

DECHLORINATION OF LIQUID AND GAS STREAMS FROM PLASTICS PYROLYSIS PROCESSES

CROSS-REFERENCE TO RELATED APPLICATION(S)

[0001] This application claims the benefit of priority of U.S. Provisional Patent Application No. 63/455,733, 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 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 NH_3 , H_2O , H_2S , and HCl . However, there are issues with higher levels of chlorides in such units (i.e. above 10 ppmw), including: (1) formation of NH_4Cl by reaction of NH_3 and HCl , which deposits and clogs equipment at temps below 100°C ; (2) catalyst deactivation; (3) and 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] One aspect of the present disclosure relates to a method of removing chlorides from a plastics pyrolysis stream comprising an initial chloride concentration of greater than about 10 ppmw. In at least one embodiment, the method comprises: contacting the stream with an alumina adsorbent, the alumina adsorbent comprising a promoter comprising sodium. In at least one embodiment, 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. In at least one embodiment, the initial chloride concentration is from about 45 ppmw to about 250 ppmw.

[0008] In at least one embodiment, the promoter is present from about 2 wt% to about 10 wt% based on the total weight of the adsorbent. In at least one embodiment, the promoter comprises the sodium in the form of Na_2O .

[0009] In at least one embodiment, the alumina adsorbent has a BET surface area of about $150 \text{ m}^2/\text{g}$ to about $300 \text{ m}^2/\text{g}$.

[0010] In at least one embodiment, the alumina adsorbent has a total pore volume from about 0.2 mL/g to about 6 mL/g .

[0011] In at least one embodiment, the alumina adsorbent exhibits a bimodal pore size distribution.

[0012] In at least one embodiment, the alumina adsorbent has a density of about 0.5 g/mL to about 1.0 g/mL .

[0013] In at least one embodiment, the alumina adsorbent is in the form of spherical particles. In at least one embodiment, the spherical particles have an average diameter of from about 2 mm to about 4 mm. In at least one embodiment, the particles exhibit a side crush strength of greater than about 40 N.

[0014] In at least one embodiment, a chlorides removal ratio is at least about 80%, at least about 85%, or at least about 90% for a temperature of the pyrolysis stream from 200°C to 350°C .

[0015] In at least one embodiment, the alumina adsorbent is regenerative.

[0016] 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 .

[0017] In at least one embodiment, the regeneration stream comprises oxygen gas at a temperature of about 250°C to about 350°C .

[0018] A further aspect of the present disclosure relates to a method of removing chlorides from a plastics pyrolysis stream comprising an initial chloride concentration of greater than about 10 ppmw. In at least one embodiment, the method comprises: contacting the stream with an adsorbent, the adsorbent comprising copper oxide, zinc oxide, and alumina. In at least one embodiment, a final chloride concentration of the treated stream is less than about 10 ppmw.

[0019] In at least one embodiment, the initial chloride concentration is from about 10 ppmw to about 45 ppmw. In at least one embodiment, the initial chloride concentration is from about 45 ppmw to about 250 ppmw.

[0020] In at least one embodiment, the copper oxide is present from about 50 wt% to about 80 wt% based on the total weight of the adsorbent.

[0021] In at least one embodiment, the zinc oxide is present from about 20 wt% to about 30 wt% based on the total weight of the adsorbent.

[0022] In at least one embodiment, the alumina is present from about 3 wt% to about 10 wt% based on the total weight of the adsorbent.

[0023] In at least one embodiment: the copper oxide is present from about 50 wt% to about 80 wt%; the zinc oxide is present from about 10 wt% to about 40 wt%; and the alumina is present as the balance of the weight of the adsorbent.

[0024] In at least one embodiment, the adsorbent is formed by co-precipitation of copper oxide and zinc oxide on alumina.

[0025] In at least one embodiment, the adsorbent has a BET surface area of about 25 m²/g to about 150 m²/g.

[0026] In at least one embodiment, the adsorbent has a total pore volume from about 0.15 mL/g to about 2 mL/g.

[0027] In at least one embodiment, the adsorbent has a density of about 1.0 g/mL to about 3.0 g/mL.

[0028] In at least one embodiment, the adsorbent is in the form of tablets. In at least one embodiment, the tablets have an average length of about 3 mm to about 6 mm, and an average width of about 2 mm to about 4 mm.

[0029] In at least one embodiment, the tablets exhibit a side crush strength of greater than about 60 N.

[0030] In at least one embodiment, a chlorides removal ratio is at least about 80%, at least about 85%, or at least about 90% for a temperature of the pyrolysis stream from 200°C to 350°C.

[0031] In at least one embodiment, the adsorbent is regenerative.

[0032] In at least one embodiment, the method further comprises: subsequently contacting the adsorbent with a regeneration stream to regenerate the 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.

BRIEF DESCRIPTION OF DRAWINGS

[0033] The disclosure described herein is illustrated by way of example and not by way of limitation in the accompanying figures.

[0034] FIG. 1 is a plot of pore volume distribution for a sample prepared in accordance with the embodiments described herein compared to a reference sample.

[0035] FIG. 2 is a plot showing chlorides removal versus temperature for samples prepared in accordance with the embodiments described herein compared to a reference sample.

[0036] FIG. 2 is a plot showing chlorides removal versus temperature for a sample prepared in accordance with the embodiments described herein compared to two reference samples.

DETAILED DESCRIPTION

[0037] 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 a promoter (e.g., sodium) 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 comprising sodium on a high-pore volume support (e.g., copper- or sodium-promoted high-pore volume alumina) are active in removal of chlorides (e.g., to below 10 ppmw or to sub-ppmw levels). Other embodiments relate to adsorbents comprising precipitated copper oxide onto a support (e.g., which may be co-precipitated with zinc oxide).

[0038] 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.

[0039] 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 promoter is dispersed on the support, for example, by impregnation. The term “dispersed form” may be synonymous with “dispersed thereon”, “impregnated in”, “supported by/on”, and the like.

[0040] In at least one embodiment, the promoter material or a precursor of the promoter material is combined with the support to facilitate incipient wetness impregnation, and the impregnated support is subsequently dried and calcined.

[0041] 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.

[0042] In at least one embodiment, the adsorbent comprises a promoter (e.g., Na_2O), which may be present from about 0.5 wt% to about 20 wt% based on the total weight of the adsorbent. In at least one embodiment, the promoter (e.g., NaO) may be present at about 0.5 wt%, about 1 wt%, about 2 wt%, about 3 wt%, about 4 wt%, about 5 wt%, about 6 wt%, about 7 wt%, about 8 wt%, about 9 wt%, about 10 wt%, about 11 wt%, about 12 wt%, about 13 wt%, about 14 wt%, about 15 wt%, about 16 wt%, about 17 wt%, about 18 wt%, about 19 wt%, about 20 wt% based on a total weight of the adsorbent, or in any range defined by and inclusive of these points (e.g., from about 2 wt% to about 10 wt%).

[0043] In at least one embodiment, the adsorbent comprises copper oxide (e.g., precipitated copper oxide), which may be present from about 50 wt% to about 80 wt% based on the total weight of the adsorbent. In at least one embodiment, the copper oxide may be present at 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%, or in any range defined by and inclusive of these points (e.g., from about 65 wt% to about 75 wt%).

[0044] In at least one embodiment, the adsorbent comprises a zinc oxide (e.g., precipitated zinc oxide), which may be present from about 10 wt% to about 40 wt% based on the total weight of the adsorbent. In at least one embodiment, the zinc oxide may be present at about 10 wt%, about 11 wt%, about 12 wt%, about 13 wt%, about 14 wt%, about 15 wt%, about 16 wt%, about

17 wt%, about 18 wt%, about 19 wt%, 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%, or in any range defined by and inclusive of these points (e.g., from about 15 wt% to about 35 wt%).

[0045] 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), which 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). In at least one embodiment, the BET surface area is at least about 25 m²/g, at least about 50 m²/g, or at least about 75 m²/g to about 150 m²/g to greater.

[0046] 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 0.15 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).

[0047] 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, about 1.6 g/mL, about 1.7 g/mL, about 1.8 g/mL, about 1.9 g/mL, about 2.0 g/mL, about 2.1 g/mL, about 2.2 g/mL, about 2.3 g/mL, about

2.4 g/mL, about 2.5 g/mL, about 2.6 g/mL, about 2.7 g/mL, about 2.8 g/mL, about 2.9 g/mL, about 3.0 g/mL, or in any range defined by and inclusive of these points (e.g., about 0.7 g/mL to about 1.0 g/mL).

[0048] The suitable components may be present in the adsorbent compositions in a bulk form, meaning in a continuous form 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, spheres, 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 copper) is in the form of spheres or 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 adsorbent 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.

[0049] 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.

[0050] 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.

[0051] 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.

[0052] 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.

[0053] The following exemplary embodiments are now described:

[0054] Embodiment 1: A method of removing chlorides from a plastics pyrolysis stream comprising an initial chloride concentration of greater than about 10 ppmw, the method comprising: contacting the stream with an alumina adsorbent, the alumina adsorbent comprising a promoter comprising sodium, wherein a final chloride concentration of the treated stream is less than about 10 ppmw.

[0055] Embodiment 2: The method of Embodiment 1, wherein the initial chloride concentration is from about 10 ppmw to about 45 ppmw.

[0056] Embodiment 3: The method of Embodiment 1, wherein the initial chloride concentration is from about 45 ppmw to about 250 ppmw.

[0057] Embodiment 4: The method of any of the preceding Embodiments, wherein the promoter is present from 2 wt% to about 10 wt% based on the total weight of the adsorbent.

[0058] Embodiment 5: The method of Embodiment 4, wherein the promoter comprises the sodium in the form of Na_2O .

[0059] Embodiment 6: The method of any of the preceding Embodiments, wherein the alumina adsorbent has a BET surface area of about $150 \text{ m}^2/\text{g}$ to about $300 \text{ m}^2/\text{g}$.

[0060] Embodiment 7: The method of any of the preceding Embodiments, wherein the alumina adsorbent has a total pore volume from about 0.2 mL/g to about 6 mL/g .

[0061] Embodiment 8: The method of any of the preceding Embodiments, wherein the alumina adsorbent exhibits a bimodal pore size distribution.

[0062] Embodiment 9: The method of any of the preceding Embodiments, wherein the alumina adsorbent has a density of about 0.5 g/mL to about 1.0 g/mL .

[0063] Embodiment 10: The method of any of the preceding Embodiments, wherein the alumina adsorbent is in the form of spherical particles.

[0064] Embodiment 11: The method of Embodiment 10, wherein the spherical particles have an average diameter of from about 2 mm to about 4 mm.

[0065] Embodiment 12: The method of either Embodiment 10 or Embodiment 11, wherein the spherical particles exhibit a side crush strength of greater than about 40 N.

[0066] Embodiment 13: The method of any of the preceding Embodiments, wherein a chlorides removal ratio is at least about 80%, at least about 85%, or at least about 90% for a temperature of the pyrolysis stream from 200°C to 350°C .

[0067] Embodiment 14: The method of any of the preceding Embodiments, wherein the alumina adsorbent is regenerative.

[0068] Embodiment 15: The method of any of the preceding Embodiments, further comprising: subsequently contacting the alumina adsorbent with a regeneration stream to regenerate the alumina adsorbent.

[0069] 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.

[0070] 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.

[0071] Embodiment 18: A method of removing chlorides from a plastics pyrolysis stream comprising an initial chloride concentration of greater than about 10 ppmw, the method comprising: contacting the stream with an adsorbent, the adsorbent comprising copper oxide, zinc oxide, and alumina, wherein a final chloride concentration of the treated stream is less than about 10 ppmw.

[0072] Embodiment 19: The method of Embodiment 18, wherein the initial chloride concentration is from about 10 ppmw to about 45 ppmw.

[0073] Embodiment 20: The method of Embodiment 18, wherein the initial chloride concentration is from about 45 ppmw to about 250 ppmw.

[0074] Embodiment 21: The method of any of Embodiments 18-20, wherein the copper oxide is present from about 50 wt% to about 80 wt% based on the total weight of the adsorbent.

[0075] Embodiment 22: The method of any of Embodiments 18-21, wherein the zinc oxide is present from about 20 wt% to about 30 wt% based on the total weight of the adsorbent.

[0076] Embodiment 23: The method of any of Embodiments 18-22, wherein the alumina is present from about 3 wt% to about 10 wt% based on the total weight of the adsorbent.

[0077] Embodiment 24: The method of any of Embodiments 18-23, wherein: the copper oxide is present from about 50 wt% to about 80 wt%; the zinc oxide is present from about 10 wt% to about 40 wt%; and the alumina is present as the balance of the weight of the adsorbent.

[0078] Embodiment 25: The method of any of Embodiments 18-24, wherein the adsorbent is formed by co-precipitation of copper oxide and zinc oxide on alumina.

[0079] Embodiment 26: The method of any of Embodiments 18-25, wherein the adsorbent has a BET surface area of about 25 m²/g to about 150 m²/g.

[0080] Embodiment 27: The method of any of Embodiments 18-26, wherein the adsorbent has a total pore volume from about 0.15 mL/g to about 2 mL/g.

[0081] Embodiment 28: The method of any of Embodiments 18-27, wherein the adsorbent has a density of about 1.0 g/mL to about 3.0 g/mL.

[0082] Embodiment 29: The method of any of Embodiments 18-28, wherein the adsorbent is in the form of tablets.

[0083] Embodiment 30: The method of Embodiment 29, wherein the tablets have an average length of about 3 mm to about 6 mm, and an average width of about 2 mm to about 4 mm.

[0084] Embodiment 31: The method of either Embodiment 29 or Embodiment 30, wherein the tablets exhibit a side crush strength of greater than about 60 N.

[0085] Embodiment 32: The method of any of Embodiments 18-20, wherein a chlorides removal ratio is at least about 80%, at least about 85%, or at least about 90% for a temperature of the pyrolysis stream from 200°C to 350°C.

[0086] Embodiment 33: The method of any of Embodiments 18-20, wherein the adsorbent is regenerative.

[0087] Embodiment 34: The method of any of Embodiments 18-20, further comprising: subsequently contacting the adsorbent with a regeneration stream to regenerate the adsorbent.

[0088] Embodiment 35: The method of Embodiment 34, wherein the regeneration stream comprises hydrogen gas at a temperature of about 450°C to about 600°C.

[0089] Embodiment 36: The method of Embodiment 34, wherein the regeneration stream comprises oxygen gas at a temperature of about 250°C to about 350°C .

ILLUSTRATIVE EXAMPLE(S)

[0090] 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.

Example 1: De-chlorination Performance

[0091] Standard dechlorination experiments were performed for various samples (described below) in a flow reactor loaded with about 1 mL of a given sample. Dechlorination was performed using a commercial waste plastics pyrolysis oil (PyOil) sample containing about 80 ppmw of chlorides, which were organic chlorides. Prior to each experiment, the reactor was purged with dry nitrogen, and samples were dehydrated at 250 °C for one hour at a gas hourly space velocity (GHSV) of 1000 hr⁻¹. After dehydration, a liquid PyOil feed was introduced into the reactor at a liquid hourly space velocity (LHSV) of 1 hr⁻¹ and a total pressure of 50 barg. The reactor temperature was increased to 200 °C at 50 barg to ensure liquid only flow. Measurements of

chlorides in the effluent liquid stream were performed in the 200 to 325 °C range with temperature increments of 25 °C. Each temperature increment was maintained for about 20 hr to allow system to equilibrate.

[0092] Sample A was a high macropore pore volume sodium promoted alumina formulation with bimodal pore size distribution in the form of a sphere. Without wishing to be bound by theory, it is believed that unique pore size distribution that features macropore volume of about 0.3 mL/g enables high performance of this product in removal of chlorides from waste plastics pyrolysis oils. The sodium oxide content was about 5.5 wt% based on a total weight of the formulation.

[0093] Reference 1 was a conventional sodium promoted alumina that did not exhibit any appreciable macropore volume (below 0.05 mL/g) or a bimodal pore size distribution, in the form of a sphere. The sodium oxide level was about 4 wt%. It is observed that performance of this formulation in removal of chlorides from waste plastics pyrolysis oils was inferior to Sample A.

[0094] Reference 2 was a conventional unpromoted high surface area activated alumina guard, in the form of a sphere. It did not exhibit any appreciable macropore volume (below 0.05 mL/g) or a bimodal pore size distribution. It was observed that performance of this formulation in removal of chlorides from waste plastics pyrolysis oils was substantially inferior to Sample A.

[0095] Sample B was a precipitated copper oxide zinc oxide based formulation in the form of a tablet, with a copper oxide content of about 70 wt% and a zinc oxide content of about 24.5 wt% balanced by alumina. Without wishing to be bound by theory, it is believed that due to exceptionally high copper oxide surface area this formulation shows high performance in removal of chlorides from waste plastics pyrolysis oils.

[0096] Properties of Samples A, B and the reference samples are summarized in Tables 1 and 2. FIG. 1 shows the mercury pore volume distributions for Sample A versus Reference 1, demonstrating a significant macropore volume peak

[0097] The chlorides removal performance of Samples A, B, and the reference samples is shown in FIGS. 2 and 3.

[0098] FIG. 2 shows performance of Samples A and B in removal of chlorides from a waste plastics pyrolysis feed. The experimental conditions were: pressure of 50 barg argon, temperature 200-325 °C, and commercial PyOil feed at 80 ppmw of chlorides.

[0099] FIG. 3 shows performance of Sample A in removal of chlorides from a waste plastics pyrolysis feed. The experimental conditions were: pressure 50 barg Argon, temperature 200-325 °C, and commercial PyOil feed at 80 ppmw of chlorides.

Table 1: Typically observed properties of Sample A, References 1 and 2.

		Sample A	Reference 1	Reference 2
Shape		sphere 3.2 mm	sphere 3.2 mm	sphere 3.2 mm
LOI (250-1100 °C)	%	6.5	6.5	6.5
Surface area	m ² /g	250	250	335
Bulk Density	kg/m ³	675	800	750
Crush strength	N	50	125	110
Water Pore volume	mL/g	0.6	0.45	0.45
Macropore Volume (d > 750Å)	mL/g	0.3	below 0.05	below 0.05
Composition				
Na ₂ O	wt%	5.5	4	below 0.25
AlO _x	wt%	balance	balance	balance

Table 2: Typically observed properties of Samples A, B and Reference 2.

		Sample A	Sample B	Reference 2
Shape		sphere 3.2 mm	tablet 3 mm x 5 mm	sphere 3.2 mm
LOI (250-1100 °C)	%	6.5	17	6.5
Surface area	m ² /g	250	70	335
Bulk Density	kg/m ³	675	1450	750
Crush strength	N	50	80	110
Water Pore volume	mL/g	0.6	0.25	0.45
Composition				
Na ₂ O	wt%	5.5	below 0.1	below 0.25
CuO	wt%	none	70	none
ZnO	wt%	none	24.5	none
AlO _x	wt%	balance	5.5	balance

[0100] 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.

[0101] 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.

[0102] 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.

[0103] 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.

[0104] 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.

[0105] 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.

[0106] 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.

[0107] 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 greater than about 10 ppmw, the method comprising:
contacting the stream with an alumina adsorbent, the alumina adsorbent comprising a promoter comprising sodium, 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 promoter is present from 2 wt% to about 10 wt% based on the total weight of the adsorbent.
5. The method of claim 4, wherein the promoter comprises the sodium in the form of Na_2O .
6. The method of claim 1, wherein the alumina adsorbent has a BET surface area of about $150 \text{ m}^2/\text{g}$ to about $300 \text{ m}^2/\text{g}$.
7. The method of claim 1, wherein the alumina adsorbent has a total pore volume from about 0.2 mL/g to about 6 mL/g .
8. The method of claim 1, wherein the alumina adsorbent exhibits a bimodal pore size distribution.
9. The method of claim 1, wherein the alumina adsorbent has a density of about 0.5 g/mL to about 1.0 g/mL .
10. The method of claim 1, wherein the alumina adsorbent is in the form of spherical particles.

11. The method of claim 10, wherein the spherical particles have an average diameter of from about 2 mm to about 4 mm.
12. The method of claim 10, wherein the spherical 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 80%, at least about 85%, or at least about 90% 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 1, 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. A method of removing chlorides from a plastics pyrolysis stream comprising an initial chloride concentration of greater than about 10 ppmw, the method comprising:
contacting the stream with an adsorbent, the adsorbent comprising copper oxide, zinc oxide, and alumina, wherein a final chloride concentration of the treated stream is less than about 10 ppmw.
19. The method of claim 18, wherein the initial chloride concentration is from about 10 ppmw to about 45 ppmw.
20. The method of claim 18, wherein the initial chloride concentration is from about 45 ppmw to about 250 ppmw.
21. The method of claim 18, wherein the copper oxide is present from about 50 wt% to about 80 wt% based on the total weight of the adsorbent.

22. The method of claim 18, wherein the zinc oxide is present from about 20 wt% to about 30 wt% based on the total weight of the adsorbent.
23. The method of claim 18, wherein the alumina is present from about 3 wt% to about 10 wt% based on the total weight of the adsorbent.
24. The method of claim 18, wherein:
the copper oxide is present from about 50 wt% to about 80 wt%;
the zinc oxide is present from about 10 wt% to about 40 wt%; and
the alumina is present as the balance of the weight of the adsorbent.
25. The method of claim 18, wherein the adsorbent is formed by co-precipitation of copper oxide and zinc oxide on alumina.
26. The method of claim 18, wherein the adsorbent has a BET surface area of about 25 m²/g to about 150 m²/g.
27. The method of claim 18, wherein the adsorbent has a total pore volume from about 0.15 mL/g to about 2 mL/g.
28. The method of claim 18, wherein the adsorbent has a density of about 1.0 g/mL to about 3.0 g/mL.
29. The method of claim 18, wherein the adsorbent is in the form of tablets.
30. The method of claim 29, wherein the tablets have an average length of about 3 mm to about 6 mm, and an average width of about 2 mm to about 4 mm.
31. The method of claim 29, wherein the tablets exhibit a side crush strength of greater than about 60 N.
32. The method of claim 18, wherein a chlorides removal ratio is at least about 80%, at least about 85%, or at least about 90% for a temperature of the pyrolysis stream from 200°C to 350°C.

33. The method of claim 18, wherein the adsorbent is regenerative.
34. The method of claim 18, further comprising:
subsequently contacting the adsorbent with a regeneration stream to regenerate the adsorbent.
35. The method of claim 34, wherein the regeneration stream comprises hydrogen gas at a temperature of about 450°C to about 600°C.
36. The method of claim 34, wherein the regeneration stream comprises oxygen gas at a temperature of about 250°C to about 350°C .