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(54) **METHOD FOR REMOVING CHLORINE FROM FEEDSTOCKS**

(57) The present invention concerns a method for removing chlorine-containing contaminants from feedstocks, *i.a.*, in edible or renewable oil, renewable fuel and plastics recycling applications, by using a combination of alkaline materials like soda and solid clay-based adsorbents like bleaching earth.

EP 4 461 787 A1

Description

[0001] The present invention concerns a method for removing chlorine-containing contaminants from feedstocks, *i.a.*, in edible or renewable oil, renewable fuel and plastics recycling applications.

[0002] Oil refining implies multiple physical and chemical processes to remove oil impurities such as color bodies, oxidation agents or contaminants like metals, halogen containing molecules or phosphorous compounds that make it not suitable for its commercialization or use in other applications. In order to remove these compounds, adsorbents are used in the so-called bleaching process, where impurities and/or contaminants are bound on the adsorbent's high surface. After bleaching, the adsorbent (typically in the form of bleaching earth)-oil mixture is separated by filtration using filters resulting in a bleached oil ready for downstream processes such as deodorization in edible oil refining or hydrogenation in case of renewable fuel applications.

[0003] Triggered by new legislations that are looking to promote the use of waste feedstocks, e.g., in renewable diesel production, the oil refining industry is moving towards the use of renewable or recyclable feedstocks.

[0004] Plastic waste today is still largely landfilled or incinerated for heat generation. Although mechanical recycling might be preferred, since it enables a more sustainable reuse of resources, there are still waste streams left where chemical recycling can be an attractive alternative to reach the recycling targets set by many countries. It encompasses converting waste plastic material into useful chemicals. An important method for chemically recycling plastic waste is pyrolysis. Pyrolysis is a thermal degradation of plastic waste in an inert atmosphere. It yields products such as pyrolysis gas, liquid pyrolysis oil and char. Depending on the process conditions, pyrolysis oil can be the major product fraction and producers seek to maximize its content in the product mix. Pyrolysis gas and char can be used as fuel for generating heat, e.g., for reactor heating. The pyrolysis oil can be used as a source for syngas production or can be processed into chemical feedstock such as ethylene, propylene, C4 cuts, etc., for example by (steam) cracking.

[0005] Plastic waste typically is mixed plastic waste composed of different types of polymers. The polymers are often composed of carbon and hydrogen in combination with other elements such as chlorine, fluorine, sulfur, and nitrogen that complicate recycling efforts. The elements other than carbon and hydrogen may be harmful during the further processing of the crude pyrolysis oil, since they may de-activate or poison catalysts used in the further processing of the pyrolysis oil and are therefore often referred to as contaminants. During (steam-) cracking, halogen-containing compounds can damage the cracker by corrosion in that they release hydrogen halide. Similar corrosion issues are reported for equipment up- and downstream of the cracker, such as heat exchangers, storage vessels etc. Sulfur-containing compounds can de-activate or poison catalysts used in the cracker or can contaminate the cracker products. Nitrogen-containing impurities may also poison downstream catalysts, or they may form explosive NO_x when heated. When mixed plastics containing polyvinyl chloride (PVC) are thermally degraded, compounds having double carbon bonds and hydrogen chloride is formed. The hydrogen chloride liberated from PVC attacks the compounds having carbon-carbon double bonds leading to the formation of chloro-organic compounds. Plastic waste typically contains heteroatom-containing additives such as pigments, stabilizers and plasticizers that have been incorporated to improve the performance of the polymers. Such additives also often comprise nitrogen, halogen and sulfur containing compounds and heavy metals. For example, waste engine oils, transformer oils, hydraulic oils and machine oils may contain heavy metal abrasion. Pyrolysis oil might also contain metals like iron (Fe) and metal oxides or other contaminants like phosphorus (P). The (heavy) metals are often toxic, and the quality of the pyrolysis oil is reduced by the presence of (heavy) metals, metal oxides and other impurities. Furthermore, plastic waste often may be uncleaned plastics with residue that may also contain elements other than carbon and hydrogen. Therefore, the reduction of the nitrogen, oxygen, phosphorus, sulfur, and halogen content in the pyrolysis oil as well as the (heavy-)metal content is essential for any meaningful processing of the pyrolysis oil. Especially, a high-quality pyrolysis oil rich in carbon and hydrogen and low in contaminants is preferred as feedstock to prevent catalyst deactivation and corrosion problems in downstream refinery processes.

[0006] Apart from plastics waste, in many cases also recycled or renewable organic material contains unwanted contaminants, such as e. g. organic oxygen and chlorine, which need to be removed from the material before catalytic treatment of the recycled or renewable organic material since such contaminants can have negative effects on the catalyst and/or can cause corrosion to process equipment, similar to the problems described *supra* for plastics waste.

[0007] Accordingly, numerous processes have been described that suggest removing the contaminants from plastics waste, recycled or renewable materials, many of them using different types of solid adsorbent materials in a purification step.

[0008] Of particular importance is the removal chlorine-containing contaminants from feedstocks.

State of the art

[0009] WO 2020/020769 A1 (Neste) discloses a method of purifying a recycled or renewable organic material (such as e. g. plant-based fats and oils, animal-based fats and oils, fossil waste-based oils, waste oils, algal oils, and microbial oils) which contains chloride (as chloride salts or as organic chloride compounds) a contaminant. The recycled or

renewable organic material is first purified and then hydrotreated in the presence of a hydrotreating catalyst at elevated temperatures (270 to 380°C) under pressure (from 4 to 20 MPa) and under continuous hydrogen flow to obtain purified hydrotreated recycled or renewable organic material. 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.

The purification step can be carried out by either using an aqueous solution of an alkaline metal hydroxide (i.e., KOH, LiOH, NaOH or mixtures thereof, NaOH being preferred) or using a solid adsorbent material, typically selected from silica-based adsorbents such as Trisyl silica or selected from metal chlorides or metal oxides. After the purification pretreatment step using the solid adsorbent material, the adsorbent material is removed from the recycled or renewable organic material, e. g. by filtration, centrifugation, and phase separation. Likewise, the organic and aqueous phase are separated if the purification step uses the aqueous solution of an alkaline metal hydroxide.

[0010] CN 106268832 discloses a dry dechlorination agent for removing HCl from various kinds of gases in a catalytic reforming section and a preparation method thereof. The dechlorination agent comprises, *i.a.*, 20 to 75 % (w/w) sodium, magnesium or calcium carbonate, oxide or hydroxide as active ingredient, 1 to 10 % (w/w) of pore additive (e.g., NH_4HCO_3) and 5 to 70 % (w/w) of carrier (such as Al_2O_3 , diaspore, kaolin or clay). The dichlorination agent is prepared by mixing, drying, and calcination at 200-700 °C for 2 to 10 h.

[0011] CN 101773768 discloses a technique for oil refining and chemical purification, in particular a dry dechlorinating agent for removing HCl from a gas and a preparation method thereof. The dechlorination agent for gases comprises alkaline materials such as a mixture of Na_2CO_3 , CaCO_3 , NaOH, MgO, CaO, plus an aluminium salt, methyl cellulose and sodium-based bentonite, in particular cross-linked bentonite as a pore additive. The dichlorination agent is prepared by mixing, drying, and roasting at 350-450 °C for 4 h. It comprises a minimum of 40 % (w/w) of alkaline materials and a maximum of 12.5 % (w/w) of bentonite clay.

[0012] CN 102485837 discloses a high-temperature dechlorination agent suitable for an environment at a temperature of 200 to 500 °C. The dechlorination agent is mainly composed of active components sodium carbonate, sodium hydroxide, ammonium carbonate and polyvinyl alcohol, and is compounded with layered bentonite as a carrier. The active component reacts with the chloride in the raw oil to generate hydrogen chloride, so that hydrogen chloride is attached to the dechlorination agent, so as to achieve the purpose of removing chloride. The high-temperature dechlorination agent is prepared from 20 to 30% of Na_2CO_3 , 20 to 30% of NaOH, 20 to 40% of bentonite, 2 to 10% of polyvinyl alcohol and 1 to 2% of $(\text{NH}_4)_2\text{CO}_3$ by mixing. The dechlorination agent uses layered bentonite as a carrier and a mixture composed of active Na_2CO_3 , NaOH and $(\text{NH}_4)_2\text{CO}_3$ as an active component. Since bentonite is a layered structure, the carbonate between the layers and the hydroxide on the plate gradually react with the hydrogen chloride in the raw oil, and chloride ions are absorbed into the layered chemical structure, which can make its chemical activity more effective. Local restrictions. Using layered bentonite as the carrier of the dechlorination agent, on the one hand, increases the dispersion area of the active component, and improves the surface adsorption activity of the dechlorination agent; on the other hand, increases the overall thermal stability and structural strength of the dechlorination agent.

[0013] Dechlorination is carried out at $T > 200$ °C. The dichlorination agent comprises from 41 to 60 % (w/w) of alkaline materials and a maximum of 40 % (w/w) of clay

[0014] WO 2023/278530 A1 (BP) describes a process for removing chloride-containing organic compounds from renewable and bio-feedstocks, especially for processing a liquid feed. The process comprises providing a liquid feed having one or more fatty acids and/or fatty acid esters with a first chloride concentration of chloride-containing organic compounds and contacting the liquid feed with a solid treatment material to remove at least a fraction of the chloride-containing organic compounds to produce a treated liquid feed with a second, lower chloride concentration. The solid treatment material comprises an alkali metal or alkaline earth metal in ionic form, e.g. disposed on a support like alumina, an aluminosilicate, a silicate, or a zeolite. The solid treatment material can e.g. be an alkali-doped alumina, a sodium- and potassium-doped zeolite, or an alkali- or alkaline earth-containing mineral.

[0015] Accordingly, there is a need for a method for removing chlorine-containing contaminants from feedstocks, *i.a.*, in edible or renewable oil and plastics recycling applications.

[0016] Chlorine removal from used cooking oil (UCO) and other renewable feedstocks is of particular importance as chlorine in hydrotreated vegetable oil (HVO) processes can lead to severe damage of the used equipment. Also with other feedstocks, like pyrolysis oil, and for other uses similar shortcomings exist.

[0017] While inorganic chloride removal can be done comparably easily by utilizing washing steps or filtration of solids, the removal of organic chlorine requires chemical processes often accompanied with negative side effects such as metal leaching, saponification etc.

Object and description of the invention

[0018] It is an objective of the present invention to provide a new method for removing chlorine-containing contaminants from organic feedstocks so that the shortcomings of the prior art approaches are overcome. Although the examples described with respect to the present invention refer to waste oils like used cooking oil and animal fat, the method of the

invention can be equally used in other fatty acid-based oils and hydrocarbon-based oils, such as bio-based oil and fossil-based oil feedstocks.

[0019] In particular, with the method of the invention it is possible to reduce chlorine content from organic feedstocks while mitigating negative side effects and simplifying the commercial application.

[0020] This and other objectives of the invention are solved by the subject matter of the independent claims. Further and preferred embodiments of the invention are the subject matter of the dependent claims.

[0021] The invention is a method for removing chlorine-containing contaminants, i.e. organic chlorine and/or inorganic chloride containing contaminants, from organic feedstocks. The method of the invention comprises

- a. providing an organic feedstock that contains at least one organic and/or inorganic chlorine-containing contaminant;
- b. optionally (and preferably) extracting the inorganic chlorine containing contaminant by washing the organic feedstock with a polar solvent and separating the organic and polar liquid phases to obtain a washed organic feedstock;
- c. adding a solid clay-based adsorbent and alkaline material to the optionally (and preferably) washed organic feedstock;
- d. heating the mixture of adsorbent, alkaline material and washed organic feedstock in non-oxidizing conditions to an adsorption temperature T_{ads} ;
- e. removing the solid components to obtain a washed organic feedstock with reduced chlorine content compared to the washed organic feedstock resulting from step c);

[0022] The method of the invention is characterized in that the adsorbent to alkaline material ratio in the heating step d) is in the range of 80 : 20 to 99 : 1 (w/w).

[0023] In a preferred embodiment, the non-oxidizing condition in the heating step is a mild vacuum, in particular a pressure of from 50 to 500 mbar. The non-oxidizing condition can also be obtained by heating under an inert gas atmosphere at ambient or elevated pressure.

[0024] Preferably, the adsorption temperature T_{ads} is chosen so that the organic feedstock is maintained in liquid state. Depending on the type and quality of organic feedstock, T_{ads} typically is between 40 °C and 280 °C, preferably between 100 °C and 240 °C.

[0025] Preferably, the heating in step d) is maintained for 10 to 120 min.

[0026] Preferably, the polar solvent for extracting inorganic chlorine (chloride) is water or a water/additive mixture. Typically, the polar solvent contains at least 90 % (w/w) water. A typical additive may be an alcohol, preferably ethanol, that acts as a co-solvent, or acids and bases. The polar solvent may originate from multi-step processes (like degumming).

[0027] In a preferred embodiment, the removing of solid components to obtain a washed organic feedstock with reduced chlorine content compared to the washed organic feedstock is done by sedimentation, filtration, centrifugation, or by using cyclonic separators like hydrocyclones.

[0028] Preferably, the optional separating of organic and polar liquid phases to obtain the washed organic feedstock is done by centrifugation or flotation. Skilled persons are able to select the proper separation method and to adjust operating parameters as needed.

[0029] The method of the present invention addresses the problem of removing chlorine-containing contaminants such as in particular inorganic chloride and/or organic chlorine containing compounds from oil and waste oil feedstocks. Such feedstocks are of special interest for the production of hydrotreated vegetable oil (HVO) and/or sustainable aviation fuels (SAF) and/or fatty acid methyl esters (FAME) production for bio-diesel.

[0030] The organic feedstock suitable for the method of the invention can be any one of bio-based oils, i.e., fatty acid-based oils, and fossil-based oils, i.e., hydrocarbon-based oils, or any combination thereof. Suitable bio-based oils include virgin oils, such as, e.g., plant-based oils, animal fats, algae oils, microbial oils, etc., as well as recycled oils, such as, e.g., used cooking oils (UCOs), fatty residues, waste oils and greases, biomass oils derived from pyrolysis, etc. Suitable fossil-based oils include technical oils, such as, e.g., engine oils, lubricants, transformer oils, etc., as well as recycled technical oils, such as, e.g., used transformer oils, polymer-based oils derived from pyrolysis, etc.

[0031] The organic feedstock according to the invention can also be a two or multi-component mixture of different individual feedstock species. While one component is a waste feedstock, the other component(s) of such feedstock mixtures can also be waste feedstock(s) and/or more easy to treat feedstocks such as vegetable oil etc.

[0032] Typical organic feedstocks suitable for the present invention contain at least 10 % (w/w) of used cooking oil (UCO), wastes from edible oil production and/or animal fat (AF) and can comprise significantly higher amounts of gums, phosphorous compounds and unknown compounds interfering with adsorption compared to (edible) vegetable oils.

[0033] The solid clay-based adsorbent suitable for the method of the present invention can be any type of clay-based adsorbent. Preferably, the clay-based adsorbent is a bleaching earth (BE).

[0034] Bleaching earths (BE) can be naturally activated or acid activated. Activation results in different types of BE, such as naturally activated bleaching earth (NABE), dry modified acid-activated bleaching earths (DMBE), surface modified bleaching earths (SMBE), and high performance bleaching earths (HPBE), as well as mixtures of two or more

of these types of BE. Such types of BE are generally known in the art and are commercially available in a wide variety of grades and for different applications.

[0035] More preferably, the solid adsorbent is selected from the group consisting of naturally activated bleaching earth (NABE), surface modified bleaching earth (SMBE) and high-performance bleaching earth (HPBE), and any combinations thereof. Most preferably, the solid adsorbent is selected from the group consisting of naturally activated bleaching earth (NABE), and high-performance bleaching earth (HPBE), and any combinations thereof.

[0036] The clay-based adsorbent of the invention can further comprise other, preferably solid, additives, such as processing aids and filter aids (e.g., silicas, perlite, diatomaceous earth, etc.), with the clay-based component being at least 50% (w/w) of the overall adsorbent.

[0037] The main difference between each type of the above-mentioned BE can be found in their bleaching activity and physical parameters. NABEs are produced only by physical processing and are pH neutral. DMBE are chemically modified with weak acids (such as citric acid). SMBE are chemically activated using strong acid (such as concentrated mineral acid, e.g., sulfuric acid or hydrochloric acid) to modify significantly their surface for higher activity. HPBE are completely activated earths chemically activated with a strong acid in a reactor to significantly modify mineral structure and obtain the highest activity.

[0038] Preferably, the alkaline material is selected from the group consisting of alkaline metal and alkaline earth metal oxide, hydroxides and carbonates, aluminum oxide/hydroxide, iron oxide/hydroxide as well as any combinations thereof.

Examples

[0039] The invention and its benefits will further be explained by the following experimental examples.

[0040] Extraction procedure for crude feedstocks ("washing"): (waste) feedstock is heated until all fat components are completely liquid (temperature range typically 25 - 100°C). A water or solvent mixture (water/EtOH; as the case may be) is added at the same temperature to a solvent : feedstock ratio of 2:1 (w/w). The resulting feedstock-solvent-mixture is mixed well by e.g. shaking or high sheer force mixing for 5 min. Afterwards, solvent and feedstock are separated by centrifugation (for 5 min at 3000 relative centrifugal force (rcf)) to obtain a washed feedstock.

[0041] Adsorption procedure: Vacuum bleaching is carried out in stirred batch reactor at an adsorption temperature T_{ads} between 100 °C and 240 °C (as given in the experimental details) using the adsorbent (type and amount (in % w/w of the feedstock) as in the experimental details), for 60 min at 100 mbar pressure. After the bleaching step, the bleached feedstock is vacuum filtrated over paper filter (Whatman No. 40) followed by ambient pressure filtration over folded filter (Whatman 595 ½).

[0042] The following analytical methods have been used:

Metals and other contaminants like phosphorus (P) and sulfur (S) in the bleached oil are determined by calibrated Inductively Coupled Plasma (ICP) with optical emission spectroscopy (OES) detection. Samples are prepared by blending the oil with kerosene. Then, the samples are injected in the ICP for concentration measurement that together with concentration ratio used in calibration and weight of the sample, final results are obtained.

[0043] Free fatty acid (FFA) determination was done using the CDR FoodLab® analysis system and method. Samples are diluted, if required, and the appropriate amount (here 2.5 µl) added for the expected measurement range (here 0.03-1.1 % FFA) in the pre-filled disposable cuvettes. Prior to the addition, the cuvette is heated to 37°C for 15 minutes and a blank reading of the absorption at 630 nm wavelength is recorded by the device. After the addition, the cuvettes are firmly shaken, placed into the measurement cell and measured after 30s settling time. The result is internally calculated by the analysis system and displayed.

[0044] Soaps content is determined according to ISO 684:1974.

[0045] Total chlorine content was determined by oxidative combustion and coulomb metric titration.

[0046] The below experiments were carried out with a used cooking oil (UCO) feedstock (in crude and washed form, as per the above procedure) having the properties as given in Table 1:

| Table 1 - Feedstock types and their contaminant contents | | | | | |
|--|----------|---------|-------------|---------------------|---------|
| Type | Cl [ppm] | FFA [%] | Soaps [ppm] | Sum of metals [ppm] | P [ppm] |
| Crude | 121.4 | 0.7 | 120 | 21.6 | 15 |
| Washed | 8.6 | 0.6 | <10 | 4.8 | 8.2 |

[0047] As can be seen from Table 1, washing of the crude feedstock leads to reduction in certain contaminant levels. In particular, inorganic chloride contaminants are removed by washing, leaving predominantly organic chloride compounds in the washed UCO feedstock.

Example 1

Reduction of Cl content from washed UCO feedstock

[0048] A UCO was washed according to the above extraction procedure for crude feedstocks using water as extraction liquid. The resulting washed feedstock was bleached in accordance with the above adsorption procedure (with and without the adsorbent and/or alkaline material; adsorbent was added to the washed feedstock as a solid, alkaline material was added in the form of an aqueous solution (0.2 mol/l or 1.0 mol/l)). The tested alkaline material for removing chlorine was sodium carbonate (technical grade; BASF SE), the tested clay-based adsorbents a bleaching earth (BE; Tonsil Optimum 210 FF, Clariant Produkte (Deutschland) GmbH) and a natural alkaline clay (from Spain). Experimental details and results are given in Table 2:

| Table 2: Chlorine reduction from washed UCO | | | | | |
|---|---|-----------------------|----------|-----------------------|----------|
| Adsorbent/Alkaline material | Adsorbent/alkaline material content [% w/w] | T _{ads} [°C] | Cl [ppm] | T _{ads} [°C] | Cl [ppm] |
| None | 0 | | | 170 | 11.7 |
| BE | 0.5 | 100 | 10.0 | 170 | 9.0 |
| Natural alkaline clay | 0.5 | | | 170 | 8.8 |
| Na ₂ CO ₃ | 0.015 | | | 170 | 5.6 |

[0049] The results shown in table 2 indicate that the predominantly organic chlorine present in washed UCO can be removed above a temperature of 100 °C, especially at 170 °C, using any of the tested adsorbents (BE, natural alkaline clay) or the alkaline material Na₂CO₃.

Example 2

Reduction of Cl content from washed feedstock using a mix of bleaching earth and alkaline material adsorbent

[0050] A UCO was washed according to the above extraction procedure for crude feedstocks using water as extraction liquid. The resulting washed feedstock was bleached in accordance with the above adsorption procedure (with and without the adsorbent; see Example 1 for details). The tested materials for removing chlorine were alkaline materials sodium carbonate (technical grade, BASF SE) and cesium carbonate (99.9% purity (metal basis), Alfa Aesar), and a bleaching earth (BE; Tonsil Optimum 210 FF, Clariant Produkte (Deutschland) GmbH) as clay-based adsorbent material, and combinations of different amounts of sodium carbonate or cesium carbonate with the BE as materials according to the invention. Experimental details and results are given in Table 3:

| Table 3: Chlorine reduction from washed UCO using BE and/or alkali carbonates | | | |
|--|--|-----------------------|----------|
| Adsorbent [% w/w] | Alkaline material [% w/w] | T _{ads} [°C] | Cl [ppm] |
| None | None | 170 | 16.5 |
| BE (0.5%) | None | 100 | 13.2 |
| BE (0.5%) | None | 170 | 15.6 |
| BE (0.5%) | None | 240 | 31.1 |
| None | Na ₂ CO ₃ (0.015%) | 170 | 8.1 |
| BE (0.5%) | Na ₂ CO ₃ (0.015%) | 170 | 5.9 |
| BE (0.5%) | Na ₂ CO ₃ (0.015%) | 220 | 14.0 |
| BE (0.5%) | Na ₂ CO ₃ (0.025%) | 240 | 7.4 |
| BE (0.5%) | Na ₂ CO ₃ (0.05%) | 170 | 6.8 |
| BE (0.5%) | Na ₂ CO ₃ (0.05%) | 220 | 3.4 |

(continued)

| Table 3: Chlorine reduction from washed UCO using BE and/or alkali carbonates | | | |
|--|--|-----------------------|----------|
| Adsorbent [% w/w] | Alkaline material [% w/w] | T _{ads} [°C] | Cl [ppm] |
| BE (0.5%) | Cs ₂ CO ₃ (0.015%) | 220 | 21.0 |
| BE (0.5%) | Cs ₂ CO ₃ (0.046%) | 220 | 11.6 |

[0051] The results shown in table 3 indicate that the predominantly organic chlorine present in washed UCO can be removed above a temperature of 100 °C, especially at 170 °C or higher, using any of the tested adsorbents or adsorbent combinations. Combinations of BE and alkaline additive (Na₂CO₃) surprisingly shows higher Cl removal effectiveness than the individual adsorbents. Higher alkaline dosing leads to higher chlorine reduction at higher temperatures. The preferred temperature for chlorine reduction using a combination of BE and alkaline material is in the range of 100 - 240 °C, ideally in the range of 170 - 240 °C.

[0052] While sodium carbonate is easily available and offers good results in combination with a BE, Cs₂CO₃ can improve efficiency even further at same molar dosing (a Cs₂CO₃ dosage of 0.046% (w/w) and a Na₂CO₃ dosage of 0.015% (w/w) both correspond to a molar dosage of 1.1 mmol/l).

[0053] Table 4 shows the result of the determination of other parameters than Chlorine for the experiments of Table 3 (unless specifically indicated, all values given in ppm):

| Table 4 | | | | | | | | | | | |
|-------------------|--|-----------------------|---------|-------|-----|-----|-----|-----|-----|-----|----|
| Adsorbent [% w/w] | Alkaline material [% w/w] | T _{ads} [°C] | FFA [%] | Soaps | P | S | Ca | Fe | K | Mg | Na |
| None | None | 170 | 0.7 | 10 | 15 | 8 | 1.3 | 0.2 | 1.6 | 2.2 | 6 |
| BE (0.5%) | None | 100 | 0.6 | 10 | 7.8 | 35 | 1 | 0.2 | 0.7 | 1.5 | 2 |
| BE (0.5%) | None | 170 | 0.7 | 10 | 7.5 | 4 | 1.7 | 0.5 | 0.9 | 2.2 | 3 |
| BE (0.5%) | None | 240 | 0.7 | 10 | 5 | 2.8 | 1.1 | 0.8 | 1 | 1.5 | 4 |
| None | Na ₂ CO ₃ (0.015%) | 170 | 0.7 | 450 | 15 | 5 | 1.4 | 0.2 | 3.1 | 2.1 | 32 |
| BE (0.5%) | Na ₂ CO ₃ (0.015%) | 170 | 0.7 | 250 | 9.2 | 4 | 2.6 | 0.3 | 0.5 | 2.3 | 18 |
| BE (0.5%) | Na ₂ CO ₃ (0.015%) | 220 | 0.7 | 100 | 8.2 | 3 | 2 | 0.7 | 0.4 | 1.9 | 15 |
| BE (0.5%) | Na ₂ CO ₃ (0.025%) | 240 | 0.7 | 250 | 10 | 5 | 2.8 | 1.6 | 0.4 | 2.3 | 21 |
| BE (0.5%) | Na ₂ CO ₃ (0.05%) | 170 | 0.7 | 600 | 11 | 4 | 4.4 | 0.3 | 0.6 | 2.3 | 27 |
| BE (0.5%) | Na ₂ CO ₃ (0.05%) | 220 | 0.7 | 650 | 8.7 | 6 | 4.4 | 1.6 | 0.4 | 2.3 | 31 |
| BE (0.5%) | Cs ₂ CO ₃ (0.015%) | 220 | 0.7 | 10 | 7.3 | 3 | 1.7 | 0.5 | 0.8 | 1.8 | 4 |
| BE (0.5%) | Cs ₂ CO ₃ (0.046%) | 220 | 0.7 | 80 | 7.7 | 5 | 2.5 | 0.7 | 1.5 | 2 | 7 |

[0054] Using sodium carbonate, while being effective in chlorine removal, has the downside of leaching sodium into the oil phase which has to be removed for further processing. This unwanted effect can effectively be mitigated by the addition of a clay-based adsorbent (in this case, a BE), as can be seen from the results in table 4. The data in table 4 also indicate that the formation of FFA is effectively suppressed at all measured temperatures and with all BE/alkaline material combinations tested; similarly, the P content is reduced in all experiments using the clay-based adsorbent (BE). Surprisingly, while the use of alkaline material Na₂CO₃ alone leads to an increase in K content in the feedstock, the combination of clay-based adsorbent (BE) and alkaline material effectively counteracts this unwanted effect.

[0055] Importantly, and as can be seen from the data for the combination of clay-based adsorbent (BE) and alkaline material Na₂CO₃, the unwanted formation of soaps when adding Na₂CO₃ to the feedstock can effectively be reduced when using the clay-based adsorbent/alkaline material combination of the present invention.

Example 3

Reduction of Cl content from pyrolysis oil feedstock using a mix of bleaching earth and alkaline material adsorbents

[0056] A pyrolysis oil feedstock from plastics pyrolysis was treated in accordance with the above adsorption procedure (with and without the adsorbent; $T_{\text{ads}} = 150\text{ }^{\circ}\text{C}$; adsorption time 240 min). The tested materials for removing chlorine were the alkaline materials sodium carbonate (technical grade, BASF SE; added in the form of an aqueous solution (0.2 mol/l or 1.0 mol/l)), potassium hydroxide (KOH; $\geq 85\%$; VWR Chemicals; added as a solid), and iron (III) oxide/hydroxide (FeO(OH); 30-63% Fe; Sigma-Aldrich; added as a solid) as well as different bleaching earth types (acid activated clay (HPBE) and naturally activated clay (NABE), both added as solids), and combinations thereof which represent the solid clay-based adsorbent and alkaline material combination of the invention. Experimental details and results are given in Table 5:

| Table 5 - Chlorine reduction from pyrolysis oil feedstock | | |
|---|--|----------|
| Adsorbent/alkaline material type/combination | Adsorbent/alkaline material dose [% (w/w)] | Cl [ppm] |
| None (crude feedstock) | 0 | 547 |
| HPBE | 5 | 458 |
| Na ₂ CO ₃ | 5 | 432 |
| HPBE (90%)/FeO(OH) (10%) | 5 | 380 |
| HPBE (99%)/FeO(OH) (1%) | 5 | 370 |
| NABE (95%)/KOH (5%) | 5 | 391 |
| HPBE (97%)/Na ₂ CO ₃ (3%) | 5 | 340 |

[0057] The results shown in table 5 indicate the increased effectiveness of different clay-based adsorbent/alkaline material combinations of the invention in removing chlorine from pyrolysis oil from plastics pyrolysis.

Claims

1. Method for removing chlorine-containing contaminants from organic feedstocks, the method comprising:

- providing an organic feedstock that contains at least one inorganic and/or organic chlorine-containing contaminant;
- optionally extracting the inorganic chlorine containing contaminant by washing the organic feedstock with a polar solvent and separating the organic and polar liquid phases to obtain a washed organic feedstock;
- adding a solid clay-based adsorbent and alkaline material to the optionally washed organic feedstock;
- heating the mixture of adsorbent, alkaline material and organic feedstock in non-oxidizing conditions to an adsorption temperature T_{ads} ;
- removing the solid components to obtain an organic feedstock with reduced chlorine content compared to the organic feedstock provided in step a);

characterized in that the adsorbent : alkaline material ratio in step d) is in the range of 80 : 20 to 99 : 1 (w/w).

2. Method according to claim 1, **characterized in that** the adsorption temperature T_{ads} is between 40 °C and 280 °C, preferably between 100 °C and 240 °C.

3. Method according to claim 1 or 2, **characterized in that** the non-oxidizing conditions are working under a mild vacuum, or under inert gas at ambient or elevated pressure.

4. Method according to claim 3, **characterized in that** the mild vacuum is a pressure of 50 to 500 mbar.

5. Method according to any one of claims 1 to 4, **characterized in that** the polar solvent is water or a water/additive mixture.

6. Method according to any one of claims 1 to 5, **characterized in that** the heating in step d) is maintained for 10 to 120 min.
7. Method according to any one of claims 1 to 6, **characterized in that** the removing of solid components in step e) is done by filtration, centrifugation, sedimentation, or by using cyclonic separators.
8. Method according to any one of claims 1 to 7, **characterized in that** the organic feedstock is selected from the group consisting of bio-based oils and fossil-based oils, and any combinations thereof.
9. Method according to claim 8, **characterized in that** the bio-based oils comprise virgin bio-based oils and/or recycled bio-based oils.
10. Method according to claim 8 or 9, **characterized in that** the fossil-based oils comprise technical oils and recycled technical oils.
11. Method according to any one of claims 1 to 10, **characterized in that** the solid clay-based adsorbent is a bleaching earth, preferably a high-performance bleaching earth or a naturally activated bleaching earth or any combinations thereof.
12. Method according to any one of claims 1 to 11, **characterized in that** the alkaline material is selected from the group consisting of alkaline metal and alkaline earth metal oxides, hydroxides and carbonates, aluminum oxide/hydroxide, iron oxide/hydroxide and any combinations thereof.



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Application Number

EP 23 38 2440

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