alcohols. The alcohols can further be converted to saturated organic compounds during the stabilization, and/or in a subsequent hydroprocessing stage such as HDO.

SUMMARY

In an aspect of the present disclosure, there is provided a process for 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 of 20-240°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 hydrogen to the flow of the liquid oil stream, of 1000-6000 NL/L, thereby forming a stabilized liquid oil stream; wherein a carbonyl number of the stabilized liquid oil stream is below 3.0 mol/kg, as measured by ASTM E 3146, and wherein a ratio of the carbonyl number of the liquid oil stream to a carbonyl number as measured by ASTM E 3146 in mol/kg of the stabilized liquid oil stream is monitored and maintained at 1.7 or higher.

DESCRIPTION

Accordingly, in a first aspect, the invention provides a process for 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 20-240°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 hydrogen to the flow of the liquid oil stream, of 1000-6000 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 H_2-to liquid oil ratio, as recited above, enables stabilization of the liquid oil by i.a. 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

It would be understood that the unit “barg” denotes pressure above atmospheric (atmospheric pressure: about 1 bar). The pressure is also referred as “hydrogen pressure”.

The temperature range 20-240°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 20, 40, 60 or 80°C. The process is exothermic thus a raise in temperature of about 100°C or more occurs. The higher the inlet temperature e.g. 80°C, the easier the ignition of the process to initiate the exotherm. The outlet temperature can for instance be 150 or 200 or 240°C. More generally, the temperature in a given step or reactor (unit) thereof, means the inlet temperature in an adiabatic step, or the reaction temperature in an isothermal step. Accordingly, suitably said temperature of 20-240°C means inlet temperature.

CLAIMS

1. A process for 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 of 20-240 °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 hydrogen to the flow of the liquid oil stream, of 1000-6000 NL/L, thereby forming a stabilized liquid oil stream; wherein a carbonyl number of the stabilized liquid oil stream is below 3.0 mol/kg, as measured by ASTM E 3146, and wherein a ratio of the carbonyl number of the liquid oil stream to a carbonyl number as measured by ASTM E 3146 in mol/kg of the stabilized liquid oil stream is monitored and maintained at 1.7 or higher.

2. The process according to claim 1, wherein the hydrogen to liquid oil ratio, defined as the volume ratio of hydrogen to the flow of the liquid oil stream, is 2000-5000 NL/L.

3. The process according to claim 1 or 2, wherein the liquid oil stream contains at least 20 wt% oxygen (O), at least 30 wt% O, or at least 45 wt% O.

4. The process according to any of claims 1-3, wherein the liquid oil stream is a pyrolysis oil stream or a hydrothermal liquefaction oil (HTL oil) stream.

5. The process according to any of claims 1-4, wherein the temperature is in the range 100-225°C, or 150-200°C; the pressure is 125-175 barg, or 150 barg; and LHSV is 0.2-1.0 h^{-1}, 0.2-0.6 h^{-1}, 0.8-1.0 h^{-1}, or 0.9 h^{-1}.

6. The process according to any of claims 1-5, wherein the Ni-Mo based catalyst is a supported catalyst having a Ni content of 3-5 wt%, and Mo content of 15-25 wt%, based on the total weight of the catalyst.

7. The process according to claim 6, wherein the Ni-Mo based catalyst is a supported catalyst having P content of 1-3 wt%, based on the total weight of the catalyst.

8. The process according to claim 6 or 7, wherein the support is selected from alumina, silica, titania and combinations thereof.

9. The process according to claim 8, wherein the support is in combination with a molecular sieve having topology MFI, BEA or FAU.

10. The process according to any of claims 1-9, wherein the Ni-Mo based catalyst is in sulfided form, i.e. NiMoS.

11. The process according to any of claims 1-10, further comprising a prior step of thermal decomposition of a solid renewable feedstock, for producing said liquid oil stream.

12. The process according to claim 11, wherein the thermal decomposition step is:
- pyrolysis, thereby producing a pyrolysis oil stream; or
- hydrothermal liquefaction, thereby producing a HTL oil stream.

13. The process according to claim 12, wherein the pyrolysis is fast pyrolysis.

14. The process according to claim 13, wherein the fast pyrolysis is suitably being conducted without the presence of a catalyst and hydrogen.

15. The process according to any of claims 11-14, wherein the solid renewable feedstock is:
- a lignocellulosic biomass including: wood products, forestry waste, and agricultural residue; and/or
- 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.

16. The process according to claim 15, wherein the municipal waste is mixed municipal waste given the waste code 200301 in the European Waste Catalog.

17. The process according to any of claims 1-16, further comprising passing the stabilized liquid oil stream through a hydrodeoxygenation (HDO) step, suitably wherein

the HDO is conducted at a higher temperature and equal or lower pressure i.e. higher temperature and equal or lower pressure than the prior step for forming said stabilized liquid oil stream.

18. The process according to claim 17, further comprising passing the stabilized liquid oil stream through one or more metal guards active in hydrometallation (HDM) and/or hydrodeoxygenation (HDO), prior to said HDO step.