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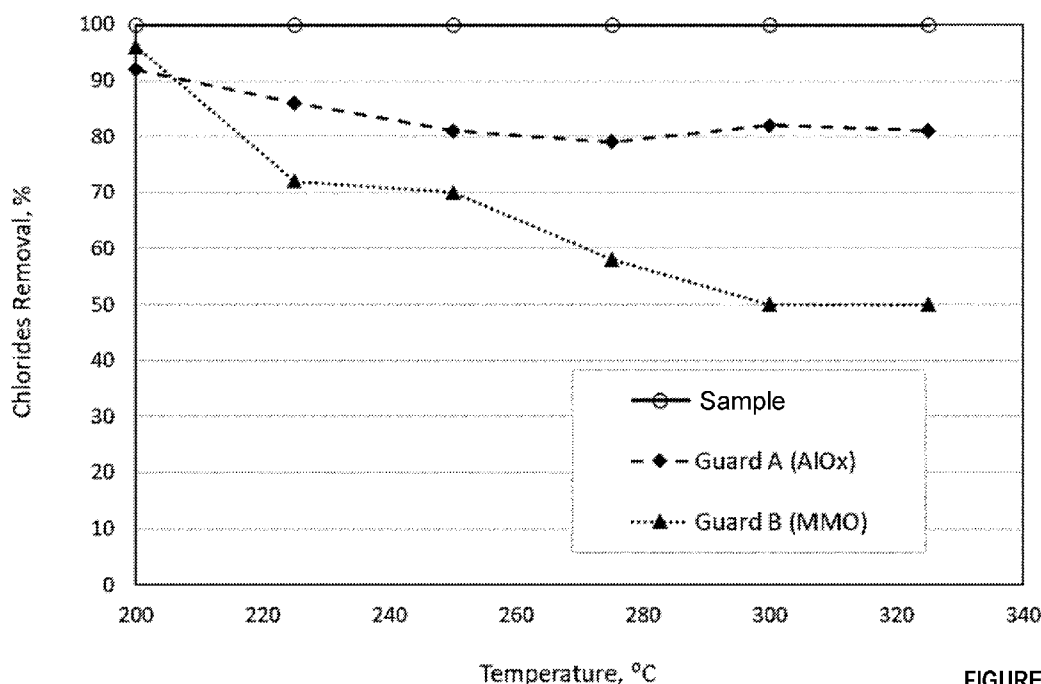


FIGURE 1

- (57) Abstract: Described herein are processes and materials for dechlorination of liquid and gas streams. In at least one embodiment, a process comprises a contacting a plastics pyrolysis stream with an alumina adsorbent, the alumina adsorbent comprising precipitated nickel.

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DECHLORINATION OF LIQUID AND GAS STREAMS FROM PLASTICS PYROLYSIS PROCESSES WITH NICKEL-BASED ADSORBENT

CROSS-REFERENCE TO RELATED APPLICATION(S)

[0001] This application claims the benefit of priority of U.S. Provisional Patent Application No. 63/455,743, filed March 30, 2023, the disclosure of which is hereby incorporated by reference herein in its entirety.

BACKGROUND

[0002] Recycling of mixed waste plastics using chemical/monomer recycling is an area of major importance. While multiple chemical recycling methods are being explored, pyrolysis remains the most technically feasible for integration into the steam cracker value chain. Plastics pyrolysis processes that have been commercialized generally prefer to use polyolefins as the feed plastics. However, pure polyolefin waste is rarely accessible in quantities relevant for full industrial scale, and/or expensive presorting needs to be implemented to reject other types of plastics (i.e., polystyrene, polyamide, polyethylene terephthalate, polyvinyl chloride, etc.). It has been shown for small-mid size pyrolysis plants that full exclusion of halogen, nitrogen, and oxygen containing polymers from feed plastics is not currently possible.

[0003] Most plastics pyrolysis plants produce liquids with average amounts of the following components: 50-400 parts per million weight (ppmw) chlorides, 1000-4000 ppmw nitrogen, 2000-20000 ppmw oxygen, and 100-1000 ppmw sulfur. These levels are too high for such liquids to be used as feeds into steam crackers without blending with conventional naphtha. Upgrading of pyrolysis liquids to remove impurities is important to ensure consistency with steam cracker naphtha specifications.

[0004] The only commercial solution accessible at scale that allows reduction of these impurities to 1-5 ppmw levels making these liquids drop-in substitute into naphtha crackers is hydroprocessing. Hydroprocessing has been standardized in refining and does not require major process tune-ups if to be used for plastics pyrolysis liquids. The only major exception is chlorides/halogens. Hydroprocessing catalysts perform hydrogenation of -N, -O, -S, and -Cl compounds which results in production of respective NH₃, H₂O, H₂S, and HCl. However, there are issues with higher levels of chlorides in such units (i.e. above 10 ppmw), including: (1) formation of NH₄Cl by reaction of NH₃ and HCl, which deposits and clogs equipment at temps below 100°C; (2) catalyst deactivation; and (3) the need for expensive steel. Therefore, there is a need for alternative and/or improved materials and processes.

SUMMARY

[0005] Disclosed and described herein are adsorbents, methods of their preparation, and methods of their use in dechlorination processes.

[0006] In one aspect of the present disclosure, a method of removing chlorides from a plastics pyrolysis stream comprising an initial chloride concentration of at least about 10 ppmw comprises: contacting the stream with an alumina adsorbent, the alumina adsorbent comprising precipitated nickel, wherein a final chloride concentration of the treated stream is less than about 10 ppmw.

[0007] In at least one embodiment, the initial chloride concentration is from about 10 ppmw to about 45 ppmw.

[0008] In at least one embodiment, the initial chloride concentration is from about 45 ppmw to about 250 ppmw.

[0009] In at least one embodiment, the nickel is present from 50-70 wt% based on the total weight of the adsorbent.

[0010] In at least one embodiment, the about 10 wt% to about 100 wt% of the nickel is present in reduced form based on the total amount of nickel present.

[0011] In at least one embodiment, the about 25 wt% to about 45 wt% of the nickel is present in reduced form based on the total amount of nickel present.

[0012] In at least one embodiment, the alumina adsorbent has a BET surface area of about 150 m²/g to about 200 m²/g.

[0013] In at least one embodiment, the alumina adsorbent has a total pore volume from about 0.3 mL/g to about 6 mL/g.

[0014] In at least one embodiment, the alumina adsorbent has a density of about 0.7 g/mL to about 1.0 g/mL.

[0015] In at least one embodiment, the alumina adsorbent is in the form of extruded particles.

[0016] In at least one embodiment, the extruded particles have an average extrudate length of about 3 mm to about 5 mm. In at least one embodiment, the extruded particles exhibit a side crush strength of greater than about 40 N.

[0017] In at least one embodiment, a chlorides removal ratio is at least about 95% for a temperature of the pyrolysis stream from 200°C to 350°C.

[0018] In at least one embodiment, the alumina adsorbent is regenerative.

[0019] In at least one embodiment, the method further comprises subsequently contacting the alumina adsorbent with a regeneration stream to regenerate the alumina adsorbent. In at least one embodiment, the regeneration stream comprises hydrogen gas at a temperature of about 450°C to

about 600°C. In at least one embodiment, the regeneration stream comprises oxygen gas at a temperature of about 250°C to about 350°C.

[0020] In another aspect of the present disclosure, an adsorbent comprises: an alumina adsorbent; and precipitated nickel supported on the alumina adsorbent, wherein the nickel is present from 50 wt% to about 70 wt% based on the total weight of the adsorbent.

[0021] In at least one embodiment, about 25 wt% to about 45 wt% of the nickel is present in reduced form based on the total amount of nickel present.

[0022] In at least one embodiment, the alumina adsorbent has a BET surface area of about 150 m²/g to about 200 m²/g. In at least one embodiment, the alumina adsorbent has a total pore volume from about 0.3 mL/g to about 6 mL/g.

BRIEF DESCRIPTION OF DRAWINGS

[0023] The disclosure described herein is illustrated by way of example and not by way of limitation in the accompanying FIGURE.

[0024] The FIGURE is a plot of chlorides removal versus temperature for a sample prepared in accordance to the embodiments described herein tested against two comparative samples.

DETAILED DESCRIPTION

[0025] Embodiments of the present disclosure relate to processes and compositions for the efficient removal of chlorides from plastics pyrolysis streams (which may be liquid or gas streams). For example, certain embodiments utilize an adsorbent comprising nickel (e.g., precipitated nickel) for removing chlorides from a plastics pyrolysis stream (e.g., having an initial chloride concentration of greater than about 10 ppmw). It has been found that formulations based on nickel precipitation and/or impregnated on a support are active in removal of chlorides down to sub-ppmw levels.

[0026] The adsorbents described may utilize a porous support and one or more active metal components supported thereon. Exemplary supports include metal oxides, metalloid oxides, activated carbons, and molecular sieves. For example, the support may include titanium oxide, ceria, alumina, silica, zirconia, magnesium oxide, zeolites, or combinations thereof. In at least one embodiment, supports include silica. In at least one embodiment, the support may include high surface area metal oxides. In at least one embodiment, the support may comprise aluminum oxide. In at least one embodiment, the support may comprise a mixture of titanium dioxide and aluminum oxide. Metal oxide mixtures, for example a mixture of titanium dioxide and aluminum oxide, may contain metal oxides in a weight/weight ratio of titanium dioxide to aluminum oxide of from any of about 9/1, about 8/1, about 7/1, about 6/1, about 5/1, about 4/1, about 3/1, about 2/1 or about

1/1 to any of about 1/2, about 1/3, about 1/4, about 1/5, about 1/6, about 1/7, about 1/8, or about 1/9.

[0027] In at least one embodiment, the adsorbent comprises a high-pore volume support, such as high-pore volume alumina. In at least one embodiment, the alumina has an Na₂O content of less than about 4000 ppmw.

[0028] The adsorbents described herein may be prepared by a variety of methods. For instance, a metal may be dispersed onto a support via an incipient-wetness technique. "Impregnated," in general, means that the materials are "in" pores of the support. In at least one embodiment, the metal is precipitated onto the support. In at least one embodiment, the metal may be reduced after being dispersed or precipitated onto the support.

[0029] In at least one embodiment, the adsorbent comprises nickel, for example, precipitated nickel or impregnated nickel. In at least one embodiment, the adsorbent comprises nickel from about 40 wt% to about 80 wt% based on the total weight of the adsorbent. In at least one embodiment, the nickel may be present at about 40 wt%, about 41 wt%, about 42 wt%, about 43 wt%, about 44 wt%, about 45 wt%, about 46 wt%, about 47 wt%, about 48 wt%, about 49 wt%, about 50 wt%, about 51 wt%, about 52 wt%, about 53 wt%, about 54 wt%, about 55 wt%, about 56 wt%, about 57 wt%, about 58 wt%, about 59 wt%, about 60 wt%, about 61 wt%, about 62 wt%, about 63 wt%, about 64 wt%, about 65 wt%, about 66 wt%, about 67 wt%, about 68 wt%, about 69 wt%, about 70 wt%, about 71 wt%, about 72 wt%, about 73 wt%, about 74 wt%, about 75 wt%, about 76 wt%, about 77 wt%, about 78 wt%, about 79 wt%, about 80 wt% based on a total weight of the adsorbent, or in any range defined by and inclusive of these points (e.g., from about 55 wt% to about 65 wt%).

[0030] In at least one embodiment, the nickel is fully/partially activated prior to treating a plastics pyrolysis stream. In at least one embodiment, the metal (e.g., nickel) is present in reduced form from about 10 wt% to about 100 wt%. In at least one embodiment, the nickel is present in reduced form from at about 20 wt%, about 21 wt%, about 22 wt%, about 23 wt%, about 24 wt%, about 25 wt%, about 26 wt%, about 27 wt%, about 28 wt%, about 29 wt%, about 30 wt%, about 31 wt%, about 32 wt%, about 33 wt%, about 34 wt%, about 35 wt%, about 36 wt%, about 37 wt%, about 38 wt%, about 39 wt%, about 40 wt%, about 41 wt%, about 42 wt%, about 43 wt%, about 44 wt%, about 45 wt%, about 46 wt%, about 47 wt%, about 48 wt%, about 49 wt%, about 50 wt%, about 51 wt%, about 52 wt%, about 53 wt%, about 54 wt%, about 55 wt%, about 56 wt%, about 57 wt%, about 58 wt%, about 59 wt%, about 60 wt% based on a total weight of nickel present, or in any range defined by and inclusive of these points (e.g., from about 25 wt% to about 45 wt%).

[0031] Surface area, as discussed herein, is determined by the Brunauer-Emmett-Teller (BET) method according to DIN ISO 9277:2003-05 (which is a revised version of DIN 66131), and may

be referred to as “BET surface area.” The specific surface area is determined by a multipoint BET measurement in the relative pressure range from 0.05–0.3 p/p_0 . In at least one embodiment, the adsorbent has a BET surface area of about 100 m²/g, about 110 m²/g, about 120 m²/g, about 130 m²/g, about 140 m²/g, about 150 m²/g, about 160 m²/g, about 170 m²/g, about 180 m²/g, about 190 m²/g, about 200 m²/g, about 210 m²/g, about 220 m²/g, about 230 m²/g, about 240 m²/g, about 250 m²/g, greater than 250 m²/g, or in any range defined by and inclusive of these points (e.g., from about 150 m²/g to about 200 m²/g).

[0032] Pore volume and average pore radius, as discussed herein, are determined by the Barret-Joyner-Halenda (BJH) method. Mercury porosimetry analysis can be used to characterize porosity. Mercury porosimetry applies controlled pressure to a sample immersed in mercury. External pressure is applied for the mercury to penetrate into the voids/pores of the material. The amount of pressure required to intrude into the voids/pores is inversely proportional to the size of the voids/pores. A mercury porosimeter generates volume and pore size distributions from the pressure versus intrusion data generated by the instrument using the Washburn equation:

$$D = \frac{-4g \cos q}{P},$$

where D = diameter, P = pressure, g = surface tension of mercury, q = contact angle. For example, porous silica microspheres containing voids/pores with an average size of about 165 nm can have an average porosity of about 0.8. In at least one embodiment, the alumina adsorbent has a total volume of about 0.1 mL/g, about 0.2 mL/g, about 0.3 mL/g, about 0.4 mL/g, about 0.5 mL/g, about 0.6 mL/g, about 0.7 mL/g, about 0.8 mL/g, about 0.9 mL/g, about 1.0 mL/g, about 1.5 mL/g, 2.0 mL/g, about 2.5 mL/g, 3.0 mL/g, about 3.5 mL/g, 4.0 mL/g, about 4.5 mL/g, 5.0 mL/g, about 5.5 mL/g, about 6.0 mL/g, greater than about 6.0 mL/g, or in any range defined by and inclusive of these points (e.g., from about 0.3 mL/g to about 6 mL/g).

[0033] In at least one embodiment, the adsorbent has a density of about 0.5 g/mL, about 0.6 g/mL, about 0.7 g/mL, about 0.8 g/mL, about 0.9 g/mL, about 1.0 g/mL, about 1.1 g/mL, about 1.2 g/mL, about 1.3 g/mL, about 1.4 g/mL, about 1.5 g/mL, or in any range defined by or inclusive of these points (e.g., about 0.7 g/mL to about 1.0 g/mL).

[0034] The suitable components may be present in the adsorbent compositions in a bulk form, meaning in a continuous form that is in general not interrupted by other materials. A bulk form may contain substantially no other materials. Accordingly, the adsorbent compositions may be in any suitable final form, for instance, tablets, extrudates, pellets, rods, moldings or monoliths, etc., in various shapes and sizes. In at least one embodiment, an adsorbent (e.g., an alumina adsorbent having precipitated or impregnated nickel) is in the form of an extruded material, such as extruded particles. In at least one embodiment, the extruded particles are elongated and may have an average extrudate length (i.e., an average largest dimension) of about 1 mm, about 2 mm, about

3 mm, about 4 mm, about 5 mm, about 6 mm, or in any range defined by and inclusive of these points (e.g., from about 3 mm to about 5 mm). In at least one embodiment, the extruded particles exhibit a side crush strength of greater than about 10 N, greater than about 20 N, greater than about 30 N, greater than about 40 N, greater than about 50 N, greater than about 60 N, greater than about 70 N, greater than about 80 N, greater than about 90 N, or greater than about 100 N.

[0035] The adsorbents described herein may be suitable for removing chlorides and/or other components from feed streams, such as plastics pyrolysis streams. As used herein, “chlorides” refers to chlorine-containing compounds that may include, but not limited to, chloroalkanes, chloroalkenes, chlorooxygenates, chloronaphthenes, and chloroaromatics. Streams suitable for treatment by the adsorbents described herein may include a chlorides content of greater than about 10 ppmw, up to about 500 ppmw (e.g., about 10 ppmw to about 45 ppmw, or about 100 ppmw to about 250 ppmw), or greater.

[0036] In at least one embodiment, the adsorbent exhibits a chlorides removal ratio of at least about 90%, at least about 91%, at least about 92%, at least about 93%, at least about 94%, at least about 95%, at least about 96%, at least about 97%, at least about 98%, or at least about 99% when contacted with a pyrolysis liquid stream (e.g., having a chlorides content of greater than about 80 ppmw) at a temperature from about 200°C to 350°C.

[0037] In at least one embodiment, the adsorbent is regenerative (i.e., the adsorbent is capable of being regenerated to restore its activity to or near its activity prior to use). In at least one embodiment, the adsorbent can be regenerated by treating the adsorbent with a regeneration stream. In at least one embodiment, the regeneration stream is at a temperature of about 450°C to about 600°C and comprises hydrogen gas. In at least one embodiment, the regeneration stream is at a temperature of about 250°C to about 350°C and comprises oxygen gas.

[0038] Unless otherwise indicated, all parts and percentages are by weight. Weight percent (wt%), if not otherwise indicated, is based on an entire composition free of any volatiles, that is, based on dry solids content.

[0039] The following exemplary embodiments are now described:

[0040] Embodiment 1: A method of removing chlorides from a plastics pyrolysis stream comprising an initial chloride concentration of at least about 10 ppmw, the method comprising: contacting the stream with an alumina adsorbent, the alumina adsorbent comprising precipitated nickel, wherein a final chloride concentration of the treated stream is less than about 10 ppmw.

[0041] Embodiment 2: The method of Embodiment 1, wherein the initial chloride concentration is from about 10 ppmw to about 45 ppmw.

[0042] Embodiment 3: The method of Embodiment 1, wherein the initial chloride concentration is from about 45 ppmw to about 250 ppmw.

- [0043] Embodiment 4: The method of any of the preceding Embodiments, wherein the nickel is present from 50-70 wt% based on the total weight of the adsorbent.
- [0044] Embodiment 5: The method of Embodiment 4, wherein the about 10 wt% to about 100 wt% of the nickel is present in reduced form based on the total amount of nickel present.
- [0045] Embodiment 6: The method of Embodiment 4, wherein the about 25 wt% to about 45 wt% of the nickel is present in reduced form based on the total amount of nickel present.
- [0046] Embodiment 7: The method of any of the preceding Embodiments, wherein the alumina adsorbent has a BET surface area of about 150 m²/g to about 200 m²/g.
- [0047] Embodiment 8: The method of any of the preceding Embodiments, wherein the alumina adsorbent has a total pore volume from about 0.3 mL/g to about 6 mL/g.
- [0048] Embodiment 9: The method of any of the preceding Embodiments, wherein the alumina adsorbent has a density of about 0.7 g/mL to about 1.0 g/mL.
- [0049] Embodiment 10: The method of any of the preceding Embodiments, wherein the alumina adsorbent is in the form of extruded particles.
- [0050] Embodiment 11: The method of Embodiment 10, wherein the extruded particles have an average extrudate length of about 3 mm to about 5 mm.
- [0051] Embodiment 12: The method of either Embodiment 10 or Embodiment 11, wherein the extruded particles exhibit a side crush strength of greater than about 40 N.
- [0052] Embodiment 13: The method of any of the preceding Embodiments, wherein a chlorides removal ratio is at least about 95% for a temperature of the pyrolysis stream from 200°C to 350°C.
- [0053] Embodiment 14: The method of any of the preceding Embodiments, wherein the alumina adsorbent is regenerative.
- [0054] Embodiment 15: The method of Embodiment 14, further comprising: subsequently contacting the alumina adsorbent with a regeneration stream to regenerate the alumina adsorbent.
- [0055] Embodiment 16: The method of Embodiment 15, wherein the regeneration stream comprises hydrogen gas at a temperature of about 450°C to about 600°C.
- [0056] Embodiment 17: The method of Embodiment 15, wherein the regeneration stream comprises oxygen gas at a temperature of about 250°C to about 350°C.
- [0057] Embodiment 18: An adsorbent comprising: an alumina adsorbent; and precipitated nickel supported on the alumina adsorbent, wherein the nickel is present from 50-70 wt% based on the total weight of the adsorbent.
- [0058] Embodiment 19: The adsorbent of Embodiment 18, wherein about 25 wt% to about 45 wt% of the nickel is present in reduced form based on the total amount of nickel present.

[0059] Embodiment 20: The adsorbent of either Embodiment 18 or Embodiment 19, wherein the alumina adsorbent has a BET surface area of about 150 m²/g to about 200 m²/g, and wherein the alumina adsorbent has a total pore volume from about 0.3 mL/g to about 6 mL/g.

ILLUSTRATIVE EXAMPLE(S)

[0060] The following example(s) are set forth to assist in understanding the disclosure and should not, of course, be construed as specifically limiting the embodiments described and claimed herein. Such variations of the embodiments, including the substitution of all equivalents now known or later developed, which would be within the purview of those skilled in the art, and changes in formulation or minor changes in experimental design, are to be considered to fall within the scope of the embodiments incorporated herein.

De-chlorination Performance

[0061] Three samples were tested with a pyrolysis oil derived from commercial waste plastics to evaluate their chlorides removal performance. An inventive sample (“Sample”) comprising reduced nickel (about 60 wt% total nickel, and about 30 wt% to about 35 wt% of total nickel being in reduced form) on a high-pore volume alumina adsorbent (BET surface area of about 170 m²/g to about 200 m²/g) was tested against two comparative samples: an alumina adsorbent with 4-5 wt% Na₂O (“Guard A”), and unreduced NiO impregnated on alumina (“Guard B”).

[0062] The pyrolysis oil had a chlorides concentration at the inlet of about 80 ppmw, and was evaluated across temperatures from 200-330 °C at a pressure of 50 barg.

[0063] As shown in the FIGURE, the Sample exhibited nearly 100% chlorides removal over the range of temperatures, demonstrating significantly improved performance over the comparative examples at higher temperatures.

[0064] In the foregoing description, numerous specific details are set forth, such as specific materials, dimensions, processes parameters, etc., to provide a thorough understanding of the embodiments of the present disclosure. The particular features, structures, materials, or characteristics may be combined in any suitable manner in one or more embodiments. The words “example” or “exemplary” are used herein to mean serving as an example, instance, or illustration. Any aspect or design described herein as “example” or “exemplary” is not necessarily to be construed as preferred or advantageous over other aspects or designs. Rather, use of the words “example” or “exemplary” is intended to present concepts in a concrete fashion. As used in this application, the term “or” is intended to mean an inclusive “or” rather than an exclusive “or”. That is, unless specified otherwise, or clear from context, “X includes A or B” is intended to mean any

of the natural inclusive permutations. That is, if X includes A; X includes B; or X includes both A and B, then “X includes A or B” is satisfied under any of the foregoing instances.

[0065] In addition, the use of the terms “a,” “an,” “the,” and similar referents in the context of describing the materials and methods discussed herein (especially in the context of the following claims) are to be construed to cover both the singular and the plural, unless otherwise indicated herein or clearly contradicted by context.

[0066] Recitation of ranges of values herein are merely intended to serve as a shorthand method of referring individually to each separate value falling within the range, unless otherwise indicated herein, and each separate value is incorporated into the specification as if it were individually recited herein. All methods described herein can be performed in any suitable order unless otherwise indicated herein or otherwise clearly contradicted by context. Moreover, any permutations of recited values are contemplated as defining the bounds of ranges. For example, a range of 1, 2, or 3 to 4, 5, or 6 is understood to include not just 1 to 4, 1 to 5, 1 to 6, 2 to 4, 2 to 5, etc., but also 1 to 2, 1 to 3, 2 to 3, 4 to 6, etc.

[0067] The term “about” used throughout is used to describe and account for small fluctuations that may be introduced via experimental or measurement error (e.g., $\pm 1\%$). All numeric values are modified by the term “about” whether or not explicitly indicated. Numeric values modified by the term “about” include the specific identified value. For example “about 5.0” includes 5.0.

[0068] The term “essentially no” or “substantially no” or “substantially free of” means “not purposefully added” and only trace or inadvertent amounts may be present, for instance ≤ 5 wt%, ≤ 4 wt%, ≤ 3 wt%, ≤ 2 wt%, ≤ 1 wt%, ≤ 0.5 wt% or ≤ 0.25 wt%, based on the weight of the composition referred to, for example the total adsorbent composition. For example, an adsorbent composition that is substantially free of lead may refer to an adsorbent composition for which lead is below a detectable limit, or its presence has a negligible effect on the performance of the adsorbent.

[0069] Reference throughout this specification to “one embodiment,” “certain embodiments,” “one or more embodiments,” “an embodiment,” or “some embodiments” means that a particular feature, structure, material, or characteristic described in connection with the embodiment is included in at least one embodiment of the present disclosure. Thus, the appearances of the phrases such as “in one or more embodiments,” “in certain embodiments,” “in one embodiment,” or “in some embodiments” in various places throughout this specification are not necessarily referring to the same embodiment of the present disclosure. Furthermore, the particular features, structures, materials, or characteristics may be combined in any suitable manner in one or more embodiments.

[0070] It is to be understood that the above description is intended to be illustrative, and not restrictive. Many other embodiments will be apparent to those of skill in the art upon reading and

understanding the above description. The scope of the disclosure should, therefore, be determined with reference to the appended claims, along with the full scope of equivalents to which such claims are entitled. The use of any and all examples, or exemplary language (e.g., “such as”) provided herein, is intended merely to better illuminate the materials and methods and does not pose a limitation on the scope unless otherwise claimed. No language in the specification should be construed as indicating any non-claimed element as essential to the practice of the disclosed materials and methods.

[0071] Although the embodiments disclosed herein have been described with reference to particular embodiments it is to be understood that these embodiments are merely illustrative of the principles and applications of the present disclosure. It will be apparent to those skilled in the art that various modifications and variations can be made to the method and apparatus of the present disclosure without departing from the spirit and scope of the disclosure. Thus, it is intended that the present disclosure include modifications and variations that are within the scope of the appended claims and their equivalents, and the above-described embodiments are presented for purposes of illustration and not of limitation.

WHAT IS CLAIMED IS:

1. A method of removing chlorides from a plastics pyrolysis stream comprising an initial chloride concentration of at least about 10 ppmw, the method comprising:
contacting the stream with an alumina adsorbent, the alumina adsorbent comprising precipitated nickel, wherein a final chloride concentration of the treated stream is less than about 10 ppmw.
2. The method of claim 1, wherein the initial chloride concentration is from about 10 ppmw to about 45 ppmw.
3. The method of claim 1, wherein the initial chloride concentration is from about 45 ppmw to about 250 ppmw.
4. The method of claim 1, wherein the nickel is present from 50-70 wt% based on the total weight of the adsorbent.
5. The method of claim 4, wherein the about 10 wt% to about 100 wt% of the nickel is present in reduced form based on the total amount of nickel present.
6. The method of claim 4, wherein the about 25 wt% to about 45 wt% of the nickel is present in reduced form based on the total amount of nickel present.
7. The method of claim 1, wherein the alumina adsorbent has a BET surface area of about 150 m²/g to about 200 m²/g.
8. The method of claim 1, wherein the alumina adsorbent has a total pore volume from about 0.3 mL/g to about 6 mL/g.
9. The method of claim 1, wherein the alumina adsorbent has a density of about 0.7 g/mL to about 1.0 g/mL.
10. The method of claim 1, wherein the alumina adsorbent is in the form of extruded particles.

11. The method of claim 10, wherein the extruded particles have an average extrudate length of about 3 mm to about 5 mm.
12. The method of claim 10, wherein the extruded particles exhibit a side crush strength of greater than about 40 N.
13. The method of claim 1, wherein a chlorides removal ratio is at least about 95% for a temperature of the pyrolysis stream from 200°C to 350°C.
14. The method of claim 1, wherein the alumina adsorbent is regenerative.
15. The method of claim 14, further comprising:
subsequently contacting the alumina adsorbent with a regeneration stream to regenerate the alumina adsorbent.
16. The method of claim 15, wherein the regeneration stream comprises hydrogen gas at a temperature of about 450°C to about 600°C.
17. The method of claim 15, wherein the regeneration stream comprises oxygen gas at a temperature of about 250°C to about 350°C.
18. An adsorbent comprising:
an alumina adsorbent; and
precipitated nickel supported on the alumina adsorbent, wherein the nickel is present from 50-70 wt% based on the total weight of the adsorbent.
19. The adsorbent of claim 18, wherein about 25 wt% to about 45 wt% of the nickel is present in reduced form based on the total amount of nickel present.
20. The adsorbent of claim 18, wherein the alumina adsorbent has a BET surface area of about 150 m²/g to about 200 m²/g, and wherein the alumina adsorbent has a total pore volume from about 0.3 mL/g to about 6 mL/g.

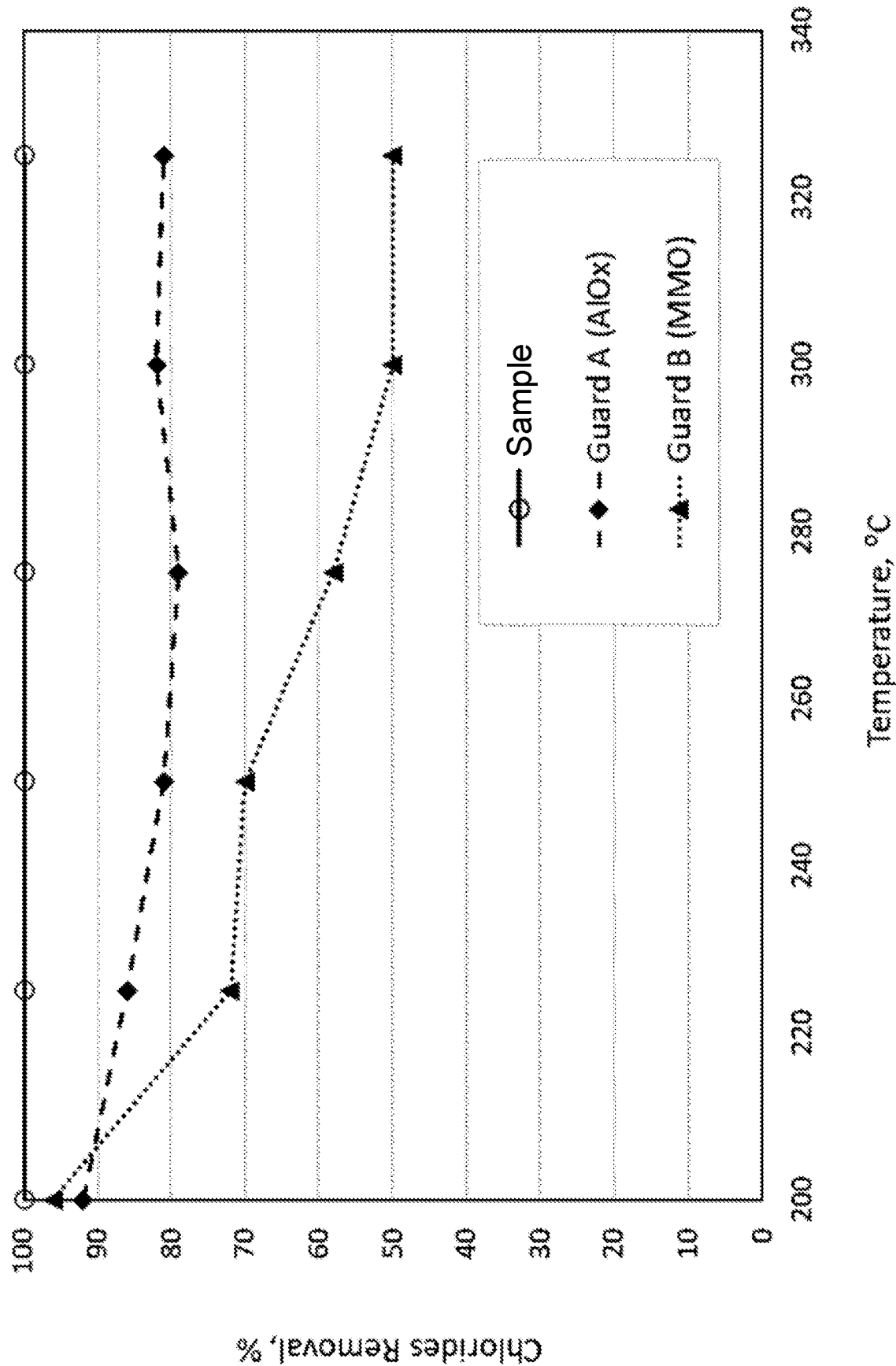


FIGURE 1