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(72) Inventeurs/Inventors:
TOUKONIITTY, BLANKA, FI;
PAASIKALLIO, VILLE, FI;
PASANEN, JUKKA-PEKKA, FI;
TOURONEN, JOUNI, FI;
HOVI, MERI, FI; ...

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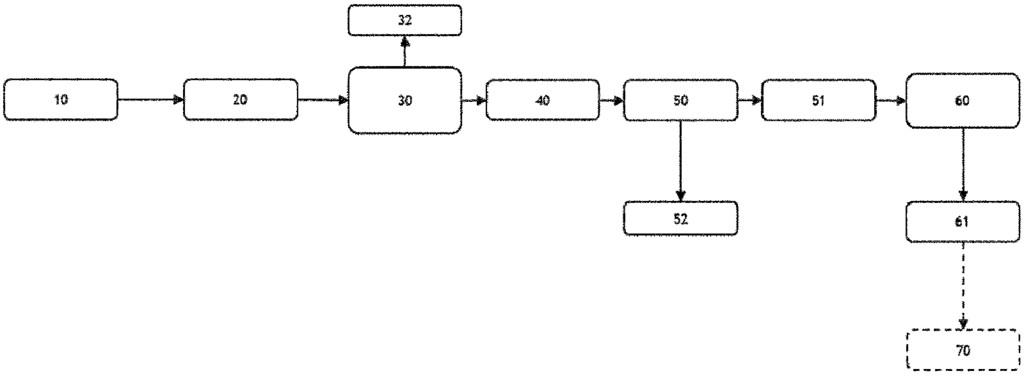

(57) Abrégé/Abstract:
There is disclosed a method of purifying a recycled or renewable organic material. The recycled or renewable organic material comprises more than 1 ppm silicon as silicon compounds and/or more than 10 ppm phosphorous as phosphorous compounds.

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(72) **Inventeurs(suite)/Inventors(continued)**: PASANEN, ANTTI, FI; LIKANDER, SALLA, FI; TOPPINEN, SAMI, FI; AALTO, PEKKA, FI; JANSSON, KARI, FI; LINDBLAD, MARINA, FI; KALDSTROM, MATS, FI; LAMMINPAA, KAISA, FI

(73) **Propriétaires(suite)/Owners(continued)**:NESTE OYJ, FI

(74) **Agent**: FASKEN MARTINEAU DUMOULIN LLP

(57) **Abrégé(suite)/Abstract(continued)**:

The method comprises the steps of providing a feed of the recycled or renewable organic material, wherein the recycled or renewable organic material is selected from a group consisting of plant based fats and oils, animal based fats and oils, fossil waste-based oils, waste oils, algal oils and microbial oils heat treating the recycled or renewable organic material in the presence of at least a silica gel at 180 to 325°C and filtering the heat treated recycled or renewable organic material, and hydrotreating the heat treated recycled or renewable organic material in a presence of a hydrotreating catalyst.

ABSTRACT

There is disclosed a method of purifying a recycled or renewable organic material. The recycled or renewable organic material comprises more than 1 ppm silicon as silicon compounds and/or more than 10 ppm phosphorous as phosphorous compounds. The method comprises the steps of providing a feed of the recycled or renewable organic material, wherein the recycled or renewable organic material is selected from a group consisting of plant based fats and oils, animal based fats and oils, fossil waste-based oils, waste oils, algal oils and microbial oils heat treating the recycled or renewable organic material in the presence of at least a silica gel at 180 to 325°C and filtering the heat treated recycled or renewable organic material, and hydrotreating the heat treated recycled or renewable organic material in a presence of a hydrotreating catalyst.

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PURIFICATION OF RECYCLED AND RENEWABLE ORGANIC MATERIAL

FIELD OF THE INVENTION

The present invention relates to a method of purifying recycled or renewable organic material, in particular recycled or renewable organic material comprising 1 ppm silicon as silicon compounds and/or more than 10 ppm phosphorous as phosphorous compounds.

BACKGROUND OF THE INVENTION

In some cases recycled or renewable organic material contains high amounts of silicon (Si) as silicon compounds and high amounts of phosphorous as phosphorous compounds such as phospholipids. Before catalytic processing of the recycled or renewable organic material these impurities need to be removed from the material as these compounds are known catalyst poisons and should therefore be removed prior to hydrotreating to maximize the cycle length and profits of the hydrotreater.

In particular tall oil pitch (TOP) contains silicon and phosphorous impurities, most likely originating from anti-fouling agents used in upstream processing. Anti-fouling agents comprise e.g. polydimethylsiloxanes (PDMS), which are soluble in oil and are therefore difficult to remove from oil. Also, some other impurities can come from sand or dirt during wood collection. Removal of silicon impurities prior to hydrotreatment is required to avoid decreased lifetime of the catalyst in the unit. Conventional purification methods such as filtration or bleaching are not adequate to remove the silicon impurities effectively.

BRIEF DESCRIPTION OF THE INVENTION

An object of the present invention is thus to provide a method so as to overcome the above problems.

The invention is based on the surprizing realization recycled or renewable organic material containing high amounts of phosphorous and silicon compounds may be purified by a method that leads to removal of phosphorous and silicon compounds from the recycled or renewable organic material as the recycled or renewable organic material is subjected to heat treating the feed of lipid material in the presence of an adsorbent at 180 to 325°C and filtering the material and hydrotreating the lipid material in a presence of a hydrotreating catalyst at a temperature from 270 to 380°C under pressure from 4 to 20 MPa and under continuous hydrogen flow.

The method allows use of low quality recycled or renewable organic material feeds as a feedstock in hydrotreating, e.g. in processes producing high quality renewable fuels and/or chemicals.

BRIEF DESCRIPTION OF THE DRAWINGS

In the following the invention will be described in greater detail by means of preferred embodiments with reference to the attached drawings, in which

Figure 1 illustrates a first exemplary process flow of the present method;

Figure 2 illustrates effect of acid treatment on Si and P removal from crude TOP samples;

Figure 3 illustrates effect of heat treatment on Si and P removal from crude TOP samples.

DETAILED DESCRIPTION OF THE INVENTION

The present invention provides a method of purifying a recycled or renewable organic material.

The term "recycled or renewable organic material" refers to organic material, i.e. material containing carbon, obtained 1) from a natural resource which replenishes to overcome recourse depletion caused by its usage and consumption or 2) from a raw or processed material that is recovered from a waste for reuse. The recycled or renewable organic material characteristically comprises aliphatic compounds having a carbon chain of from 4 to 30 carbon atoms, particularly from 12 to 22 carbon atoms. Typical examples of such aliphatic compounds are fatty acids or esters thereof, in particular wherein the fatty acids have an aliphatic chain of from 4 to 30 carbon atoms, more particularly from 12 to 22 carbon atoms.

The recycled or renewable organic material typically comprises at least 50 wt% aliphatic compounds of the total weight of the recycled or renewable organic material.

Typically the recycled or renewable organic material refers to fats and/or oils of plant, microbial, algal, and/or animal origin. It also refers to any waste stream received from processing of such oils and/or fats. The recycled or renewable organic material may be in an unprocessed form (e.g. animal fat), or a processed form (used cooking oil).

Plant based fats and/or oils can originate directly from plants or they can be byproducts from various industrial sectors such as agriculture or forest industry. For example bio-oils and biocrudes can be produced from biomass, also known as lignocellulosic biomass, with various liquefying methods such as fast pyrolysis or hydrothermal liquefaction. Fast pyrolysis is the thermochemical decomposition of biomass through rapid heating in absence of oxygen. Hydrothermal liquefaction (HTL) is a thermal depolymerization process used to convert wet biomass into crude-like oil under moderate temperature and high pressure. Examples of bio-oil and biocrude produced from lignocellulosic biomass, e.g. materials like forest harvesting residues or byproducts of a saw mill, are lignocellulose pyrolysis liquid (LPL), which is produced via fast pyrolysis and HTL-biocrude, which is produced via hydrothermal liquefaction. Further example of plant based oil is tall oil, which is obtained as a by-product of the Kraft process of wood pulp manufacture as crude tall oil (CTO), and its derivates such as tall oil pitch (TOP), crude fatty acids (CFA), tall oil fatty acids (TOFA) and distilled tall oil (DTO). Tall oil comprises resin acids, fatty acids, and unsaponifiables. Resin acids are a mixture of organic acids derived from oxidation and polymerization reactions of terpenes. The main resin acid in tall oil is abietic acid but abietic derivatives and other acids such as primaric acid are also found. Fatty acids are long chain monocarboxylic acids and are found in hardwoods and softwoods. The main fatty acids in tall oil are oleic, linoleic and palmitic acids. Unsaponifiables cannot be turned into soaps as they are neutral compounds which do not react with sodium hydroxide to form salts. They include sterols, higher alcohols and hydrocarbons. Sterols are steroids derivatives which also include a hydroxyl group.

The term “tall oil pitch (TOP)” refers to residual bottom residual bottom fraction from tall oil distillation processes. Tall oil pitch typically comprises from 34 to 51 wt% free acids, from 23 to 37 wt% esterified acids, and from 25 to 34 wt% unsaponifiable neutral compounds of the total weight of the tall oil pitch. The free acids are typically selected from a group consisting of dehydroabietic acid, abietic and other resin acids. The esterified acids are typically selected from a group consisting of oleic and linoleic acids. The unsaponifiables neutral compounds are typically selected from a group consisting of diterpene sterols, fatty alcohols, sterols, and dehydrated sterols.

The term "crude fatty acid (CFA)" refers to fatty acid-containing materials obtainable by purification (e.g., distillation under reduced pressure, extraction, and/or crystallization) of CTO.

The term "tall oil fatty acid (TOFA)" refers to fatty acid rich fraction of crude tall oil (CTO) distillation processes. TOFA typically comprises mainly fatty acids, typically at least 80 wt% of the total weight of the TOFA. Typically TOFA comprises less than 10 wt% rosin acids.

The term "distilled tall oil (DTO)" refers to resin acid rich fraction of crude tall oil (CTO) distillation processes. DTO typically comprises mainly fatty acids, typically from 55 to 90 wt%, and rosin acids, typically from 10 to 40 wt% rosin acids, of the total weight of the DTO. Typically DTO comprises less than 10 wt% unsaponifiable neutral compounds of the total weight of the distilled tall oil.

The term "microbial oils" refers to triglycerides (lipids) produced by microbes. The term "algal oils" refers to oils derived directly from algae. The term "animal fats and oils" refers to lipid materials derived from animals.

Examples of the recycled or renewable organic material of the present invention include, but are not limited to, animal based oils and fats, vegetable or plant based oils and fats such as sludge palm oil, used cooking oil, microbial oils, algal oils, free fatty acids, any lipids containing phosphorous and/or metals, oils originating from yeast or mold products, oils originating from biomass, rapeseed oil, canola oil, colza oil, sunflower oil, soybean oil, hemp oil, olive oil, linseed oil, cottonseed oil, mustard oil, palm oil, arachis oil, castor oil, coconut oil, animal fats such as suet, tallow, blubber, recycled alimentary fats, starting materials produced by genetic engineering, and biological starting materials produced by microbes such as algae and bacteria, tall oil, tall oil fatty acid TOFA), crude fatty acids (CFA), tall oil pitch (TOP), and any mixtures of said feedstocks.

In particular, the recycled or renewable organic material is crude tall oil (CTO) or tall oil pitch (TOP).

The recycled or renewable organic material to be treated by the present method contains high amounts of silicon compounds. The recycled or renewable organic material of the present invention comprises more than 1 ppm silicon compounds. In particular the recycled or renewable organic material of the present invention comprises more than 10 ppm silicon compounds, more particularly the recycled or renewable organic material of the present invention comprises more than 15 ppm silicon compounds, and even more particularly the recycled or renewable organic material of the present invention comprises more than 20 ppm silicon compounds.

The recycled or renewable organic material to be treated by the present method further contains high amounts of phosphorous compounds. The phosphorous compounds present in the biomass-based lipid material are typically phospholipids. The phospholipids present in the biomass-based lipid material are in particular one or more of phosphatidyl ethanolamines, phosphadityl cholines, phosphatidyl inositols, phosphatidic acids, and phosphatidyl ethanolamines.

In particular the recycled or renewable organic material of the present invention comprises more than 10 ppm, especially more than 20 ppm, particularly more than 50ppm phosphorous.

The recycled or renewable organic material to be treated by the present method may also comprise further impurities e.g. impurities comprising phosphorus and/or metals in the form of phospholipids, soaps and/or salts. The impurities may for example be in the form of phosphates or sulfates, iron salts or organic salts, soaps or phospholipids. The metal impurities that may be present in the biomass-based lipid material are for example alkali metals or alkali earth metals, such as sodium or potassium salts, or magnesium or calcium salts, or any compounds of said metals.

Accordingly provided herein is method of purifying a recycled or renewable organic material, wherein the recycled or renewable organic material comprises more than 1 ppm silicon as silicon compounds and/or more than 10 ppm phosphorous as phosphorous compounds,

comprising the steps of

(a) providing a feed of the recycled or renewable organic material;

(b) optionally pre heat treating the recycled or renewable organic material at 180 to 325°C and optionally adding acid before or after the heat treatment process and optionally filtering the pre heat treated recycled or renewable organic material;

(c) heat treating the recycled or renewable organic material in the presence of an adsorbent at 180 to 325°C and filtering the heat treated recycled or renewable organic material, and optionally adding acid before or after the heat treatment process;

(d) optionally blending the heat treated recycled or renewable organic material with a hydrocarbon or lipid-based stream;

(e) optionally evaporating the volatile silicon compounds from the heat treated recycled or renewable organic material; and

(f) hydrotreating the heat treated recycled or renewable organic material in a presence of a hydrotreating catalyst;

to obtain purified hydrotreated recycled or renewable organic material comprising less than 20%, preferably less than 10 %, more preferably less than 5%, of the original silicon content of the recycled or renewable organic material provided in step (a) and/or less than 30% of the original phosphorous content of the recycled or renewable organic material provided in step (a).

In step (c) the recycled or renewable organic material is heated at any temperature from 180 to 325°C. For achieving optimal results, step (c) is performed at 200 to 300°C, preferably at 240 to 280°C.

The time during which the recycled or renewable organic material is heated and held at the desired temperature, i.e. residence time, is typically from 1 to 300 min, preferably from 5 to 240 min, more preferably from 30 to 90 min in step (c).

The pressure in step (c) is typically from 500 to 5000 kPa, preferably from 800 to 2000 kPa.

In step (c) the recycled or renewable organic material is heated to cause thermal reactions that disrupt the structure of the impurity containing compounds comprised in the recycled or renewable organic material thus forming material that adsorbs into the adsorbent present in the heating step (c), or material that forms solid precipitates and that can thus be subsequently removed from the recycled or renewable organic material.

The adsorbent present in step (c) may be selected from silica-based adsorbents. Preferably the adsorbent is selected from a group consisting of alumina silicate, silica gel and mixtures thereof. In step (c) the amount of adsorbent is typically from 0.1 to 10.0 wt-%, preferably 0.5 to 2.0 wt%, of the total weight of the treated recycled or renewable organic material.

The process can be further enhanced by acid addition before or after heat treatment in step (c). This removes any remaining sodium impurities. The acid is preferably selected from citric acid and phosphoric acid.

After the heat treatment the adsorbent comprising the undesired impurities is removed. Accordingly in step (c) the recycled or renewable organic material is subjected to removal of the solid adsorbent material. Removal of the solid material may be achieved for example by any separation method found suitable by a skilled person for separation of the solid material from the heat treated recycled or renewable organic material. Suitable examples include, but are not limited to, filtration, centrifugation, and phase separation. It is also to be understood that several separation methods, e.g. filtration and centrifugation, may be combined. The removal is preferably performed at any temperature from 100 to 180°C.

Prior to step (c) the recycled or renewable organic material may be subjected to a pre heat treatment in absence of adsorbent material. In optional step (b) the recycled or renewable organic material is pre heated to cause thermal reactions that disrupt silicon containing impurities comprised in the recycled or renewable organic material creating volatile silicon compounds material that can be subsequently removed from the h recycled or renewable organic material. In particular polydimethylsiloxanes (PDMS) resulting from anti-fouling agents degrade to volatile polydimethylcyclosiloxanes (PDMCS) under the process conditions.

The pre heat treatment of step (b) takes place at any temperature from 180 to 325°C. For achieving optimal results, step (b) is performed at 200 to 300°C, preferably at 240 to 280°C.

The time during which the recycled or renewable organic material is heated and held at the desired temperature, i.e. residence time, is typically from 1 to 300 min, preferably from 5 to 90 min, more preferably from 20 to 40 min in step (b).

The pressure in the pre heat treatment in step (b) is typically from 500 to 5000 kPa, preferably from 800 to 2000 kPa.

Optionally, the process can be further enhanced by acid addition before or after pre heat treatment in step (b). This removes any remaining sodium impurities. The acid is preferably selected from citric acid and phosphoric acid.

In step (b) the solid material created due to the heat treatment may be removed. Removal of the solid material may be achieved for example by any separation method found suitable by a skilled person for separation of the solid material from the heat treated recycled or renewable organic material. Suitable examples include, but are not limited to, filtration, centrifugation and phase separation. It is also to be understood that several separation methods, e.g. filtration and centrifugation, may be combined. Preferably the removal is accomplished by filtration. The removal is preferably performed at any temperature from 100 to 180°C.

Removal or solids/precipitates avoids deactivation of the hydrotreating catalyst in hydrotreatment of the recycled or renewable organic material.

After the heat treatment in step (c) the volatiles created due to the heat treatment and/or otherwise present in the recycled or renewable organic material may be removed. Accordingly in step (e) the heat treated recycled or renewable organic material is optionally subjected to evaporation of the volatile silicon compounds from the heat treated recycled or renewable organic material in one or more stages. In step (e) the evaporation is achieved at any temperature from 145 to 250°C, in particular at from 150°C to 225°C. For achieving optimal results, the evaporation in step (e) is performed at from 160°C to 200°C, preferably at from 160 to 180°C.

The reduced pressure in the evaporation in step (e) is such that evaporation of volatile Si compounds is achieved. Typically the pressure is from 0.1 to 5 kPa, preferably from 0.1 to 3 kPa.

The evaporated mass should advantageously be arranged to evaporation of 1 to 10 wt%, preferably from 1 to 8 wt%, more preferably from 1 to 5 wt%, even more preferably from 1 to 3 wt%, of the heat treated recycled or renewable organic material.

The time during which the heat treated recycled or renewable organic material is heated and evaporated at the desired temperature, i.e. residence time, is typically from 100 to 600 min, preferably from 180 to 300 min in the evaporation phase of step (e).

An applicable step (e) provides (i) a vapor fraction comprising the major part of volatile silicon compounds, and (ii) a heat treated recycled or renewable organic material fraction comprising less than 50 %, preferably less than 30 %, of the original silicon content of the recycled or renewable organic material provided in step (a).

The evaporation in step (e) may be accomplished by any evaporation method found suitable by a skilled person for separation of the volatiles from the heat treated recycled or renewable organic material. Suitable examples include, but are not limited to, falling film evaporation, rising film evaporation, thin film evaporation and flash evaporation, for example. The evaporation may be accomplished in one or more stages. It is also to be understood that several evaporation methods, e.g. thin film evaporation and flash evaporation, may be combined. Preferable evaporation method of the present invention is one or multi stage flash evaporation. Due to high pressure difference in flash vessel, less evaporation mass is needed in flash evaporation to provide better mass transfer as compared to thin film evaporation. For example, applying the same method and equipment as in a typical crude tall oil (CTO) thin film evaporation process for tall oil pitch (TOP) after heat treatment remarkably increases heat consumption as compared to flash evaporation.

The optimum temperature, pressure, evaporated mass and how many flash stages to use depends on composition and quality of the recycled or renewable organic material and also on the heat treatment parameters (temperature, pressure and residence time) of step (c) and optional steps (b) and (e).

Furthermore, it is preferable to add water to the initial mixture of the heat treated recycled or renewable organic material. Adding a small percentage of water to the initial heat treated recycled or renewable organic material allows use of lower temperature and higher vacuum pressure while achieving the same level of Si removal than in normal evaporation. Even more importantly, there is less loss of volatile fatty acids, which reduces the amount of fatty acid waste to half compared to evaporation without water.

Accordingly in an example of the present invention water is added to the heat treated recycled or renewable organic material so that water content before evaporation step (e) is from 1 to 5 wt%, preferably from 1.5 to 4 wt% more preferably from 2 to 3 wt% of the total weight of the heat treated recycled or renewable organic material.

The purified recycled or renewable organic material is subjected to (f) to hydrotreatment in presence of a hydrotreating catalyst to further remove silicon from the recycled or renewable organic material.

The heat treated recycled or renewable organic material may be (d) blended with a hydrocarbon or lipid-based stream if so desired. The hydrocarbon or lipid-based stream is preferably vacuum gas oil (VGO).

The term "hydrotreating" refers to a chemical engineer process in which reaction of hydrogen is used to remove impurities, such as oxygen, sulfur, nitrogen, phosphorous, silicon and metals, especially as part of oil refining.

Hydrotreating can be performed in one or several steps in one or more reactor units or catalyst beds.

Step (f) is typically achieved under continuous hydrogen flow. For achieving optimal results the continuous hydrogen flow is step (f) preferably has H_2/feed ratio from 500 to 2000 n-L/L, more preferably from 800 to 1400 n-L/L.

In step (f) hydrotreatment is advantageously performed at a temperature from 270 to 380°C, preferably from 275 to 360°C., more preferably from 300 to 350°C. Typically the pressure in step (f) is from 4 to 20 MPa.

The hydrotreating catalyst is step (f) preferably comprises at least one component selected from IUPAC group 6, 8 or 10 of the Periodic Table.. Preferably the hydrotreating catalyst in step (f) is a supported Pd, Pt, Ni, NiW, NiMo or a CoMo catalysts and the support is zeolite, zeolite-alumina, alumina and/or silica, preferably NiW/Al_2O_3, NiMo/Al_2O_3 or CoMo/Al_2O_3. In particular the hydrotreating catalyst is a sulfided NiW, NiMO or CoMo catalyst.

The time during which the recycled or renewable organic material is heated and held at the desired temperature, i.e. residence time, is typically from 1 to 300 min, preferably from 5 to 240 min, more preferably from 30 to 90 min in step (c).

An applicable hydrotreatment step (f) provides a purified hydrotreated recycled or renewable organic material. The purified hydrotreated recycled or renewable organic material advantageously comprises less than 20%, more preferably less than 10%, even more preferably less than 5%, of the original silicon content content of the recycled or renewable organic material provided in step (a) and/or less than 30% of the original phosphorous content of the recycled or renewable organic material provided in step (a).

For achieving optimal results part of the hydrotreated recycled or renewable organic material may be recycled in step (f). Preferably the ratio of the fresh feed i.e. purified recycled or renewable organic material obtained in step (c) to the recycled hydrotreated recycled or renewable organic material is from 2:1 to 20:1.

In a particular example step (f) is accomplished by (f1) hydrodeoxygenating (HDO) the heat treated recycled or renewable organic material fraction. This is preferably achieved in a presence of a HDO catalyst at a temperature from 290 to 350°C under pressure from 4 to 20 MPa and under continuous hydrogen flow.

The term “hydrodeoxygenation (HDO)” refers to removal of oxygen as water by the means of molecular hydrogen under the influence of a (HDO) catalyst.

The HDO catalyst may for example be selected from a group consisting of NiMO-, CoMo-, NiW-catalysts and any mixtures thereof. Preferably the HDO catalyst is sulfided NiW, NiMo or CoMo catalyst.

Advantageously, the continuous hydrogen flow has H2/feed ratio from 500 to 2000 n-L/L, preferably from 800 to 1400 n-L/L.

Preferably step (f1) is performed to obtain purified recycled or renewable organic material comprising less than 1 wt% oxygen.

In another example step (f) is accomplished by (f2) hydrodesulfurizing (HSD) the heat treated recycled or renewable organic material fraction. The term “hydrodesulfurisation (HDS)” refers to removal of sulfur as hydrogensulfide by the means of molecular hydrogen under the influence of a (HDS) catalyst.

In another example step (f) is accomplished by (f3) hydrometaillizing (HDM) the heat treated recycled or renewable organic material fraction. The term “hydrodemetallization (HDM)” refers to removal of metals by trapping them with a (HDM) catalyst.

In another example step (f) is accomplished by (f4) hydrodenitrificating (HDN) the heat treated recycled or renewable organic material fraction. The term “hydrodenitrification (HDN)” refers to removal of nitrogen by the means of molecular hydrogen under the influence of a (HDN) catalyst.

In another example step (f) is accomplished by (f5) hydrodearomatizing (HDA) the heat treated recycled or renewable organic material fraction. The term “hydrodearomatisation (HDA)” refers to saturation or ring opening of aromatics by the means of molecular hydrogen under the influence of a (HDA) catalyst.

Figure 1 illustrates a first exemplary process flow of the present method.

Referring to Figure 1, a feed of recycled or renewable organic material, in particular tall oil pitch (TOP), 10 is subjected to a step of heat treating 20 the recycled or renewable organic material as discussed herein for step (b). The heat treated feed of recycled or renewable organic material may then be then evaporated 30 as discussed herein for step (e) and a bottom containing a heat treated recycled or renewable organic material fraction 31 comprising less than 50 % of the original silicon content of the recycled or renewable organic material provided in step (a), and a vapor fraction 32 comprising the major part of volatile silicon compounds is obtained. The heat treated recycled organic material 31 is then subjected to heating 40 the recycled or renewable organic material the presence of adsorbent to adsorb the impurities to the adsorbent and to render the mixture separable as discussed herein for step (c). The adsorbent is then separated 50 from the treated feed of recycled or renewable organic material as discussed herein for step (c) to obtain a purified recycled or renewable organic material 51 and an adsorbent 52 comprising the major part of the impurities. The purified recycled or renewable organic material is then hydrotreated 60, as discussed herein for step (f) to obtain a purified hydrotreated recycled or renewable organic material 61, wherein the purified hydrotreated recycled or renewable organic material comprises less than 20%, preferably less than 10%, more preferably less than 5%, of the original silicon content of the recycled or renewable organic material provided in step (a) and/or less than 30 % of the original phosphorous content of the recycled or renewable organic material provided in step (a). The hydrotreated recycled or renewable organic material 61 may then be subjected to catalytic upgrading 70.

After the recycled or renewable organic material has been purified in accordance with the present method, it may be subjected to further processing e.g. catalytic upgrading. Such catalytic upgrading processes include, but are not limited to, catalytic cracking, catalytic hydrocracking, thermo-catalytic cracking, catalytic hydrotreatment, fluid catalytic cracking, catalytic ketonization, and catalytic esterification. Such processes require the recycled or renewable organic material to be sufficiently pure and free from impurities that may otherwise hamper the catalytic process or poison the catalyst(s) present in the process.

Accordingly the present invention further provides a process for producing recycled or renewable hydrocarbons, comprising steps of (x) purifying the recycled or renewable organic material as discussed herein, and (y) subjecting the purified recycled or renewable organic material to an oil refinery conversion process, wherein the oil refinery conversion process comprises altering the molecular weight of the feed, such hydrocracking, or steamcracking, removal of heteroatoms from the feed, such as thermal catalytic cracking, fluid catalytic cracking, or hydrotreating, in particular hydrodeoxygenating, or hydrodesulfurizing, altering the degree of saturation of the feed, such as hydrotreating, thermal catalytic cracking, or fluid catalytic cracking, rearranging the molecular structure of the feed, such as isomerizing, or any combination thereof to obtain at least one recycled or renewable hydrocarbon.

In a typical example of the present process the recycled or renewable hydrocarbon is a renewable traffic fuel or fuel component.

In an example of the present process, step (y) is hydrocracking. In such example, step (y) is preferably performed in a mild hydrocracking (MHC) refinery unit, in particular in a presence of a hydrocracking catalyst.

In another example of the present process, step (y) is steamcracking. In such example step (y) is preferably performed in a steamcracking unit.

In yet another example of the present process, step (y) is isomerization. In such example, step (y) is preferably performed in an isomerization unit.

In yet another example of the present process, step (y) is hydrotreating. In such example, step (y) is preferably performed in a hydrotreating unit.

In yet another example of the present process, step (y) is thermal catalytic cracking (TCC). In such example, step (y) is preferably performed in a thermal catalytic cracking unit.

In yet another example of the present process, step (y) is fluid catalytic cracking (FCC). In such example, step (y) is preferably performed in a fluid catalytic cracking unit.

EXPERIMENTAL

Example 1

Crude TOP was treated in the presence of two adsorbents: alumina silicate (Tonsil 9194 FF) and silica gel (Trisyl). The amount of each adsorbent was 1.5 wt-%. Crude TOP samples from different producers were tested. Water addition of 0.4 wt.-% was made prior the high temperature adsorption treatment.

During high temperature adsorption treatment the sample materials were heated to temperature 280°C for 60 minutes. After this treatment the sample materials were cooled to 100°C and filtered through a 0.45 µm filter paper.

From the obtained results it can be seen that Si and other impurities can be very efficiently removed from the feed at elevated temperatures in presence of both alumina silicate and silica gel adsorbent. However, more efficient purification was obtained using silica gel material. The results are listed in Table 1. As can be seen from Table 2 and Figure 2 and Figure 3, efficient Si and P removal cannot be achieved by mere acid + heat treatment nor acid + adsorption purification method.

Table 1. Effect of heat treatment adsorption on Si and P removal from different types of crude TOP samples. Adsorbent addition 1.5 wt-%.

		14144865	14225369	14225368
		Crude TOP A	280°C, 1 hour	280°C, 1 hour
⍰	⍰			
⍰	⍰		1.5 wt.-% Tonsil 9194	1.5 wt.-% Trisyl
Al	mg/kg	7.1	3.7	<0.2
Fe	mg/kg	27	32	2.4
Na	mg/kg	580	150	150
Si	mg/kg	27	3	1.3
Ca	mg/kg	56	13	0.82
Mg	mg/kg	6.2	14	<0.3
P	mg/kg	50	14	<0.6

		14177357	14225371	14225370
		Crude TOP B	280°C, 1 hour	280°C 1.5 wt.-% Trisyl
			1.5 wt.-% Tonsil 9194	
Al	mg/kg	10	4	<0,2
Fe	mg/kg	71	50	0.62
Na	mg/kg	740	180	170
Si	mg/kg	130	12	4.4
Ca	mg/kg	41	13	0.57
Mg	mg/kg	7.4	13	<0.3
P	mg/kg	137	21	1.3

Table 2 Effect of acid treatment (Citric acid addition 2000 ppm) and adsorption on Si and P removal from crude TOP sample. Adsorbent addition 2.0 wt-%.

		14151662	14151646
		Crude TOP C	120°C bleaching + cake filtration
☐	☐		
☐	☐		2 wt.-% Tonsil 9194
Al	mg/kg	5	0.64
Fe	mg/kg	29	1.1
Na	mg/kg	490	6.9
Si	mg/kg	41	15
Ca	mg/kg	25	4.5
Mg	mg/kg	4.2	1.5
P	mg/kg	73	9.5

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

CLAIMS

1. A method of purifying a recycled or renewable organic material, wherein the recycled or renewable organic material comprises more than 1 ppm silicon as silicon compounds and/or more than 10 ppm phosphorous as phosphorous compounds,

comprising the steps of

(a) providing a feed of the recycled or renewable organic material, wherein the recycled or renewable organic material is selected from a group consisting of plant based fats and oils, animal based fats and oils, fossil waste-based oils, waste oils, algal oils and microbial oils;

(b) heat treating the recycled or renewable organic material in a presence of an adsorbent at 180 to 325°C and filtering the heat treated recycled or renewable organic material, the adsorbent comprising at least a silica gel; and

(c) hydrotreating the heat treated recycled or renewable organic material in a presence of a hydrotreating catalyst;

to obtain purified hydrotreated recycled or renewable organic material comprising less than 20% of the original silicon content of the recycled or renewable organic material provided in step (a) and/or less than 30% of the original phosphorous content of the recycled or renewable organic material provided in step (a).

2. A method as claimed in claim 1, further comprising step (d) pre heat treating the recycled or renewable organic material at 180 to 325°C to form a pre heat treated recycled or renewable organic material.

3. A method as claimed in claim 2, further comprising adding acid before or after the pre heat treatment process.

4. A method as claimed in claim 2 or 3, further comprising filtering the pre heat treated recycled or renewable organic material.

5. A method as claimed in any one of claims 1 to 4, further comprising adding acid before or after the heat treatment process.

6. A method as claimed in any one of claims 1 to 5, further comprising step (e) blending the heat treated recycled or renewable organic material with a hydrocarbon or lipid-based stream.

7. A method as claimed in claim 6, wherein in step (e) the hydrocarbon or lipid-based stream is vacuum gas oil or animal fat.

8. A method as claimed in any one of claims 1 to 7, further comprising

step (f) evaporating volatile silicon compounds from the heat treated recycled or renewable organic material.

9. A method as claimed in any one of claims 1 to 8, wherein the purified hydrotreated recycled or renewable organic material comprises less than 10% of the original silicon content of the recycled or renewable organic material provided in step (a).

10. A method as claimed in claim 9, wherein the purified hydrotreated recycled or renewable organic material comprises less than 5% of the original silicon content of the recycled or renewable organic material provided in step (a).

11. A method as claimed in any one of claims 2 to 10, wherein pre heat treatment in step (d) is performed at 200 to 300°C.

12. A method as claimed in claim 11, wherein pre heat treatment in step (d) is performed at 240 to 280°C.

13. A method as claimed in any one of claims 2 to 12, wherein a residence time in step (d) is from 1 to 300 min.

14. A method as claimed in claim 13, wherein the residence time in step (d) is from 5 to 90 min.

15. A method as claimed in claim 14, wherein the residence time in step (d) is from 20 to 40 min.

16. A method as claimed in any one of claims 8 to 15, wherein evaporation in step (f) is performed at 150°C to 225°C.

17. A method as claimed in claim 16, wherein evaporation in step (f) is performed at 160°C to 200°C.

18. A method as claimed in claim 17, wherein evaporation in step (f) is performed at 160 to 180°C.

19. A method as claimed in any one of claims 8 to 18, wherein a pressure in evaporation of step (f) is from 0.1 to 5 kPa.

20. A method as claimed in claim 19, wherein the pressure in evaporation of step (f) is from 0.1 to 3 kPa.

21. A method as claimed in any one of claims 8 to 20, wherein in evaporation of step (f), from 1 to 10 wt% of the heat treated recycled or renewable organic material is evaporated.

22. A method as claimed in claim 21, wherein in evaporation of step (f), from 1 to 8 wt% of the heat treated recycled or renewable organic material is evaporated.

23. A method as claimed in claim 22, wherein in evaporation of step (f), from 1 to 5 wt% of the heat treated recycled or renewable organic material is evaporated.

24. A method as claimed in claim 23, wherein in evaporation of step (f), from 1 to 3 wt% of the heat treated recycled or renewable organic material is evaporated.

25. A method as claimed in any one of claims 8 to 24, wherein water is added to the heat treated recycled or renewable organic material so that a water content of the heat treated recycled or renewable organic material before evaporation step (f) is from 1 to 5 wt%.

26. A method as claimed in claim 25 wherein the water content is from 1.5 to 4 wt%.

27. A method as claimed in claim 26 wherein the water content is from 2 to 3 wt%.

28. A method as claimed in any one of claims 1 to 27, wherein heat treatment in step (b) is performed at 200 to 300°C.

29. A method as claimed in claim 28, wherein heat treatment in step (b) is performed at 240 to 280°C.

30. A method as claimed in any one of claims 1 to 29, wherein a residence time in step (b) is from 1 to 300 min.

31. A method as claimed in claim 30, wherein, the residence time in step (b) is from 5 to 240 min

32. A method as claimed in claim 31, wherein, the residence time in step (b) is from 30 to 90 min.

33. A method as claimed in any one of claims 1 to 32, wherein a pressure in step (b) is from 500 to 5000 kPa.

34. A method as claimed in claim 33, wherein the pressure in step (b) is from 800 to 2000 kPa.

35. A method as claimed in claim 34, wherein the adsorbent further comprises an alumina silicate.

36. A method as claimed in any one of claims 1 to 35, wherein an amount of adsorbent is from 0.1 to 10.0 wt-% of a total weight of the recycled or renewable organic material.

37. A method as claimed in claim 36, wherein the amount of adsorbent is from 0.5 to 2.0 wt%,

38. A method as claimed in any one of claims 1 to 37, wherein hydrotreating step (c) takes place under continuous hydrogen flow.

39. A method as claimed in any one of claims 1 to 38, wherein step (c) is performed at 270 to 380°C.

40. A method as claimed in claim 39, wherein step (c) is performed at 275 to 360°C.

41. A method as claimed in any one of claims 1 to 40, wherein step (c) is performed under pressure from 4 to 20 MPa.

42. A method as claimed in any one of claims 1 to 41, wherein the hydrotreating catalyst in step (c) comprises at least one component selected from IUPAC group 6, 8 or 10 of the Periodic Table.

43. A method as claimed in any one of claims 1 to 42, wherein the hydrotreating catalyst in step (c) is a supported Pd, Pt, Ni, NiW, NiMo or a CoMo catalyst and the support is zeolite, zeolite-alumina, alumina and/or silica.

44. A method as claimed in claim 43, wherein the hydrotreating catalyst in step (c) is a supported NiW/Al_2O_3, $NiMo/Al_2O_3$ or $CoMo/Al_2O_3$.

45. A method as claimed in any one of claims 1 to 44, wherein step (c) is accomplished by hydrodeoxygenating the heat treated recycled or renewable organic material fraction.

46. A method as claimed in claim 45, wherein step (c) is accomplished by hydrodeoxygenating the heat treated recycled or renewable organic material fraction in a presence of a hydrodeoxygenating catalyst at a temperature from 290 to 350°C under pressure from 4 to 20 MPa and under continuous hydrogen flow.

47. A method as claimed in claim 46, wherein step (c) is performed at 300 to 350°C.

48. A method as claimed in claim 47, wherein less than 10 % of the original silicon content of the recycled or renewable organic material is provided in step (a).

49. A method as claimed in claim 48, wherein less than 5% of the original silicon content of the recycled or renewable organic material is provided in step (a).

50. A method as claimed in any one of claims 46 to 49, wherein in step (c) the hydrodeoxygenating catalyst is sulfided NiW, NiMO or CoMo catalyst.

51. A method as claimed in any one of claims 46 to 50, wherein in step (c) the continuous hydrogen flow has H2/feed ratio from 500 to 2000 n-L/L.

52. A method as claimed in claim 51, wherein in step (c) the continuous hydrogen flow has H2/feed ratio from 800 to 1400 n-L/L.

53. A method as claimed in any one of claims 1 to 52, wherein a part of the hydrotreated product from step (c) is recycled to step (a).

54. A method as claimed in claim 53, wherein a ratio of the feed to the hydrotreated product is from 2:1 to 20:1.

55. A process for producing recycled or renewable hydrocarbons, comprising steps of

(x) purifying the recycled or renewable organic material as claimed in any one of claims 1 to 54, and

(y) subjecting the purified recycled or renewable organic material to a oil refinery conversion process, wherein the oil refinery conversion process comprises altering a molecular weight of the feed, removal of heteroatoms from the feed, altering a degree of saturation of the feed, rearranging a molecular structure of the feed, or any combination thereof to obtain at least one recycled or renewable hydrocarbon.

56. A process as claimed in claim 55 wherein step (y) is hydrocracking.

57. A process as claimed in claim 56, wherein step (y) is performed in a mild hydrocracking refinery unit.

58. A process as claimed in claim 56 or 57, wherein step (y) is performed in a presence of a hydrocracking catalyst.

59. A process as claimed in claim 55 wherein step (y) is steamcracking.

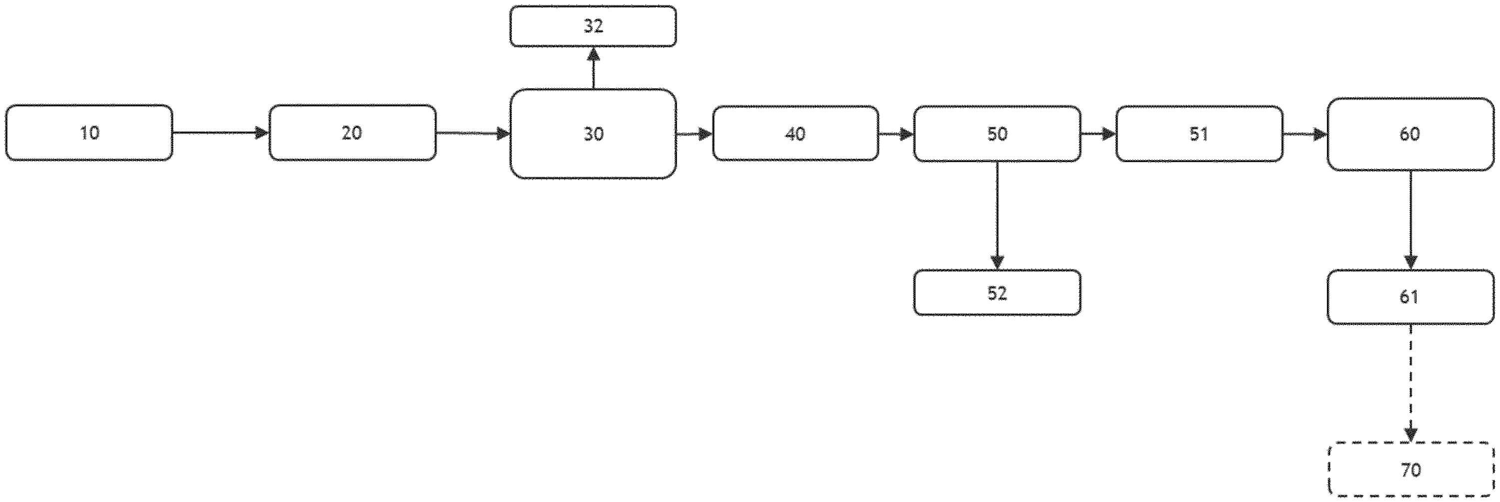
60. A process as claimed in claim 55 wherein step (y) is isomerization.

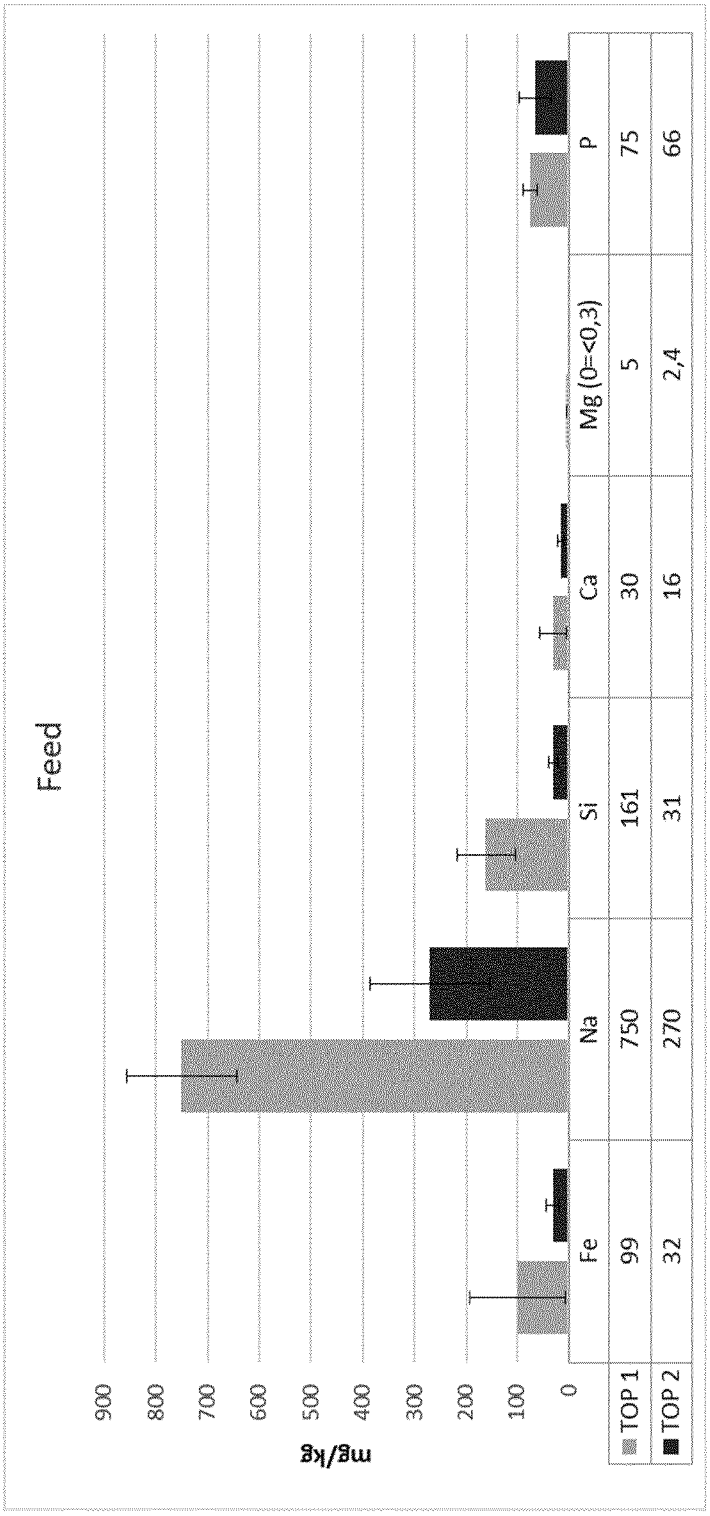
61. A process as claimed in claim 55 wherein step (y) is hydrotreating.

62. A process as claimed in claim 55 wherein step (y) is thermal catalytic cracking.

63. A process as claimed in claim 55 wherein step (y) is fluid catalytic cracking.

Figure 1

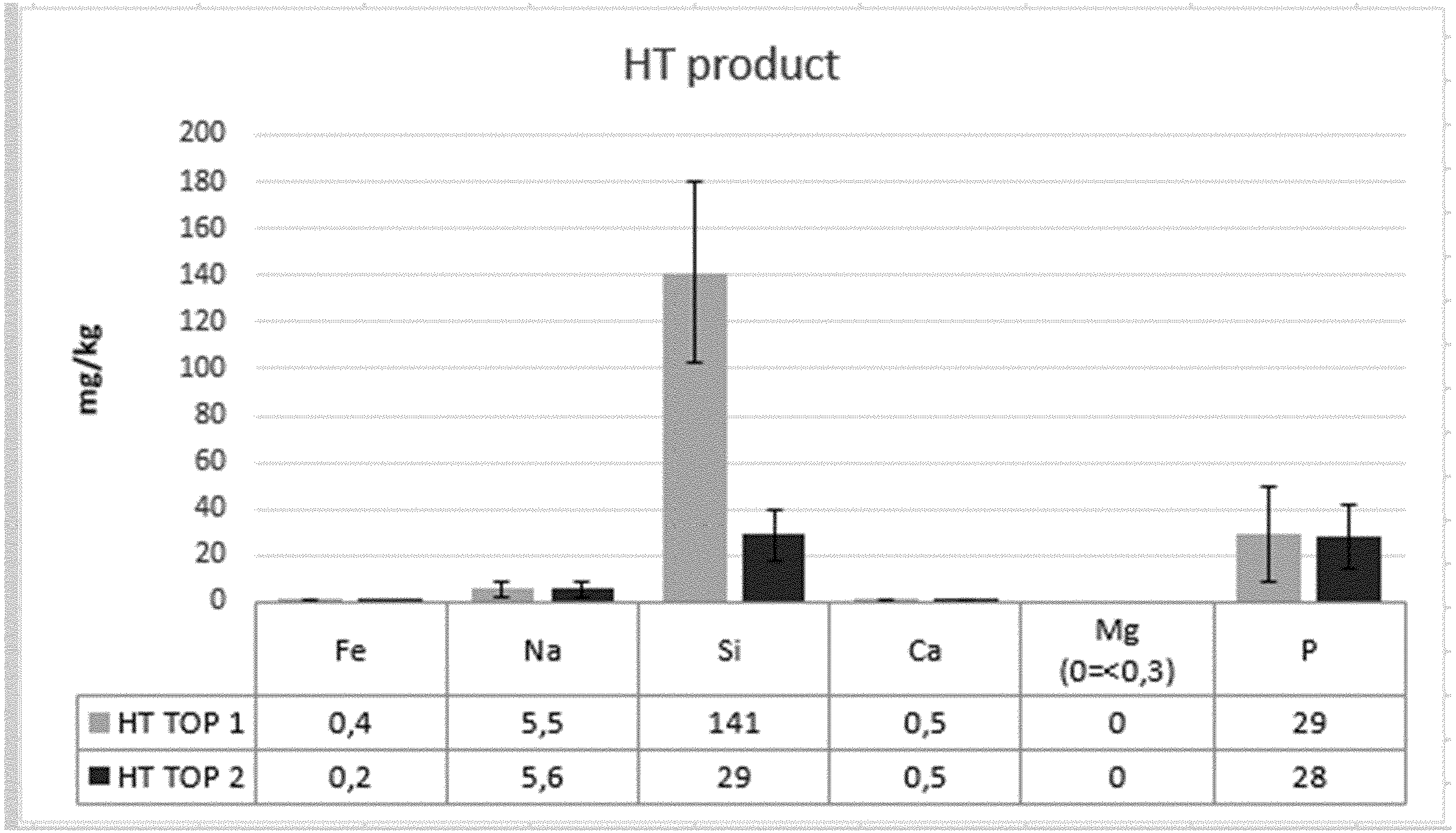




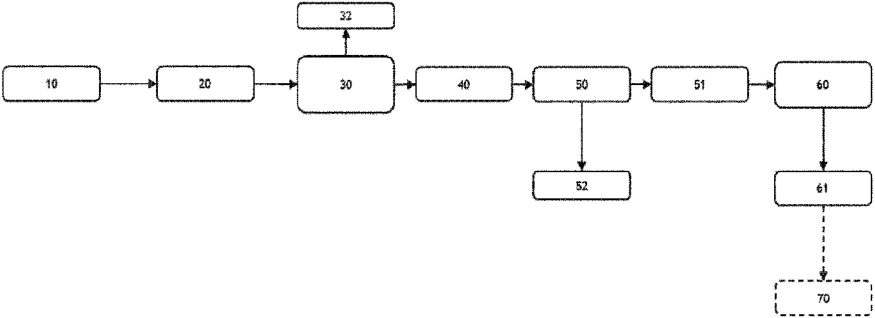
	Fe	Na	Si	Ca	Mg (0=<0,3)	P
▨ TOP 1	99	750	161	30	5	75
■ TOP 2	32	270	31	16	2,4	66

Figure 2

Figure 3



	Fe	Na	Si	Ca	Mg (0=<0,3)	P
▨ HT TOP 1	0,4	5,5	141	0,5	0	29
■ HT TOP 2	0,2	5,6	29	0,5	0	28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