# Description

# Title of Invention : A process for stabilization of an unstable raw hydrocarbonaceous product.

## Technical Field

[0001] Thermal decomposition of solid feedstocks, such as mixed municipal waste, mixed or sorted plastic waste and forestry waste provides a liquid product (for simplicity pyrolysis oil or raw pyrolysis oil) which may be upgraded to quality hydrocarbons and be used as transportation fuels or petrochemical raw materials.

[0002] Thermal decomposition is a process of moderate complexity and may be carried out in plants converting a moderate amount of solid feedstock. As the transport of solid feedstock is a significant cost in this respect, thermal decomposition in moderate sized decentralized plants may be convenient, but the requirements for processing the product, pyrolysis oil, to current trade standards requires extensive processing which is unsuited for small scale operation.

[0003] The raw pyrolysis oil – the immediate liquid product of most thermal decomposition methods is highly unstable and has a high propensity for solidification, e.g. by polymerization, and therefore the upgrading is commonly preferred to be carried out in the same plant as the thermal decomposition. The upgrade process is however beneficially carried out in large scale hydroprocessing plants, since provision of process support, including utilities such as hydrogen and steam, is required.

[0004] To bridge these contradictory demands, we propose an overall process involving decentralized stabilization of the raw pyrolysis oil, transport of stabilized pyrolysis oil to a central upgrade hydroprocessing plant including a cost effective process for decentralized production of such a stabilized pyrolysis oil.

## Summary

[0004a] In one aspect, the present disclosure provides a process for production of a stabilized hydrocarbonaceous product from solid feedstock, said method comprising the steps of

(a) providing a solid feedstock for thermal decomposition

(b) directing said solid feedstock for thermal decomposition to a thermal decomposition process to provide a fluid product of thermal decomposition and a solid phase,

(c) directing to a catalytic process as raw liquid feedstock at least an amount of said fluid product of thermal decomposition and an amount of hydrogen to contact a material catalytically active in hydrogenation of conjugated diolefinic carbon-carbon bonds under active conditions for hydrogenation of conjugated diolefinic carbon-carbon bonds to provide said stabilized hydrocarbonaceous product, wherein said catalytic process may have several catalytically distinct steps, and where raw liquid feedstock and hydrogen are added together or independently in one or more positions,

(d) and withdrawing said stabilized hydrocarbonaceous product for transport or storage optionally after removal of an aqueous phase or other impurities,

characterized in the ratio of the total amount of added hydrogen to the amount of raw liquid feedstock is from 1 $Nm^3/m^3$ to 100 $Nm^3/m^3$.

[0004b] In another aspect, the present disclosure provides a process plant for carrying out a process as described herein.

## Definitions

[0005] It would be understood that the listed pressures are gauge pressure, i.e. pressure above surroundings.

[0006] The term continuous operation, as is well known in the art, means that during a given production cycle feedstock is provided and product withdrawn without

interruption. This contrasts a batch 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.

[0007] It would be understood, that the unit $Nm^3$ means “normal” $m^3$, i.e. the amount of gas taken up this volume at 0°C and 1 atmosphere.

[0008] As used herein, the term “hydrogen to liquid oil ratio” or “$H_2$/oil ratio” means the volume ratio of hydrogen to the flow of the liquid oil stream, and is reported as $Nm^3/m^3$, where the gas phase is reported at normal conditions and the liquid phase is reported at standard conditions (at 25°C and 1 atmosphere).

[0009] Where concentrations are stated in wt% this shall be understood as weight/weight %.

[0010] As used herein, the term “thermal decomposition” shall for convenience be used broadly for any decomposition process, in which a solid material is partially decomposed at elevated temperature (typically 250°C to 800°C or even 1000°C), in the presence of substoichiometric amount of $O_2$ (including no added oxygen). The product will typically be a combined liquid and gaseous stream, as well as an amount of solid char. The term shall be construed to include processes known as pyrolysis and hydrothermal liquefaction, both in the presence and absence of a catalyst. For convenience the product of such a thermal decomposition process may be called pyrolysis oil, but shall be understood to cover any thermal decomposition process.

[0011] As used herein, the term “section” means a physical section comprising a unit or combination of units for conducting one or more steps and/or sub-steps.

[0012] The term a feedstock of polymeric origin or waste polymer may be understood as including a mixed sorted waste comprising at least 50 wt%, 80 wt% or 90 wt% plastic and other artificial polymers.

[0013] A feedstock of biological origin may be defined by tracing the origin, but it may also be defined by the $^{14}C$ content being above 0.5 parts per trillion of the total carbon content.

[0014] Where hydrogen and hydrogen concentration is mentioned this shall in general be understood as molecular elemental hydrogen, unless it is implied that hydrogen is part of other molecules.

[0015] Where oxygen content is mentioned this shall in general be understood as atomic oxygen as part of other molecules, unless referred to as $O_2$.

## Technical Problem

[0016] The cost-effective operation of a plant for thermal decomposition of e.g. plastic waste, commonly produces a raw pyrolysis oil product which is unsuited for transportation, since the raw pyrolysis oil is highly reactive and likely to solidify during transportation, especially at moderately elevated temperatures and or presence of $O_2$. Processes for conversion and stabilization of such reactive materials would typically require high hydrogen consumption and multiple process steps, and thus benefit from large scale operation, which does not match the fact that such process plants are commonly preferred to be local plants, to minimize the transport of solid feedstock to the plant. Therefore it is desirable to establish a process for decentralized stabilization, and thus to identify a stabilization process suitable for such intermediate products in small scale, to facilitate their production and storage.

## Solution to Problem

[0017] Commonly the composition of oil originating from thermal decomposition of artificial polymers may involve 0.5-5 wt% of conjugated di-olefins and as much as 30-90 wt% such as 65 wt% olefins. The atomic oxygen content may typically be below 1 wt%, but if the solid feedstock contains high amounts of organic material such as in mixed household waste the atomic content of oxygen may be as much as 50 wt%.

[0018] By the present invention, a raw product of thermochemical decompositon, e.g. pyrolysis oil, is stabilized with minimal hydrogen consumption, at low pressures and moderate temperatures by the conversion of at least the most reactive compounds in the pyrolysis oil. For feedstocks of polymeric origin, such as waste plastic, the raw pyrolysis product may often contain hydrocarbon molecules with a conjugated di-olefinic structure, including a vinyl-aromatic and styrene type of structure, i.e. where two double bonds or aromatic bonds between carbon atoms

are separated by a single bond. These conjugated diolefins may, especially at temperatures above 50°C and/or in the presence of $O_2$, polymerize under formation of larger molecules, which may not be liquid at the conditions used during storage, transport or processing. Especially low molecular weight diolefins are prone to such polymerization, as conjugated double bonds near the end of the molecules are more reactive.

[0019] Similar problems also exist for materials of biological origin, but here carbonylic oxygenates such as furfural, furans, aldehydes, ketones and acids are the compounds which may polymerize, and commonly the pyrolysis oil may comprise both molecules with di-olefinic structure and carbonylic oxygen.

[0020] To stabilize these reactive compounds at moderate cost, we have identified the possibility of providing a limited amount of hydrogen which is only in a low excess with respect to hydrogenation of the most reactive groups. The amount of hydrogen provided may possibly only consider the conjugated di-olefins, which for oil originating from thermal decomposition of artificial polymers may be present in amounts of 0.5-5 wt%, and we propose limiting the conditions (temperature and pressure) such that only reactive groups are converted and in accordance, the amount of hydrogen may also be limited. As an example the hydrogen to liquid oil may be 4 $Nm^3/m^3$ which is sufficiently low that the hydrogen may be virtually completely dissolved in the oil. This also has the benefit that the reactor and process lines do not have to be designed for contacting of gas and liquid in a two phase flow.

[0021] Conversion of plastic waste, biomass and municipal waste to liquid products by thermochemical decomposition, such as pyrolysis and hydrothermal liquefaction, is, especially with subsequent hydrotreatment, considered an environmentally friendly source for alternatives to petroleum products, especially from a global warming perspective. Due to the nature of these liquid products (for simplicity pyrolysis oil, irrespective of the originating process) they will require upgrading, e.g. by hydrotreatment to remove heteroatoms, such as sulfur and oxygen, and to hydrogenate olefinic structures. The nature of formation means that the products are not stabilized, and therefore, contrary to typical fossil raw feedstocks, they may be very reactive, demanding high amounts of hydrogen, releasing significant amounts of heat during reaction and furthermore having a

high propensity towards polymerization. The release of heat may increase the polymerization further, and at elevated temperature catalysts may also be deactivated by coking.

[0022] The thermochemical decomposition process plant section providing the hydrocarbonaceous feedstock according to the present disclosure may be in many forms, including rotary oven, fluidized bed, transported bed, or circulating fluid bed, as is well known in the art. This decomposition converts a pyrolysis feedstock into a solid (char), a high boiling liquid (tar) and fraction being gaseous at elevated temperatures. The gaseous fraction comprises a fraction condensable at standard temperature (pyrolysis oil or condensate, C5+ compounds) and a non-condensable fraction (pyrolysis gas, including pyrolysis off-gas). For instance, the thermochemical decomposition process plant section (the pyrolysis section) may comprise a pyrolizer unit (pyrolysis reactor), cyclone(s) and/or filters to remove particulate solids such as char, and a cooling unit for thereby producing pyrolysis off-gas stream and said pyrolysis oil stream, i.e. condensed pyrolysis oil. The pyrolysis gas stream comprises light hydrocarbons e.g. C1-C4 hydrocarbons, and commonly also $H_2O$, CO and $CO_2$. Typically, the term pyrolysis oil comprises condensate and tar, and the pyrolysis oil stream from pyrolysis of biomass may also be referred to as bio-oil or bio-crude. The pyrolysis oil is a liquid substance rich in blends of molecules, usually consisting of more than two hundred different compounds mainly oxygenates such as acids, sugars, alcohols, phenols, guaiacols, syringols, aldehydes, ketones, furans, and other mixed oxygenates, resulting from the depolymerization of the solids treated in pyrolysis. Thermochemical decomposition of non-biological waste comprising suitable compositions, such as plastic fractions or rubber, including end of life tires will in general only provide products which have low contents of oxygen, unless $O_2$ is added to the decomposition process and will commonly provide a hydrocarbonaceous feedstock which has a structure reflecting the solid pyrolysis feedstock.

[0023] For the purposes of the present invention, the pyrolysis section may be fast pyrolysis, also referred to in the art as flash pyrolysis. Fast pyrolysis means the thermochemical decomposition of a solid feedstock typically in the absence of $O_2$, at temperatures typically in the range 350-650°C e.g. about 500°C and reaction

times of 10 seconds or less, such as 5 seconds or less, e.g. about 2 sec. Fast pyrolysis may for instance be conducted by autothermal operation e.g. in a fluidized bed reactor. The latter is also referred to as autothermal pyrolysis and is characterized by employing air, optionally with an inert gas or recycle gas, as the fluidizing 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. In so-called catalytic fast pyrolysis, a catalyst may be used. An acid catalyst, commonly comprising a zeolite, without active metals, may be used to upgrade the pyrolysis vapors, and it can both be operated in an in-situ mode (the catalyst is located in the pyrolysis reactor) and an ex-situ mode (the catalyst is placed in a separate reactor). The use of a catalyst conveys the advantage of helping to stabilize the pyrolysis oil and thereby making it easier to hydroprocess. In addition, increased selectivity towards desired pyrolysis oil compounds may be achieved.

[0024] In some cases, hydrogen is added to the catalytic pyrolysis which is then called reactive catalytic fast pyrolysis. If the catalytic pyrolysis is conducted at a high hydrogen pressure, such as above 0.5 MPa, it is often called catalytic hydropyrolysis. The catalyst for upgrading in the presence of hydrogen, will typically comprise one or more metals active in hydrogenation, such as a metal from Group 6 or Group 8,9 or 10.

[0025] The pyrolysis stage may be fast pyrolysis which is conducted without the presence of a catalyst and hydrogen, i.e. the fast pyrolysis stage is not catalytic fast pyrolysis, hydropyrolysis or catalytic hydropyrolysis. This enables a much simpler and inexpensive process.

[0026] In an embodiment, the thermal decomposition is hydrothermal liquefaction. Hydrothermal liquefaction means the thermochemical conversion of solid feedstocks, such as plastic waste, biomass, municipal solid waste or sewer sludge into liquid fuels by processing in a hot, pressurized water environment for sufficient time to break down the solid biopolymeric structure to mainly liquid components. Typical hydrothermal processing conditions are temperatures in the range of 200-500°C, especially 300-450°C and operating pressures in the range of 4-40 MPa especially 25-35 MPa. This technology offers the advantage of

operation of a lower temperature, higher energy efficiency and lower tar yield compared to pyrolysis, e.g. fast pyrolysis.

[0027] In an embodiment, the thermal decomposition further comprises passing said solid feedstock through a solid feedstock preparation section comprising for instance drying for removing water and/or comminution for reduction of particle size. Any water/moisture in the solid feedstock which vaporizes in for instance the pyrolysis section condenses in the pyrolysis oil stream and is thereby carried out in the process, which may be undesirable. Furthermore, the heat used for the vaporization of water withdraws heat which otherwise is necessary for the pyrolysis. By removing water and also providing a smaller particle size in the solid feedstock the thermal efficiency of the pyrolysis section is increased.

[0028] Finally, other relevant thermochemical decomposition methods are intermediate or slow pyrolysis, in which the conditions involve a lower temperature and commonly higher residence times – these methods may also be known as carbonization or torrefaction. The major benefit of these thermochemical decomposition methods is a lower investment, but they may also have specific benefits for specific feedstocks or for specific product requirements, such as a desire for bio-char as an associated product.

[0029] When high amounts of solid product are produced, such as processes producing bio-char or when retrieval of unconverted carbon black particles from thermochemical conversion of end-of-life tires is desired, it may be beneficial to filter the liquid product as part of the thermochemical conversion process, which will also have the benefit of minimizing deactivation of downstream catalyst.

[0030] The hydrotreatment of reactive compounds is by the chemical nature of the process exothermal. This means that as long as the temperature is sufficient for ignition of the hydrogenation of the most reactive compounds, an increase in temperature will occur, ensuring further reaction of other compounds, but by limiting the availability of hydrogen, the increase in temperature will not proceed to levels where hydrocarbons would be converted to solid carbon deposits, which would deactivate the catalyst.

[0031] As mentioned the reactivity of large molecules in general is lower than smaller molecules. Accordingly sufficient stabilization for transportation, while minimizing

local process volume and hydrogen consumption, may be obtained by only directing the lightest and least stable fraction of the pyrolysis product for stabilization. In practice such fractionation may either be carried out by fractionation of a product with a broad boiling point range in fractionator, or by condensation of a high boiling fraction e.g. at 250°C, while a less stable lower boiling fraction is either hydrotreated in vapor state or condensed prior to hydrotreatment.

[0032] Accordingly, we propose a process for hydrotreating a liquid oil stream by, in a continuous operation, reacting the liquid oil stream with hydrogen in the presence of a hydrotreatment catalyst having moderate sulfur resistance. This catalyst may be a sulfided catalyst comprising one or more of nickel, cobalt, molybdenum and tungsten typically operating at an inlet temperature of 130-200°C or it may be a metallic catalyst comprising one or more of nickel, palladium and platinum typically operating at an inlet temperature of 80-130°C. In most cases the the pressure may be 0.5-2 MPa, but it may be up to 35 MPa, and the liquid hourly space velocity (LHSV) of 0.1-5 $h^{-1}$, which conditions enable forming a stabilized liquid oil stream.

[0033] The process is moderately exothermic thus a raise in temperature of 5-20°C typically occurs .

[0034] By the present invention, a continuous operation process is used, since contrary to a batch operation, there is no dependency on the outcoming product (stabilized liquid oil) being fluid at all times. The process may inter alia be conducted in a fixed bed reactor, a slurry bed reactor, trickle bed reactor, and fluidized bed reactor.

[0035] The provision of hydrogen for hydroprocessing is a significant cost, and the reduction of the requirements for hydrogen may be a driver for cost reduction. In hydroprocessing, an amount of hydrogen is consumed per volume of oil, which is termed the $H_2$:oil consumption ratio. Depending on the nature of the raw product, for complete hydroprocessing the $H_2$:oil consumption ratio may be from 50 $Nm^3/m^3$ to 1000 $Nm^3/m^3$. However, to minimize the risk of coke deposits on the catalyst, it is common to operate with a safety factor of 2, 4 or even 8, such that an $H_2$:oil consumption ratio of 200 $Nm^3/m^3$ results in operation with up to 1000

$Nm^3/m^3$ $H_2$:oil – and if the purity of the $H_2$ rich gas in the process is only 80 vol%, the resulting gas:oil ratio would be 500 $Nm^3/m^3$. Such an excess of gas will naturally cause equipment size to be higher, and the excess of $H_2$ may also result in increased reactivity such that the actual $H_2$ consumption is higher due to the availability alone.

[0036] With such elevated hydrogen levels, it becomes economically relevant to recycle the gas and the related costs in equipment (such as a recycle gas compressor) and process size leads to a requirement for increased processing volumes.

[0037] The requirement for a high excess of $H_2$ is mainly relevant at elevated temperatures, close to complete hydrotreatment. Therefore, we propose to limit the $H_2$ to less than the amount required for complete hydrotreatment, as this would protect the process against thermal runaway and limit the hydrogen consumption at the same time, which will result in a reduced cost of operation, a reduced process volume and reduced capital investment as no recycle and recycle compressor would be required.

[0038] In an embodiment, the catalyst is in sulfided form, e.g. NiMoS or CoMoS. The catalyst may be pre-sulfided by exposure of to a sulfur containing stream or it may be sulfided in-situ i.e. during operation, for instance by sulfur present in the pyrolysis oil, such that the sulfided catalyst remains sulfided and thus active due to the presence of sulfur.

[0039] The process may further comprise passing the stabilized pyrolysis oil stream through a further hydrotreatment step, possibly after transportation to a central site where the stabilized pyrolysis oil can be further treated for either producing hydrocarbons suitable for conversion in a steam cracker or for producing products boiling in the transportation fuel range, such as diesel, jet fuel and naphtha. The further treatment may include hydrodewaxing, hydrocracking, or isomerization, as is well known in the art of fossil oil refining.

[0040] The material catalytically active in initial hydrotreating especially of conjugated double bonds, e.g. hydrogenation, typically comprises an active metal (sulfided base metals such as nickel, cobalt, tungsten and/or molybdenum, but possibly also either elemental metals both nickel and noble metals such as platinum

and/or palladium) and a refractory support (such as alumina, silica or titania, or combinations thereof). Initial hydrotreating conditions may involve a moderate temperature in the interval 120-200°C, a moderate pressure in the interval 0.5-5 MPa, and a liquid hourly space velocity (LHSV) in the interval 0.1-5. For certain conditions an elevated pressure up to 35 MPa may be required.

[0041] Final hydrotreating e.g. hydrogenation conditions commonly involve a higher temperature in the interval 250-400°C, a higher pressure in the interval 3-15 MPa, and a liquid hourly space velocity (LHSV) in the interval 0.1-4, optionally together with intermediate cooling by quenching with cold hydrogen, feed or product.

[0042] 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).

[0043] Isomerization conditions involve a temperature in the interval 250-400°C, a pressure in the interval 2-10 MPa, and a liquid hourly space velocity (LHSV) in the interval 0.5-8.

[0044] 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.

[0045] Hydrocracking conditions may involve a temperature in the interval 250-400°C, a pressure in the interval 3-20MPa, and a liquid hourly space velocity

(LHSV) in the interval 0.5-8, optionally together with intermediate cooling by quenching with cold hydrogen, feed or product.

[0046] Other types of hydrotreating are also envisaged, for instance hydrodearomatization (HDA). 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).

[0047] Hydrodearomatization conditions involve a temperature in the interval 200 - 350°C, a pressure in the interval 2-10 MPa, and a liquid hourly space velocity (LHSV) in the interval 0.5-8.

[0048] Any of the embodiments and associated benefits of the first aspect of the invention may be used with the second aspect of the invention, and vice versa.

## Advantageous Effects of Invention

[0049] A first aspect of the invention relates to a process for production of a stabilized hydrocarbonaceous product from solid feedstock, said method comprising the steps of, providing a solid feedstock for thermal decomposition, directing said solid feedstock for thermal decomposition to a thermal decomposition process to provide a fluid product of thermal decomposition and a solid phase, directing to a catalytic process as raw liquid feedstock at least an amount of said fluid product of thermal decomposition and an amount of hydrogen to contact a material catalytically active in hydrogenation of conjugated diolefinic carbon-carbon bonds under active conditions for hydrogenation of conjugated diolefinic carbon-carbon bonds to provide said stabilized hydrocarbonaceous product, wherein said catalytic process may have several catalytically distinct steps, and where raw liquid feedstock and hydrogen are added together or independently in one or more positions, and withdrawing said stabilized hydrocarbonaceous product for transport or storage optionally after removal of an aqueous phase or other impurities, characterized in the ratio of the total amount of added hydrogen to the amount of raw liquid feedstock is from 1 $Nm^3/m^3$ to 100 $Nm^3/m^3$.

[0050] This has the associated benefit of such a process requiring only a low amount of hydrogen, while still providing a stabilized hydrocarbon product for transport or storage.

[0051] A second aspect of the invention relates to a process according to the first aspect wherein the characterized in the ratio of the total amount of added hydrogen to the amount of raw liquid feedstock is from 1, 2, 5 or 10 $Nm^3/m^3$ to 20 $Nm^3/m^3$ or 50 $Nm^3/m^3$.

[0052] This has the associated benefit of such amounts of hydrogen corresponding to the amounts of reactive compounds in the fluid product of thermal decomposition.

[0053] A third aspect of the invention relates to a process according to the first or second aspect wherein the solid feedstock comprises at least 50% waste polymer.

[0054] This has the associated benefit of such a process being highly suited for processing of waste polymer feedstock for use of the stabilized product in a steam cracker, optionally after further processing.

[0055] A fourth aspect of the invention relates to a process according to the first or second aspect further involving separating said fluid product of thermal decomposition in at least a polar liquid phase and a non-polar liquid phase.

[0056] This has the associated benefit of providing a process suited for handling a feedstock with a high content of oxygen being converted to water, such as a feedstock comprising a high amount of feedstock of biological origin.

[0057] A fifth aspect of the invention relates to a process according to the first, second, third or fourth aspect wherein the active hydrogenation conditions involving a pressure being from ambient pressure or 0.5 MPa to 10 MPa, 20 MPa or 35 MPa.

[0058] This has the associated benefit of reducing the cost of equipment, without negative impact on performance, as the pressure is not limiting for hydrogen solubility.

[0059] A sixth aspect of the invention relates to a process according to the first, second, third, fourth or fifth aspect wherein the active hydrogenation conditions involving an inlet temperature from 80 to 210 °C.

[0060] This has the associated benefit of providing sufficient temperature for process ignition, while maintaining a low temperature such that only the most reactive compounds are converted.

[0061] A seventh aspect of the invention relates to a process according to the first, second, third, fourth, fifth or sixth aspect wherein said material catalytically active in hydrogenation comprises at least one of Ni, Co, Mo, W and Pd.

[0062] An eighth aspect of the invention relates to a process according to the first, second, third, fourth, fifth, sixth or seventh aspect wherein said hydrogen being provided at least in part by reaction of an amount of said fluid product of thermal decomposition product stream, optionally employing electrical heating.

[0063] This has the associated benefit of converting waste gases from the pyrolysis stream into process hydrogen, with minimal $CO_2$ emission, especially if the electricity is produced from excess process heat or from a renewable energy source, such as solar energy, wind energy or wave energy.

[0064] A ninth aspect of the invention relates to a process according to the first, second, third, fourth, fifth, sixth, seventh or eighth aspect wherein said hydrogen being produced at least in part by electrolysis optionally employing electricity produced from excess process heat or from a renewable energy source, such as solar energy, wind energy or wave energy.

[0065] This has the associated benefit of converting waste gases from the pyrolysis stream into process hydrogen, with minimal $CO_2$ emission.

[0066] A tenth aspect of the invention relates to a process according to the first, second, third, fourth, fifth, sixth, seventh, eighth or ninth aspect wherein the thermal decomposition product prior to contacting the material catalytically active in hydrotreatment is cooled to at a temperature between 20°C and 150°C, 180°C or 230°C.

[0067] This has the associated benefit of avoiding solidification by polymerization.

[0068] An eleventh aspect of the invention relates to a process according to the first, second, third, fourth, fifth, sixth, seventh, eighth, ninth or tenth aspect in which the amount of solid feedstock is at least 10 ton/day or 50 ton/day and less than 2000 ton/day, less than 1000 ton/day or less than 500 ton/day.

[0069] This has the associated benefit of such a size process being well suited for decentralized stabilization but too small for optimal operation with full conversion.

[0070] A twelfth aspect of the invention relates to a process according to the first, second, third, fourth, fifth, sixth, seventh, eighth, ninth, tenth or eleventh aspect in which the stabilized hydrocarbon product is transferred to a means of transportation such as a tank or a pipeline and transported to an upgrade facility for upgrading into a final hydrocarbon product.

[0071] This has the associated benefit of such a process being well suited for centralized finalization of the processing, with the aim of producing a hydrocarbon product for use in steam cracking or as a part of a transportation fuel.

[0072] Further aspects relate to process plants including means for carrying out any of the aspects above, where said means are configured accordingly.

## Brief Description of Drawings

[0073] Figure 1 shows a thermochemical decomposition process in which all liquid hydrocarbon product is stabilized by hydrotreatment.

[0074] Figure 2 shows a thermochemical decomposition process in which only the light hydrocarbons are stabilized by hydrotreatment.

## Fig.1

[0075] In Fig.1 a solid feedstock (102) is directed to a thermochemical decomposition reactor (PYR). The thermochemical decomposition produces three streams; a high temperature gas stream (104), solid char (106) and liquid pyrolysis oil (108). The thermochemical decomposition process may have internal recycle or additional inlets, such as gases, water and solvents, but these are not illustrated in Fig.1.

[0076] The full range of pyrolysis oil (108) is combined with a moderate amount hydrogen (114) and optionally heated, either by heating a single stream or by heating a combined raw feedstock stream (116). The raw feedstock stream is

directed to contact a material catalytically active in hydrotreatment a hydrotreatment reactor (HYD) at a moderate temperature such as 150°C and moderate pressure such as 2 MPa. This hydrotreatment reactor (HYD) is illustrated as separate, but it may also be integrated in the thermochemical decomposition reactor (PYR).

[0077] The product stream (118) will typically be directed to a gas-liquid product separator (SEP), separating light gases (120) from stabilized hydrocarbon product (124) and if the raw product comprises oxygen, this product separator may be a three way separator, as the liquid would comprise a hydrocarbon phase and an aqueous phase. In the illustration, the separator (SEP) is a reboiled stripper, with the benefit of driving dissolved hydrogen and other gases from the product.

[0078] The stabilized hydrocarbon phase will be sufficiently stable for transportation and storage, but not of sufficiently quality for use as transportation fuel or feedstock for chemical processes such as steam cracking.

[0079] If the process involves a significant excess of hydrogen, the recovery of this hydrogen by a gas recycle is of economical relevance, although such a recycle circuit involves capital and operational cost. If the excess of hydrogen is low, the gas may be directed to the thermochemical decomposition for use as a heat source.

## Fig.2

[0080] In Fig.2 a solid feedstock (202) is directed to a thermochemical decomposition reactor (PYR). The thermochemical decomposition produces three streams; a high temperature gas stream (204), solid char (206) and liquid pyrolysis oil (208). The thermochemical decomposition process may have internal recycle or additional inlets, such as gases, water and solvents, but these are not illustrated in Fig.2.

[0081] In this figure the pyrolysis oil (208) is fraction in a light range pyrolysis oil (210) and a heavy range pyrolysis oil (212). The fractionation is illustrated to take place in a fractionator, but the process for condensation of pyrolysis oil may also be employed for a similar fractionation.

[0082] The light range pyrolysis oil (210) is combined with a moderate amount hydrogen (214) and optionally heated, either by heating a single stream or by heating a combined raw feedstock stream (216). The raw feedstock stream is directed to contact a material catalytically active in hydrotreatment a hydrotreatment reactor (HYD) at a moderate temperature such as 150°C and moderate pressure such as 2 MPa. This hydrotreatment reactor (HYD) is illustrated as separate, but it may also be integrated in the thermochemical decomposition reactor (PYR).

[0083] The product stream (218) will typically be directed to a gas-liquid product separator (SEP), separating light gases (220) from stabilized light product (222) and if the raw product comprises oxygen, this product separator may be a three way separator, as the liquid would comprise a hydrocarbon phase and an aqueous phase. In the illustration, the separator (SEP) is a reboiled stripper, with the benefit of driving dissolved hydrogen and other gases from the product.

[0084] The stabilized light product (222) is combined with the range pyrolysis oil (212) to form a stabilized hydrocarbon product (224) will be sufficiently stable for transportation and storage, but not of sufficiently quality for use as transportation fuel or feedstock for chemical processes such as steam cracking.

## Fig.3

[0085] Fig.3, according to the prior art, shows a highly simplified layout for quantitative hydrogenation. While the layout is illustrated as similar to Fig.1, in practice an increased flow of hydrogen, elevated temperatures and elevated pressures causes a need for larger equipment and multiple modifications.

[0086] As in Fig.1 a solid feedstock (302) is directed to a thermochemical decomposition reactor (PYR). The thermochemical decomposition produces three streams; a high temperature gas stream (304), solid char (306) and liquid pyrolysis oil (308). The thermochemical decomposition process may have internal recycle or additional inlets, such as gases, water and solvents, but these are not illustrated in Fig.3.

[0087] The full range of pyrolysis oil (308) is combined with an amount of hydrogen (314) and optionally heated, either by heating a single stream or by heating a combined raw feedstock stream (316). As the objective is full hydrogenation of

the pyrolysis oil (308) the amount of hydrogen directed to the process must correspond to the total chemically required amount, and in addition, as a safety measure an excess amount must be provided to minimize the risk of coke formation on the catalyst. The raw feedstock stream (316) is directed to contact a material catalytically active in hydrotreatment a hydrotreatment reactor (HYD) at a moderate temperature such as 150°C, which further downstream is increased to e.g 350°C by heat release in the process and possibly also external heating. The pressure is preferably elevated such as 20 MPa. Here a single hydrotreatment reactor (HYD) is illustrated as separate, but commonly several reactors would be required, and the first reactor may be integrated in the thermochemical decomposition reactor (PYR).

[0088] The product stream (318) will typically be directed to a gas-liquid product separator (SEP), separating light gases (320) from stabilized hydrocarbon product (324) and if the raw product comprises oxygen, this product separator may be a three way separator, as the liquid would comprise a hydrocarbon phase and an aqueous phase. In the illustration, the separator (SEP) is a reboiled stripper, with the benefit of driving dissolved hydrogen and other gases from the product.

[0089] The stabilized hydrocarbon phase will be highly stable and useful as a transportation fuel or feedstock for chemical processes such as steam cracking.

[0090] Since the process involves a significant excess of hydrogen, the recovery of this hydrogen by a gas recycle is of economical relevance, although such a recycle circuit involves capital and operational cost. Therefore the light gases (320) are directed to be pressurized in a recycle compressor (CMP) and combined with hydrogen (314). Commonly this light gases stream is purified by appropriate means (not shown).

## Examples

[0091] To illustrate the invention 3 examples were compared. Tables 1, 2 and 3 shows the boiling point curves and the content of conjugated diolefins and olefins in a process treating 1200 t/day (50 t/hr) of a product of hydrothermal liquefaction of plastic waste, which is treated by mild hydrotreatment in accordance with one of Figures 1 or 2. Due to the presence of diolefins, the feedstock has a tendency

to polymerization and solidification during transport, especially if heated above 50°C.

[0092] In Example 1 according to Figure 1, reported in Table 1, the full range pyrolysis oil is directed to mild hydrotreatment at 150°C, with an amount of hydrogen corresponding to 2 times the theoretical hydrogen consumption for diolefin saturation, which is an amount which may be 99% dissolved in the oil, ensuring good contact and avoiding practical challenges of a large gas flow. This corresponds to a hydrogen to oil ratio of 4 $Nm^3/m^3$. The amount of conjugated diolefins is reduced from 1.9 wt% to 0.095 wt%, which will result in a product which is stable for transport.

[0093] In Example 2 according to Figure 2, reported in Table 2, only the naphtha range pyrolysis oil is directed to mild hydrotreatment at 150°C, with an amount of hydrogen corresponding to 2 times the theoretical hydrogen consumption for diolefin saturation, which also in this Example is substantially dissolved in the oil. This corresponds to a hydrogen to oil ratio of 4 $Nm^3/m^3$ in the stream for hydrotreatment. The amount of conjugated diolefins is only reduced from 1.9 wt% to 1.35 wt%, but the most reactive small conjugated diolefins are reduced by 95%, and therefore the product will be sufficiently stable for transport.

[0094] In Example 3 according to Figure 3, reported in Table 3, the full range pyrolysis oil is directed to hydrotreatment at 180°C to 350°C, with 35200 $Nm^3/h$ of hydrogen corresponding to about 7 times the theoretical hydrogen consumption of 5200 $Nm^3/h$ for full hydrogenation and to a hydrogen to oil ratio of 560 $Nm^3/m^3$. In a simplified manner this process corresponds to Figure 1 and Example 1, but additional equipment will in practice be required to optimize the thermal efficiency, ensuring good contacting between hydrogen and oil, as a significant amount of gas is not dissolved in the oil, to optimize hydrogen consumption by provision of a gas recycle circuit, including a recycle line and a compressor and multiple reactors to allow for different temperatures and pressures. As an amount of hydrogen is withdrawn with purge, 5850 $Nm^3/hr$ make-up hydrogen is required, even though excess hydrogen is recycled.

[0095] Comparing the three examples shows that the required addition of make-up hydrogen varies from 77.5 $Nm^3/hr$ in Example 2 to 5850 $Nm^3/hr$ in Example 3.

The relative amount of hydrogen withdrawn as off gas is lower in Example 3, since recycle reduces this, but the higher absolute level also causes a higher amount of hydrogen withdrawn as off-gas.

[0096] In all three examples an amount of off-gas is withdrawn. This off-gas may beneficially be directed to the hydrogen plant, in order to produce hydrogen with a minimal requirement of resources.

**Table 1**

| | | *102* | *110* | *112* | *118* |
|---|---|---|---|---|---|
| *Boiling point* | | | | | |
| *IBP* | [°C] | 80.3 | 73.0 | 73.8 | 83.2 |
| *5%* | [°C] | 104.2 | 100.9 | 101.9 | 105.1 |
| *10%* | [°C] | 121.2 | 119.6 | 120.4 | 121.6 |
| *30%* | [°C] | 180.6 | 178.7 | 179.7 | 181.0 |
| *50%* | [°C] | 244.4 | 243.7 | 244.0 | 244.5 |
| *70%* | [°C] | 292.9 | 292.6 | 292.7 | 293.0 |
| *90%* | [°C] | 348.2 | 348.2 | 348.2 | 348.2 |
| *95%* | [°C] | 358.6 | 358.7 | 358.9 | 358.8 |
| *EBP* | [°C] | 362.8 | 362.9 | 362.3 | 362.2 |
| *Volume flow* | [m3/hr] | 63.3 | 63.6 | 64.0 | 63.8 |
| *Olefins* | [wt%] | 65.0 | 65.0 | 64.4 | 64.3 |
| *Conj.diolefins* | [wt%] | 1.9 | 1.9 | 0.095 | 0.095 |

**Table 2**

| | | *202* | *204* | *206* | *210* | *212* | *218* |
|---|---|---|---|---|---|---|---|
| *Boiling point* | | | | | | | |
| *IBP* | [°C] | 80.3 | 72.4 | 205.5 | 58.9 | 73.6 | 49.0 |
| *5%* | [°C] | 104.2 | 79.7 | 220.0 | 76.5 | 101.8 | 123.4 |
| *10%* | [°C] | 121.2 | 86.2 | 230.6 | 85.4 | 120.3 | 201.9 |
| *30%* | [°C] | 180.6 | 102.0 | 257.4 | 101.7 | 179.6 | 243.7 |
| *50%* | [°C] | 244.4 | 114.5 | 285.8 | 114.2 | 244.0 | 276.9 |
| *70%* | [°C] | 292.9 | 129.1 | 313.3 | 128.9 | 292.7 | 307.9 |
| *90%* | [°C] | 348.2 | 152.3 | 348.7 | 152.2 | 348.2 | 348.1 |
| *95%* | [°C] | 358.6 | 159.2 | 357.0 | 159.1 | 358.9 | 358.8 |
| *EBP* | [°C] | 362.8 | 175.0 | 358.8 | 175.0 | 362.3 | 359.6 |
| *Volume flow* | [m3/hr] | 63.3 | 19.4 | 43.9 | 19.5 | 17.9 | 61.8 |
| *Olefins* | [wt%] | 65.0 | 65.0 | 65.0 | 65.0 | 64.35 | 63.3 |
| *Conj.diolefins* | [wt%] | 1.90 | 1.90 | 1.90 | 1.90 | 0.10 | 1.35 |

**Table 3**

| | | *302* | *310* | *312* | *318* |
|---|---|---|---|---|---|
| *Boiling point* | | | | | |
| *IBP* | [°C] | 80.3 | 71.5 | 52.5 | 75.4 |
| *5%* | [°C] | 104.2 | 98.7 | 106.7 | 104.3 |
| *10%* | [°C] | 121.2 | 117.2 | 138.0 | 121.8 |
| *30%* | [°C] | 180.6 | 173.4 | 232.0 | 180.5 |
| *50%* | [°C] | 244.4 | 242.2 | 273.8 | 241.8 |
| *70%* | [°C] | 292.9 | 292.0 | 308.1 | 289.7 |
| *90%* | [°C] | 348.2 | 348.3 | 347.1 | 345.5 |
| *95%* | [°C] | 358.6 | 358.8 | 356.2 | 356.5 |
| *EBP* | [°C] | 362.8 | 363.0 | 358.2 | 360.9 |
| | | | | | |
| *Volume flow* | [m3/hr] | 63.3 | 111.7 | 233.2 | 63.1 |
| *Olefins* | [wt%] | 65.0 | 65.0 | 3.25 | 3.25 |
| *Conj.diolefins* | [wt%] | 1.9 | 1.9 | 0.019 | 0.019 |