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(57) Abstract: The invention relates to an integrated system for the preparation of purified terephthalic acid (PTA) and the use of the PTA for the production of poly(ethylene terephthalate) (PET). Advantageously, the integrated system design described herein can minimize the possibility of contamination of the PTA production operation with reactant, catalysts, or impurities from the PET production operation. Methods of using the integrated system for the production of PET are also described.



CONTAMINATION PREVENTION IN INTEGRATED PURIFIED TEREPHTHALIC ACID PRODUCTION AND POLYESTER POLYMERIZATION PLANT

FIELD OF THE INVENTION

[0001] The invention is related to a modified integrated purified terephthalic acid (PTA) and poly(ethylene terephthalate) (PET) polymerization plant.

BACKGROUND OF THE INVENTION

[0002] Poly(ethylene terephthalate) (PET) resins are widely produced and used, for example, in the form of fibers and in the form of bottle resin. PET is commonly used in the production of beverage and food containers, thermoforming applications, textiles, and as engineering resins. PET is a polymer that is commonly formed from a diol (e.g., ethylene glycol) and terephthalic acid (or dimethyl terephthalate).

[0003] The raw materials for PET production are thus ethylene glycol and phthalic acids. The phthalic acids are typically 100% terephthalic acid for the production of polyester fibers, but may contain up to 5% isophthalic acid for bottle resins. Catalysts and other additives may be added to the process at any point. In a first stage of the process, ethylene glycol and terephthalic acid are combined in a cold state and then heated to undergo an esterification reaction to form an oligomer and water vapor as a byproduct. The oligomer is then polymerized to form the PET polymer product with ethylene glycol and water as byproducts. The resulting polymer can, for example, then be formed into chips to be sold or can be fed directly into a downstream polyester spinning facility.

[0004] The terephthalic acid used in the PET production process is typically in the form of purified terephthalic acid (PTA). PTA is prepared in a two-stage process, wherein para-xylene is oxidized to give a crude terephthalic acid product and the crude terephthalic acid product is purified and isolated from the impurities associated therewith to give PTA. The PTA is generally isolated in the form of a wet cake of PTA, which is then fed to a drier (e.g., a rotary steam tube drier) to generate dry PTA, which is cooled and stored for later use in PET polymerization or is directly transported to a PET polymerization plant.

[0005] This process for the production of dry PTA which can be used in the PET polymerization plant requires a significant amount of upfront capital cost associated with the

facilities required, the raw materials, and the energy requirements of the multi-step process. Furthermore, a significant amount of water is required and a large amount of aqueous waste effluent must be treated and may present problems with disposal. Additionally, dissolved PTA and other valuable materials in the waste effluent may be lost. The wet cake of PTA crystals is in pure form following separation from the para-toluic acid-rich mother liquor stream but cannot be used directly in this wet form. Accordingly, additional energy input is required simply to dry the starting material prior to use in PET production. Even more energy is used to transfer the PTA from the drier to storage silos and subsequently from the silos to downstream polymerization plants and later to reheat the PTA powder for reaction with the ethylene glycol within the polymerization plant.

BRIEF SUMMARY OF THE INVENTION

[0006] It would therefore be beneficial to provide a means by which PTA could be used directly in a PET production plant to reduce both capital and operating costs. Integrating a PTA purification plant with a PET production plant has heretofore been hindered in that such integration runs the intrinsic risk that diol (*e.g.*, ethylene glycol), which is a reagent in the PET production plant, may contaminate the PTA purification plant. The ethylene glycol used and recycled in a PET polymerization plant contains trace amounts of various catalyst materials used in PET production and contaminants already present in such catalyst materials (including, but not limited to, antimony, phosphate, and arsenic). Many of these catalysts and contaminants are capable of poisoning precious metal catalysts (including one or more catalysts typically used in the purification of terephthalic acid). If these catalysts and contaminants contaminate the PTA purification process, this will lead to rapid poisoning of the purification plant palladium catalyst, which can significantly decrease the efficiency of the process.

[0007] Therefore, it is desirable to provide an integrated terephthalic acid purification plant and PET production plant that reduces or prevents the likelihood of the terephthalic acid purification plant becoming contaminated with catalysts and contaminants from the PET production plant.

[0008] The present invention provides an integrated terephthalic acid (TA) purification plant and poly(ethylene terephthalate) (PET) production plant. Advantageously, the integrated plant is designed so as to minimize or effectively eliminate transfer of reagents and/or contaminants

associated with the PET production process to the TA purification plant. Such integration can, in certain embodiments, provide improvements in overall efficiency of PET production by eliminating one or more steps typically associated with providing the purified terephthalic acid (PTA) reagent for the production of PET.

[0009] In one aspect of the invention is provided an integrated method for the purification of crude terephthalic acid and the production of poly (ethylene terephthalic acid), comprising: (a) providing a stream of crystallized purified terephthalic acid in an aqueous medium; (b) separating at least a portion of the aqueous medium in a filter device to provide wet purified terephthalic acid; (c) transferring the wet purified terephthalic acid directly from the filter device to a vessel and contacting the purified terephthalic acid with a diol in the vessel to give a reactant slurry; (d) conveying the reactant slurry directly to a polymerization reactor for the production of poly(ethylene terephthalate); and (e) maintaining the vessel at a pressure equal to or less than the pressure of the filter device.

[0010] In some embodiments, the maintaining step comprises integration of a vapor balance line connecting the vessel to the filter device. In some embodiments, the maintaining step comprises applying a positive pressure to the filter device. For example, positive pressure can, in certain embodiments, be applied by one or more steps of: controlling a first pressure control valve that is associated with the filter device; and venting the vessel. Optionally, the venting can be controlled by a second pressure control valve that is associated with the vessel that is set at a lower pressure than that of the first pressure control valve.

[0011] In certain embodiments, the providing step comprises: (i) dissolving crude terephthalic acid in an aqueous medium to produce a terephthalic acid-containing solution comprising one or more impurities; (ii) contacting the terephthalic acid solution with hydrogen to reduce at least a portion of the impurities present in the crude terephthalic acid to produce pure terephthalic acid and hydrogenated impurities; and (iii) crystallizing the pure terephthalic acid. In certain embodiments, the contacting step further comprises exposing the terephthalic acid solution to elevated temperature and pressure and introducing a hydrogenation catalyst. The hydrogenation catalyst can vary, and can be, for example, a supported palladium catalyst.

[0012] In some embodiments, the separating step comprises one or more of filtering the pure terephthalic acid on a filter surface, washing the pure terephthalic acid, and drying the pure

terephthalic acid. The method can, in certain embodiments, further comprise applying a pressure differential across the filter surface.

[00013] The transferring step can, in some embodiments, comprise passing the purified terephthalic acid through a non-sealed transfer line. The non-sealed transfer line can optionally comprise a direct line to the vessel. The non-sealed transfer line can, in certain embodiments, comprise one or more screw conveyors. Advantageously, in some embodiments, the diol is heated prior to combination with the purified terephthalic acid according to the methods disclosed herein. For example, in specific embodiments, the diol is heated to a temperature of between about 130°C and about 150°C.

[00014] In another aspect of the invention is provided an integrated system for the purification of crude terephthalic acid and the production of poly(ethylene terephthalic acid), comprising: (a) a filter device comprising a filtration zone and a washing zone to remove at least a portion of the impurities from crude terephthalic acid and to provide wet purified terephthalic acid; (b) a vessel in direct fluid connection with the filter device, comprising a first inlet for addition of the wet purified terephthalic acid and a second inlet for the addition of a diol; (c) one or more lines adapted to maintain the vessel at a pressure equal to or less than the pressure of the filter device; and (d) a poly(ethylene terephthalate) polymerization reactor in direct fluid connection with the vessel.

[00015] The one or more lines can, in certain embodiments, comprise a vapor balance line in fluid connection with the vessel and the filter. In some embodiments, the vapor balance line comprises an in-line condenser. The one or more lines can, in some embodiments, comprise: (i) a first pressure control valve adapted to control an in-flow of a pressure stream into the filter device; and (ii) a second pressure control valve adapted to control an out-flow of a pressure stream from the vessel. The second pressure control valve can advantageously be set at a pressure lower than that of the first pressure control valve. In some embodiments, the one or more lines can further comprise an in-line condenser.

[00016] In certain embodiments, the integrated system described herein can further comprise a conveying device to provide the direct fluid connection between the filter device and the vessel. The conveying device can advantageously in certain embodiments, not be sealed against vapor transfer. In specific embodiments, the conveying device comprises a screw conveyor (*e.g.*, an unsealed screw conveyor).

BRIEF DESCRIPTION OF THE DRAWINGS

[00017] Having thus described the invention in general terms, reference will now be made to the accompanying drawings, which are not necessarily drawn to scale, and wherein:

[00018] FIG. 1 is a diagram showing the application of a rotary filter to separation of PTA from a slurry;

[00019] FIG. 2 is a schematic illustration of an exemplary filter in the context of a larger portion of the integrated plant described herein;

[00020] FIG. 3 is a schematic illustration of an optional arrangement of components for the production and scrubbing of steam to be used within the filter device of the integrated plant described herein;

[00021] FIG. 4 is a schematic illustration of one embodiment of the present disclosure, wherein a vapor balance line is used to maintain a similar pressure in the return slurry vessel (e.g., a reslurry vessel) and the filter;

[00022] FIG. 5 is a schematic illustration of one embodiment of the present disclosure, wherein two pressure control units are used to maintain similar pressures in the return slurry vessel (e.g., a reslurry vessel) and the filter; and

[00023] FIG. 6 is a schematic illustration of one embodiment of the present disclosure, wherein a vapor balance line is used to maintain a similar pressure in the return slurry vessel (e.g., a reslurry vessel) and the filter and a condenser is provided in the balance line.

DETAILED DESCRIPTION OF THE INVENTION

[00024] The present invention now will be described more fully hereinafter with reference to the accompanying drawings, in which some, but not all embodiments of the inventions are shown. Indeed, these inventions may be embodied in many different forms and should not be construed as limited to the embodiments set forth herein; rather, these embodiments are provided so that this disclosure will satisfy applicable legal requirements. Like numbers refer to like elements throughout. As used in the specification, and in the appended claims, the singular forms “a”, “an”, “the”, include plural referents unless the context clearly dictates otherwise.

[00025] Briefly, the present invention provides systems and methods for the production of purified terephthalic acid (PTA) and polyethylene terephthalate (PET). More specifically, the

invention provides a means for integrating these systems and methods for the production of PTA and PET to afford an integrated system offering energy and costs savings as compared with a system in which these processes operate independently.

[00026] Generally, the present invention involves a step of providing and/or producing crude terephthalic acid (CTA), which is subsequently purified to provide PTA. Crude terephthalic acid can be provided, for example, as described in the background section of the present application. Also see, for example, International Application Publication Nos. WO/1993/024440 to Turner *et al.* and WO 1995/019335 to Hindmarsh *et al.*, which are incorporated herein by reference in their entireties. Commonly, CTA is produced by the air oxidation of para-xylene. The specific means by which this oxidation is achieved can vary. In some embodiments, the oxidation of para-xylene is conducted at elevated pressure and temperature. The solvent can vary and commonly comprises an aliphatic carboxylic acid, such as acetic acid. The catalyst can vary and is any hydrogenation catalyst sufficient to ensure oxidation of the para-xylene. For example, in certain embodiments, the hydrogenation catalyst can comprise cobalt and manganese acetates. Under certain such conditions, CTA is formed and can precipitate in a main reactor, co-precipitating reaction intermediates, organic byproducts, and catalyst. These reaction intermediates, organic byproducts, and catalyst must be removed before the material can be used in the manufacture of polyester products (*i.e.*, the CTA must be purified to form PTA).

[00027] The method or methods by which removal of reaction intermediates, organic byproducts, and catalyst can, in some embodiments, comprise selective hydrogenation of an aqueous solution of the CTA. When an aqueous medium is added to the CTA, a slurry is generally formed, which can then be heated at elevated temperature to dissolve the CTA. In certain embodiments, the resulting CTA solution can be hydrogenated using gaseous hydrogen at elevated pressure (between about 60 and about 100 bar, *e.g.*, about 80 bar) and elevated temperature (*e.g.*, between about 250 °C and about 350 °C, *e.g.*, about 285 °C). A hydrogenation catalyst is typically employed in the process, *e.g.*, a supported noble metal catalyst (*e.g.*, palladium on carbon). The method by which the hydrogenation is conducted can vary, but can in certain embodiments suitably be conducted by passing the CTA solution (*e.g.*, a 20% – 50% solution of terephthalic acid by weight) through a flooded bed of catalyst at elevated temperature in the presence of hydrogen. This hydrogenation step generally results in the reduction of various organic impurities in the CTA, including 4-carboxy benzaldehyde (4CBA), one of the

predominant impurities of CTA. The 4CBA can advantageously be hydrogenated under such conditions to para-toluic acid.

[00028] The resulting solution containing terephthalic acid, water, and impurities is then typically subjected to reduced temperatures and/or pressures, resulting in crystallization of the terephthalic acid from solution (while at least a portion of the impurities remain in solution). For example, in some embodiments, a series of recrystallizer stages is used, wherein the pressure of each recrystallizer stage is progressively reduced. Any number of stages can be employed for this purpose (*e.g.*, between about 1 and about 10, such as at least about one, at least about two, at least about three, or at least about four). In one particular embodiment, a first crystallizer stage can operate in the range of about 35 – 50 bar, a second crystallizer stage can operate in the range of about 20-33 bar, a third crystallizer stage can operate in the range of about 10-19 bar, a fourth crystallizer stage can operate in the range of about 6-10 bar, and a fifth crystallizer stage can operate in the range of about 3-9 bar. The temperature of the slurry following the crystallizer stages can be, for example, in the range of about 100°C to about 220°C (*e.g.*, typically about 135°C to about 180°C).

[00029] The resultant slurry of terephthalic acid in aqueous solution can, in certain embodiments, be passed into a filter device, wherein PTA can be recovered by one or more liquid/solid separation steps. The means by which the slurry of terephthalic acid is introduced into the filter device can vary. In one embodiment, terephthalic acid slurry stored in a tank can be fed by a pump and flow controlled valve to the filter device (*e.g.*, rotary drum/pressure filter). In some embodiments, the slurry is introduced into the filter device at a temperature of at least about 60°C (*e.g.*, between about 100°C and about 200°C, such as between about 120°C and about 180°C). In some embodiments, the slurry is introduced into the filter device at a pressure of between about 3-9 bar (*e.g.*, about 8 bar). In preferred embodiments, the slurry is deposited in such a way that the saturation pressure of the feed is less than the absolute pressure on the lower (downstream) side of a filter medium contained within the filter device. Deposition of the terephthalic acid stream into the filter device at elevated temperature and/or pressure is advantageous, as improved filtration may be afforded due to the aqueous medium being less viscous at elevated temperature. Furthermore, there is less co-crystallization of impurities (including, but not limited to, para-toluic acid) when the terephthalic acid product is filtered at elevated temperature and/or pressure. Thus, a higher purity terephthalic acid product can be

obtained in some embodiments, and there is a correspondingly higher level of impurities (for example, para-toluic acid) in the aqueous medium removed therefrom, which is desirably recycled within the process. The elevated temperature may also permit heat recovery and hence provide a reduction in variable costs. The elevated temperature also means that the heat required to raise the temperature of the PTA/ethylene glycol slurry within the subsequent PET production process is minimized.

[00030] The para-toluic acid impurity noted above is commonly present in the terephthalic acid slurry in one or more forms, including in the forms of dissolved para-toluic acid in the water, para-toluic acid which has been crystallized on the surface of the PTA crystals, and para-toluic acid which has been co-crystallized with the PTA and is therefore present within the body of the PTA crystal. The crystallized PTA is generally separated from the water and impurities by a filter device. Because para-toluic acid is more soluble in water than terephthalic acid, the para-toluic acid impurity remains predominantly in the aqueous solution during crystallization and product recovery stages to provide PTA. The purpose of the filter device in certain embodiments is thus to remove as much para-toluic acid as possible from the terephthalic acid by displacement removal of the mother liquor and by displacement washing of the mother liquor from the cake, thereby also removing para-toluic acid which is present on the surface of the crystals.

[00031] According to the present disclosure, one exemplary filter device comprises an integrated wash facility, as illustrated in FIG. 1. The filter device may comprise a number of different zones wherein filtering, washing, and/or drying can be performed. For example, FIG. 1 depicts a filter device with a filtration zone, drying zone, washing zone, drying zone, and discharge zone. In other embodiments, filter devices can be employed which include a greater or lesser number of zones. In some embodiments, two or more zones can be combined to form a section of the filter device. For example, filtering and drying zones may be combined within a single section and washing and drying zones may be combined within a single section.

[00032] The filter material of the filter device can comprise any material sufficient to separate solid PTA from para-toluic acid. In one exemplary embodiment, the filter device employed (e.g., the filter device with integrated wash facility) comprises a rotary pressure filter, which is commercially available. A rotary pressure filter can comprise an outer casing within which a cylindrical support carrying a filter medium is mounted for rotation about a horizontal axis perpendicular to the plane of the filter medium. In certain embodiments, the filter material can

be a metal gauze or a cloth comprising a plastic such as polyester, polypropylene, polyetheretherketone, combinations thereof, or the like. The filter surface may suitably be in the form of a band, preferably a continuous band which can be moved (*e.g.*, continuously or intermittently) to convey material comprising terephthalic acid. The slurry can be, for example, supplied to the lower region of the filter casing, which forms a reservoir. In one embodiment, the reservoir is bordered by a weir on one side so that the slurry contained within the reservoir is of constant depth. Overflow can pass (as shown in FIG. 1) into an overflow section. In some embodiments, the overflow can be withdrawn and recirculated via a level controlled valve to the slurry holding tank, the control being affected in dependence on the level of slurry within the slurry overflow section.

[00033] The rotary pressure filter can further comprise a suction unit located within the interior of the cylindrical support carrying the filter medium is mounted, so as to exhaust fluid from the interior of the filter material. This arrangement is such that, as the support rotates in a clockwise direction, successive parts of the periphery of the cylindrical filter dip into the reservoir (illustrated as “Feed” in FIG. 1) and slurry is drawn against the filter medium, forming a cake of solid materials (*e.g.*, crystals of terephthalic acid, *i.e.*, a “PTA cake”) on the upstream face of the filter medium. (Note that the rotation can also be in the counter-clockwise direction, which is not depicted in FIG. 1). The filtration process is advantageously driven by the application of differential pressure across the filter medium. Such pressure can be developed by the supply of pressurized fluid to the space between the casing of the filter and the filter medium. The pressure exerted by the fluid in such embodiments is such that a small pressure differential is established through the thickness of the filter cake. Typically, this pressure differential is of the order of about 0.1 bar to 2 bar. With reference to the typical slurry pressure noted above, the pressurized fluid may be supplied at a pressure of the order of 8.5 bar and the pressure at the downstream side of the filter medium is typically of 0.1 to 2 bar less but at least substantially the same as or greater than the pressure prevailing in the final stage of the crystallization process.

[00034] In some embodiments, the fluid used to pressurize the upstream side of the filter medium comprises a solvent present in liquid form and/or the solvent used for the purpose of establishing the pressure differential is present in its vapor phase (*e.g.*, including but not limited to, steam). In one embodiment, the pressurized fluid that provides the differential pressure across the filter medium in the filter device comprises heated steam that is provided from

elsewhere in the integrated plant described herein. For example, in a specific embodiment, as illustrated in FIG. 2, steam can be pressurized by compressor 346 and introduced into the filter casing 320 of the filter device via a line 348. The steam can circulate around a path within the filter device in which it passes through the filter cake and the filter medium, enters suction unit 332 (along with filtrate), and returns to the compressor 346 via line 347 and line 352. Filtrate removed by suction unit 332 can collect in the tank 350, from which it is withdrawn for further processing via level controlled valve 354. The supply of steam to the rotary filter is controlled by valve 356 and pressure differential sensor 358 coupled between lines 347 and 348. Excess steam may be purged, as necessary, from the system via valve 360 while make-up steam may be supplied, as necessary, via valve 362, which are both under the control of pressure sensor 364. The supply of pressurized fluid (*e.g.*, steam) supply to the system may be derived from any suitable source; for instance, it may in some embodiments comprise steam derived from the purification process at a point upstream of the filtration system. One exemplary source of such steam is steam produced during a conventional PTA crystallization process applied to the liquor withdrawn from the hydrogenation reactor, as described in greater detail above.

[00035] The pressurized fluid (*e.g.*, steam) employed as the pressurizing fluid is typically at a temperature slightly above that at which the liquor is introduced into the filter. Thus, for example, where the liquor is introduced at a pressure of 8 bar and at 170°C, the steam admitted as the pressurizing steam will be at about 173°C to 175°C and, in particular, at a temperature which ensures that there is no tendency for condensation. In such embodiments, the arrangement is such that the temperature of the pressurizing fluid on the upstream and downstream sides of the filter cake are substantially the same and the equipment will be thermally insulated to avoid heat losses as the pressurizing fluid circulates around the system. In practice, the compression of the circulating fluid by compressor 346 introduces heat into the circulating steam and means may be provided for moderating or controlling the temperature of the steam entering the filter. For instance, this may be achieved by passing the pressurized fluid (*e.g.*, steam) through a heat exchanger following compression or by controlled injection of further pressurized fluid in liquid or gas phase (*e.g.*, steam or water), depending on whether heating or cooling is required, into the recirculating vapor to adjust the temperature thereof so that the pressurized fluid (*e.g.*, steam) entering the filter is within a desired temperature range.

[00036] As shown in FIG. 3, the pressurizing fluid (*e.g.*, steam) leaving compressor 346 can, in some embodiments contain volatile para-toluic acid, which would contaminate the PTA cake after it has been washed with wash fluid from nozzles 336. To prevent such contamination from occurring, in certain embodiments, a scrubbing column 371 is incorporated into the disengagement pot 370, such that the pressurizing fluid leaving disengagement pot 370 is contacted in a counter current manner with scrubbing medium over a series of trays, or a section of packing within scrubbing column 371. The scrubbing medium is typically water which is added through nozzle 372. The detailed arrangement is shown in FIG. 3. After use, the scrubbing medium can be combined with material leaving tank 350 (including filtrate removed by suction unit 332).

[00037] Within the filter device itself, with reference to the embodiment illustrated in FIG. 1, the slurry from the Feed section is carried by the rotating filter medium to a first zone comprising a filtration unit, wherein the terephthalic acid crystals are separated from the aqueous medium by filtration of the slurry through the filter medium to obtain a wet mass of crystals. The filter drum is typically rotated through this slurry feed, which is circulated around the lower section of the exterior of the drum and a pressure differential maintained between the interior and exterior of the drum can cause water (including, in certain embodiments, dissolved impurities) from the slurry to be drawn through the drum, while a filter cake of wet crystals is formed on the exterior of the drum.

[00038] In the second zone of the embodiment of FIG. 1, the filter cake is subjected to a first drying stage. As the filter drum is further rotated, gas is drawn through the drum, causing the wet crystals of the filter cake to be dried by partial displacement of the para-toluic acid-rich mother liquor (which remains between the crystals after cake formation in the first filtration step). In certain embodiments, the gas can comprise steam (*e.g.*, may be predominantly steam), wherein the steam can have a small degree of superheat. The resulting filter cake can then be transferred to the next zone without reslurrying.

[00039] In the third zone of the embodiment of FIG. 1, a washing step occurs wherein a washing fluid is brought into contact with the filter cake to remove further impurities (*e.g.*, para-toluic acid) from the crystals. The washing fluid can be supplied, *e.g.*, through nozzles as shown above the washing stage 3 of FIG. 1. The washing fluid can vary and in certain embodiments, may comprise demineralized water which is heated to substantially the same temperature as the

filter feedstream. The use of a washing fluid at similar temperature as the crystals can, in certain embodiments, help to avoid problems with flashing or quenching (with the consequent risk of precipitating impurities). This washing step can be conducted, for example, on a filter surface, wherein the washing fluid is applied to the filter cake while effecting filtration, whereby the washing liquid can displace remaining mother liquor through the filter cake and through the filter surface. This zone advantageously in certain embodiments comprises a single stage wash, in which the wash liquor passes through the filter surface only once, either as a single stream or, following splitting of the wash liquor, as a plurality of streams. If desired, this zone may alternatively comprise a succession of wash stages, wherein the wash liquid is passed through the filter surface more than once. In such embodiments, the succession of wash stages may be concurrent or counter-current in which in each stage, the incoming aqueous was passed through the terephthalate crystals and the filter surface is the aqueous wash which has passed through the crystals and the filter surface in one or more previous stages. However, in the last stage, the washing fluid is preferably fresh (*i.e.*, clean solvent, *e.g.*, water). Within the filter, the washing fluid can optionally be segregated and collected separately from the main filtrate, allowing for its reuse within the process to minimize water usage.

[00040] The fourth zone of the embodiment illustrated in FIG. 1 comprises a second drying zone. In this zone, the filter cake from zone three enters a drying zone in which the washing fluid used in zone three and any residual liquor from the slurry is removed from the filter cake. When the filter device comprises a filter drum, the filter drum is further rotated, thereby drawing gas through the drum and further drying the filter cake. The expected cake wetness is in the range of about 5-15%, with a target of less than 10%. The drying gas in this zone can comprise an inert gas (*e.g.*, predominantly nitrogen) or superheated steam or preferably a mixture of inert gas and steam.

[00041] As noted above, a differential pressure is preferably maintained across the filter surface in at least one of these zones, such that on the lower pressure side of the filter surface, the pressure is substantially the same as or greater than the pressure prevailing immediately prior to introducing the terephthalic acid slurry into the filter device. For example, the pressure differential of this second drying step can, in some embodiments, be such that, on the lower pressure side of the filter surface, the pressure is at least equal to the pressure prevailing in the final crystallizer stage (which will commonly be superatmospheric, *e.g.*, between about 1.5 and

15 bar, or about 3 to about 10 bar). Preferably, in certain embodiments, the pressure differential will be such that, on the lower side of the filter surface in each of said zones, the pressure is at least equal to the pressure prevailing in the final crystallizer stage (*i.e.*, in the terephthalic acid slurry following the crystallizer stages). Typically, the pressure differential across the filter surface in each of said zones is at least about 0.05 bar, with the side of the filter surface on which the mass of terephthalic acid crystals is located being at a higher pressure than the other side of the filter. Preferably, the pressure differential is about 0.1 to 10 bar, more preferably, 0.2 to 3 bar and especially 0.2 to 1 bar, for example 0.3 bar. The actual pressure on the lower pressure side of the filter is maintained at such a pressure that the washing fluid in the third zone and, if applicable, the para-toluic acid-rich mother liquor in the first zone, which are removed through the filter surface, remain substantially in the liquid phase. The higher pressure side of the filter surface is preferably maintained at elevated pressure, desirably at 2 to 15 bar and especially 3 to 10 bar and is desirably above the pressure of the preceding pressure-reducing step in the process.

[00042] Advantageously, each of these steps (*i.e.*, the steps described herein with reference to zones 1-4 as illustrated in FIG. 1) is carried out by filtering said slurry on a rotating filter drum, which is movable to transport the terephthalic acid through the zones. In this way, a reslurry of the terephthalic acid is avoided and by effecting filtration through a filter surface so that the lower pressure side of the filter surface is at a pressure no less than said superatmospheric pressure, liquid removal from the terephthalic acid can be effected substantially without accompanying flashing, thereby reducing the tendency for soluble impurities to precipitate and contaminate the mass of purified terephthalic acid. In addition, any tendency for material to precipitate and foul the filter medium is reduced. The separation (*i.e.*, the one or more filtration, washing, and/or drying steps described herein) advantageously can remove at least a portion of the para-toluic acid from the PTA crystals, and most advantageously can remove a majority of the para-toluic acid from the PTA crystals, including substantially all of the para-toluic acid from the PTA crystals. The resulting PTA, after being passed through the filter device, is preferably at a purity suitable for direct manufacture of polyester.

[00043] In a final zone of the filter device (illustrated as zone 5 in the embodiment of FIG. 1), the filter cake is discharged such that it can be directly combined with ethylene glycol in a separate vessel. The PTA can be discharged from the filter device by any suitable means, for

example, by scraping, by gravity, and/or by means of gas blowoff from the inside of the filter drum. Although not required according to the present disclosure, the filter device can optionally be further equipped with a suitable means to pass liquid (*e.g.*, water or alkaline solution) through the returning part of the band to wash off downwardly facing adhering deposits into a receiver or into the feed slurry of the filter device. Furthermore, at least a portion of the aqueous medium recovered in the filtration and/or washing steps (*i.e.*, the para-toluic acid-rich mother liquor and/or the washing fluid) can be recovered and combined, directly or indirectly, with additional CTA and accordingly, this liquid can in some embodiments desirably constitute at least a part of the aqueous medium with which the CTA is combined. If both the para-toluic acid-rich mother liquor and the washing fluid are recycled in this way, they may optionally be mixed together to form a single stream prior to combination with the CTA. The para-toluic acid-rich mother liquor and the washing fluid can optionally be treated (separately or together) by such methods as distillation, filtration, and/or evaporation to produce substantially pure water or to at least partially eliminate para-toluic acid. Such treatment can, in some embodiments, further comprising cooling or evaporation to produce a less pure precipitate and a residual mother liquor which are then suitably separated. In certain embodiments, such a less pure precipitate can be returned to the oxidation step of the oxidation plant (*e.g.*, where the CTA is produced by an oxidation plant integrated with the purification plant). The residual mother liquor can then be treated further and/or used as an aqueous medium to be combined with the CTA. It is noted that, where recycle of any liquid within this system is employed, it may be necessary to provide a purge to allow some degree of control over the level of components in the recycled stream.

[00044] The PTA filter cake resulting from the filtration, washing, and drying steps within the filter device (*i.e.*, the wet PTA discharged from the filter device) is not further dried, stored, or processed prior to being combined with ethylene glycol. In particular, with reference to the embodiments illustrated in FIGS. 4, 5, and 6, the filter cake is dislodged from the filter 316 and falls into a collection section 344, from which it is recovered. In the illustrated embodiment, the PTA filter cake leaving the filter 316 is discharged either directly or via one screw conveyor or a series of screw conveyors 382, into a reslurry vessel 380 where it is mixed directly with ethylene glycol. Advantageously, the means for conveying the wet PTA from the filter device to the reslurry vessel is unsealed (*e.g.*, the means for conveying does not create a vapor seal).

[00045] The optional screw conveyors (or other means) used for transport of the PTA to the reslurry vessel generally comprise a relatively large opening therethrough to allow the PTA to be conveyed. In certain embodiments, the screw conveyors useful according to the present disclosure can comprise conveyors other than typical solids-conveying extruders or sealed type conveyors. One exemplary screw conveyor for use in the integrated systems described herein is a ribbon-type screw. Such a screw conveyor comprises a vapor path through the screw, without a vapor seal. Although the present disclosure does not explicitly exclude other types of screw conveyors (*e.g.*, sealed conveyors, such as the Peters X-pump, which include an integral vapor seal), it is understood that the integrated systems disclosed herein preferably use screw conveyors that do not include a vapor seal.

[00046] The ethylene glycol provided to the reslurry vessel, which is combined with the wet PTA from the filter device preferably already in heated form. For example, in some embodiments, the ethylene glycol is advantageously heated to a temperature above about 100°C, *e.g.*, between about 130°C and about 150°C, such as around 140°C prior to combination with the PTA filter cake. In some embodiments, the ethylene glycol is pre-heated prior to introduction into the reslurry vessel 380. The energy to heat the ethylene glycol can be provided from various sources. However, in certain embodiments, at least a portion of the energy can be provided by indirect heat exchange with flash steam produced from the crystallizers of the PTA plant. Any residual water remaining with the PTA cake will subsequently be removed as water vapor along with water of reaction, which is produced in the initial polymerization vessel of the polymerization plant portion of this integrated plant system.

[00047] In preferred embodiments, the reslurry vessel is operated at approximately the same pressure as the casing of the filter 316. For example, in certain embodiments, the reslurry vessel and casing of the filter operate within 0.01 to 0.5 bar, including 0.01 to 0.1 bar, of each other. The pressure balance line 381 illustrated in FIG. 4 can be provided within the system to ensure roughly equal pressures between the reslurry vessel and the casing of the filter. In particular, the reslurry vessel is beneficially maintained at a pressure equal to or less than that in the casing of the filter device. As such, no vapor seal is necessary to prevent vapor flowback from the reslurry vessel (*e.g.*, into the PTA production process). Typically, the pressure in vapor balance line 381 is maintained at the same pressure as that in the reslurry vessel 380. A condenser unit 390 can also be incorporated into the system to condense and knock down any water or ethylene glycol

vapor that forms and is collected, further minimizing the possibility of ethylene glycol vapor from the reslurry vessel contaminating the PTA production process, as illustrated in FIG. 6. The condenser can be located, for example, immediately above the reslurry vessel 380 in the vapor balance line 381. In some embodiments, an inert gas (*e.g.*, nitrogen) can be added to the vapor space of the reslurry vessel to ensure that the necessary vapor pressure is maintained (*i.e.*, a vapor pressure that is roughly equal to that in the casing of the filter 316). The resulting slurry of wet PTA crystals in ethylene glycol can then be transferred directly from reslurry vessel 380 to the first stage of a polymerization reactor to begin the process of PTA production.

[00048] In another embodiment, as depicted in FIG. 5, a nitrogen sweep process with controlled pressure differential is used to prevent contamination of the PTA process. Briefly, this process employs a gaseous flow (*e.g.*, comprising nitrogen or a mixture of nitrogen and superheated steam) to decrease the likelihood of contamination. For example, a gas can be added to the pressure casing of a rotary pressure filter through a pressure control valve, which is controlled by pressure controller PC1.

[00049] Again, a PTA filter cake is formed and filtered as described above, and is discharged from the system (*e.g.*, from the rotary pressure filter). The discharged PTA filter cake is again combined in a reslurry vessel 380 with ethylene diol to form a PTA-ethylene glycol slurry. The gas added to the rotary pressure filter and passing into the reslurry vessel is vented through a pressure control valve, which is controlled by pressure controller PC2. The pressure of PC2 is maintained at a pressure lower than that of pressure controller PC1, such that there is a positive gas flow (*e.g.*, comprising nitrogen or a mixture of nitrogen and superheated steam) from the rotary pressure filter to the reslurry vessel. Typically, the pressure difference is 0.05 to 0.5 bar, including 0.1 to 0.2 bar. The gas flow can pass from the filter through a screw conveyor or through a PTA discharge route to the reslurry vessel. This positive gas flow is thus designed to prevent the flow of diol vapor from the reslurry vessel back into the filter.

[00050] Again, a condenser unit 390 can be incorporated into the system shown in FIG. 5 to condense and knock down any water or ethylene glycol vapor that forms and is collected, further minimizing the possibility of ethylene glycol vapor from the reslurry vessel contaminating the PTA production process. The condenser can be located, for example, anywhere upstream of the pressure control valve on the reslurry vessel 380, such that any steam vented from the reslurry vessel is condensed prior to the steam being vented. The condenser is typically arranged such

that any water condensed therein returns to the reslurry vessel after condensation. A vertical upflow condenser can be particularly useful according to this embodiment, such that the water or glycol condensed in the condenser is at the same temperature as the vapor entering the condenser and, as such, will not cause excessive cooling of the PTA-diol slurry upon reintroduction to the reslurry vessel. Any gas vented from the reslurry vessel pressure control valve can, in some embodiments, be scrubbed prior to discharge to the atmosphere, to prevent emissions of glycol vapor to the atmosphere.

[00051] The pressure control between the reslurry vessel and the filter casing in the embodiment shown in FIG. 5 not only prevents any ethylene glycol (in vapor or liquid form) from flowing back from the reslurry vessel to the rotary pressure filter, but can also prevent the water content of the hot PTA cake from flashing when it enters the reslurry vessel and can also ensure that the majority of the enthalpy available in the hot PTA cake is transferred directly into the polyester production portion of the integrated plant. As such, there is an overall beneficial reduction in the heat required in the first stage of the polymerization process.

[00052] Experimental - Typical flowrates of different components into the reslurry system

Comparative example (baseline data)

Flowrate in kg/h	PTA Product	Esterifier Hot well Glycol	CP Recycle Tank Glycol	Mixed slurry
PTA	92100			92100
Water		589.0	2320.5	2910
Ethylene Glycol		18919.3	36118.7	55039
Diethylene Glycol		98.2	154.7	253
Acetaldehyde		0.8	19.3	20
2 Methyl 1,3, Dioxalane		1.4	38.7	40
Ethylene Glycol monoacetate		23.6	15.5	39
Ethylene Glycol diacetate			7.7	8

Temperature (C°)	40	165	45	67.8
Pressure (barA)	1.01	1.01	1.01	1.01
Total kg/h	92100	19632	38675	150408
enthalpy KJ/h	4052400	8990859	4906181	17949440

Example 1:

Flowrate in kg/h	Wash stream	PTA Cake	Esterifier Hot well Glycol	CP Recycle Tank Glycol	Overall stream
PTA		92100			92100
Water	32235	8009	589.0	2320.5	10918
Ethylene Glycol			18919.3	36118.7	55039
Diethylene Glycol			98.2	154.7	253
Acetaldehyde			0.8	19.3	20
2 Methyl 1,3, Dioxalane			1.4	38.7	40
Ethylene Glycol monoacetate			23.6	15.5	39
Ethylene Glycol diacetate				7.7	8
Temperature (°C)	148	148	165	45	113.5
Pressure (bar)	5	4.5	4.5	4.5	4.5
Total kg/h	32235	100109	19632	38675	158417
enthalpy KJ/h	19941860	19948379	8990859	4906181	33845419

Example 2:

Flowrate in kg/h	Wash stream	PTA Cake	Esterifier Hot well Glycol	CP Recycle Tank Glycol	Overall stream
PTA		92100			92100
Water	32235	8009	589.0	2320.5	10918
Ethylene Glycol			18919.3	36118.7	55039
Diethylene Glycol			98.2	154.7	253
Acetaldehyde			0.8	19.3	20
2 Methyl 1,3, Dioxalane			1.4	38.7	40
Ethylene Glycol monoacetate			23.6	15.5	39
Ethylene Glycol diacetate				7.7	8
Temperature (°C)	170	170	165	130	154.5
Pressure (bar)	8	8	8	8	8
Total kg/h	32235	100109	19632	38675	158417
enthalpy KJ/h	22906191	19948379	8990859	16135885	45075123.57

[00053] Comparative example shows a heat and mass balance for the PET slurry tank when cold PTA at 40°C is mixed with recycled glycol from the PET plant. This shows that the combined slurry temperature is 67.8°C.

[00054] Example 1 shows the comparable heat and mass balance for the PET slurry tank when hot PTA cake is combined with recycled glycol in the reslurry tank. The benefit of adding hot PTA is that the temperature of the mixed stream is around 113°C, showing that the benefit of discharging PTA cake directly into the slurry tank reduces the heat load on the esterifier reboiler by 4.4 MW.

[00055] Example 2 shows the comparable heat and mass balance for the PET slurry tank when hot PTA cake is combined with recycled glycol in the reslurry tank. In this case the cooler of the glycol streams has been heated using waste low-grade heat from the PTA Plant, whilst the

Rotary Filter is operated at a higher temperature. In this case, the user of a higher pressure filter combined with heated glycol increased the temperature of the slurry drum to 154°C, and the heat load on the esterifier reboiler is reduced by 7.5 MW compared to the comparative example. This further shows the energy benefit of integrating the PTA and PET plants.

[00056] Many modifications and other embodiments of the invention will come to mind to one skilled in the art to which this invention pertains having the benefit of the teachings presented in the foregoing description. Therefore, it is to be understood that the invention is not to be limited to the specific embodiments disclosed and that modifications and other embodiments are intended to be included within the scope of the appended claims. Although specific terms are employed herein, they are used in a generic and descriptive sense only and not for purposes of limitation.

THAT WHICH IS CLAIMED:

1. An integrated method for the purification of crude terephthalic acid and the production of poly (ethylene terephthalic acid), comprising:
 - (a) providing a stream of crystallized purified terephthalic acid in an aqueous medium;
 - (b) separating at least a portion of the aqueous medium in a filter device to provide wet purified terephthalic acid;
 - (c) transferring the wet purified terephthalic acid directly from the filter device to a vessel and contacting the purified terephthalic acid with a diol in the vessel to give a reactant slurry;
 - (d) conveying the reactant slurry directly to a polymerization reactor for the production of poly(ethylene terephthalate); and
 - (e) maintaining the vessel at a pressure equal to or less than the pressure of the filter device.
2. The method of claim 1, wherein the maintaining step comprises integration of a vapor balance line connecting the vessel to the filter device.
3. The method of claim 1, wherein the maintaining step comprises applying a positive pressure to the filter device.
4. The method of claim 3, wherein the applying comprises controlling a first pressure control valve that is associated with the filter device.
5. The method of claim 4, wherein the applying further comprises venting the vessel.
6. The method of claim 5, wherein the venting is controlled by a second pressure control valve that is associated with the vessel that is set at a lower pressure than that of the first pressure control valve.

7. The method of claim 1, wherein the providing step comprises:
 - (i) dissolving crude terephthalic acid in an aqueous medium to produce a terephthalic acid-containing solution comprising one or more impurities;
 - (ii) contacting the terephthalic acid solution with hydrogen to reduce at least a portion of the impurities present in the crude terephthalic acid to produce pure terephthalic acid and hydrogenated impurities; and
 - (iii) crystallizing the pure terephthalic acid.
8. The method of claim 7, wherein the contacting step further comprises exposing the terephthalic acid solution to elevated temperature and pressure and introducing a hydrogenation catalyst.
9. The method of claim 8, wherein the hydrogenation catalyst is a supported palladium catalyst.
10. The method of claim 1, wherein the separating step comprises one or more of filtering the pure terephthalic acid on a filter surface, washing the pure terephthalic acid, and drying the pure terephthalic acid.
11. The method of claim 10, further comprising applying a pressure differential across the filter surface.
12. The method of claim 1, wherein the transferring step comprises passing the purified terephthalic acid through a non-sealed transfer line.
13. The method of claim 12, wherein the non-sealed transfer line comprises a direct line to the vessel.
14. The method of claim 12, wherein the non-sealed transfer line comprises one or more screw conveyors.

15. The method of claim 1, further comprising heating the diol prior to combination with the purified terephthalic acid.

16. The method of claim 15, wherein the diol is heated to a temperature of between about 130°C and about 150°C.

17. An integrated system for the purification of crude terephthalic acid and the production of poly(ethylene terephthalic acid), comprising:

(a) a filter device comprising a filtration zone and a washing zone to remove at least a portion of the impurities from crude terephthalic acid and to provide wet purified terephthalic acid;

(b) a vessel in direct fluid connection with the filter device, comprising a first inlet for addition of the wet purified terephthalic acid and a second inlet for the addition of a diol;

(c) one or more lines adapted to maintain the vessel at a pressure equal to or less than the pressure of the filter device; and

(d) a poly(ethylene terephthalate) polymerization reactor in direct fluid connection with the vessel.

18. The integrated system of claim 17, wherein the one or more lines comprise a vapor balance line in fluid connection with the vessel and the filter.

19. The integrated system of claim 18, wherein the vapor balance line comprises an in-line condenser.

20. The integrated system of claim 17, wherein the one or more lines comprise

(i) a first pressure control valve adapted to control an in-flow of a pressure stream into the filter device; and

(ii) a second pressure control valve adapted to control an out-flow of a pressure stream from the vessel.

21. The integrated system of claim 20, wherein the second pressure control valve is set at a pressure lower than that of the first pressure control valve.
22. The integrated system of claim 20, wherein the one or more lines further comprise an in-line condenser.
23. The integrated system of claim 17, further comprising a conveying device to provide the direct fluid connection between the filter device and the vessel.
24. The integrated system of claim 23, wherein the conveying device is not sealed against vapor transfer.
25. The integrated system of claim 23, wherein the conveying device comprises a screw conveyor.
26. An integrated method or integrated system as substantially described herein with reference to and as illustrated by the accompanying drawings.
27. A poly (ethylene terephthalate) made from the integrated method of claim 1 or the integrated system of claim 17.
28. The poly (ethylene terephthalate) of claim 27, wherein said PET is spun into fibres, blow-molded or extruded.
29. An integrated method for the purification of crude terephthalic acid and the production of poly (ethylene terephthalic acid), comprising:
- (a) a step for mixing crystallized crude terephthalic acid with water to form an aqueous slurry of crude terephthalic acid;

- (b) a step for processing the crude terephthalic acid in a hydrogenation reaction and multistage crystallizer train to convert the crude terephthalic acid to purified terephthalic acid, so producing an aqueous slurry of purified terephthalic acid;
- (c) a step for partitioning at least a portion of the aqueous slurry of purified terephthalic acid to a filter device;
- (d) a step for transferring the wet purified terephthalic acid directly from the filter device to a vessel and a step for mixing the purified terephthalic acid with a diol in the vessel to give a reactant slurry;
- (e) a step for transferring the reactant slurry directly to a polymerization reactor for the production of poly(ethylene terephthalate); and
- (f) a step for pressurizing the vessel at a pressure equal to or less than the pressure of the filter device.

30. An integrated method for the purification of crude terephthalic acid and the production of poly (ethylene terephthalic acid), comprising:

- (a) a step for purifying and crystallizing terephthalic acid in aqueous medium;
- (b) a step for partitioning at least a portion of the aqueous medium to a filter device;
- (c) a step for relocating the wet purified terephthalic acid directly from the filter device to a vessel and a step for mixing the purified terephthalic acid with a diol in the vessel to give a reactant slurry;
- (d) a step for relocating the reactant slurry directly to a polymerization reactor for the production of poly(ethylene terephthalate); and
- (e) a step for pressurizing the vessel at a pressure equal to or less than the pressure of the filter device.

FIG. 1

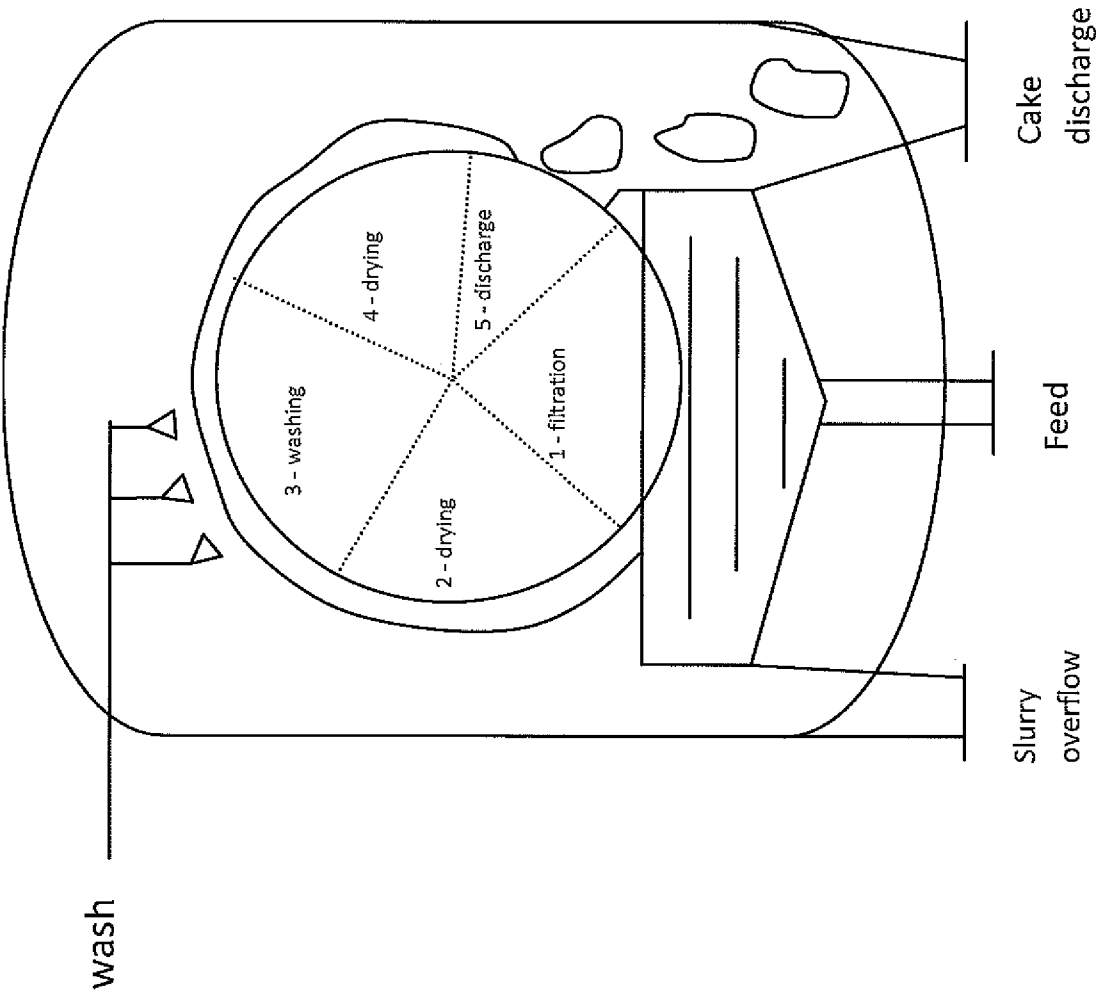


FIG. 2

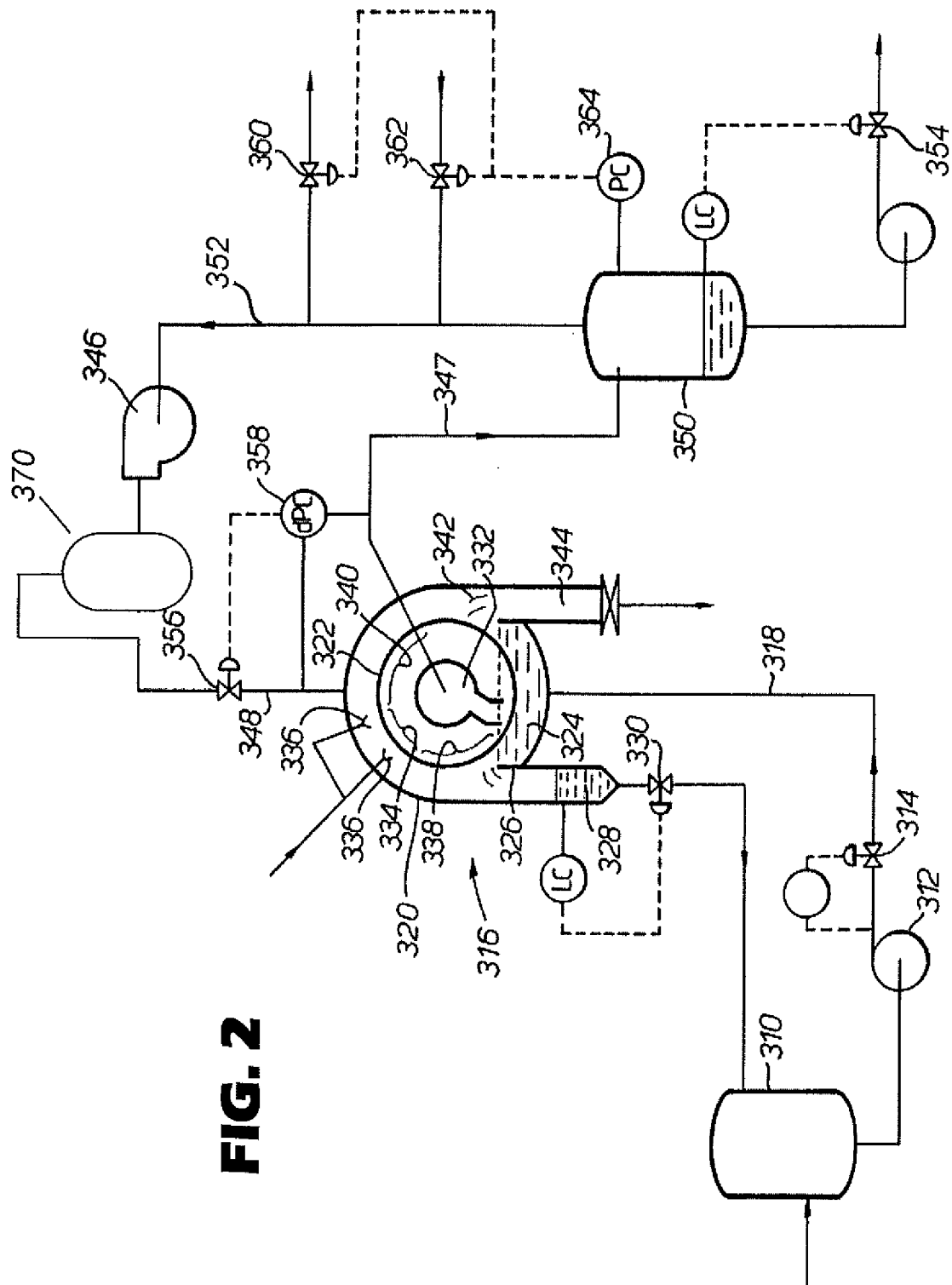
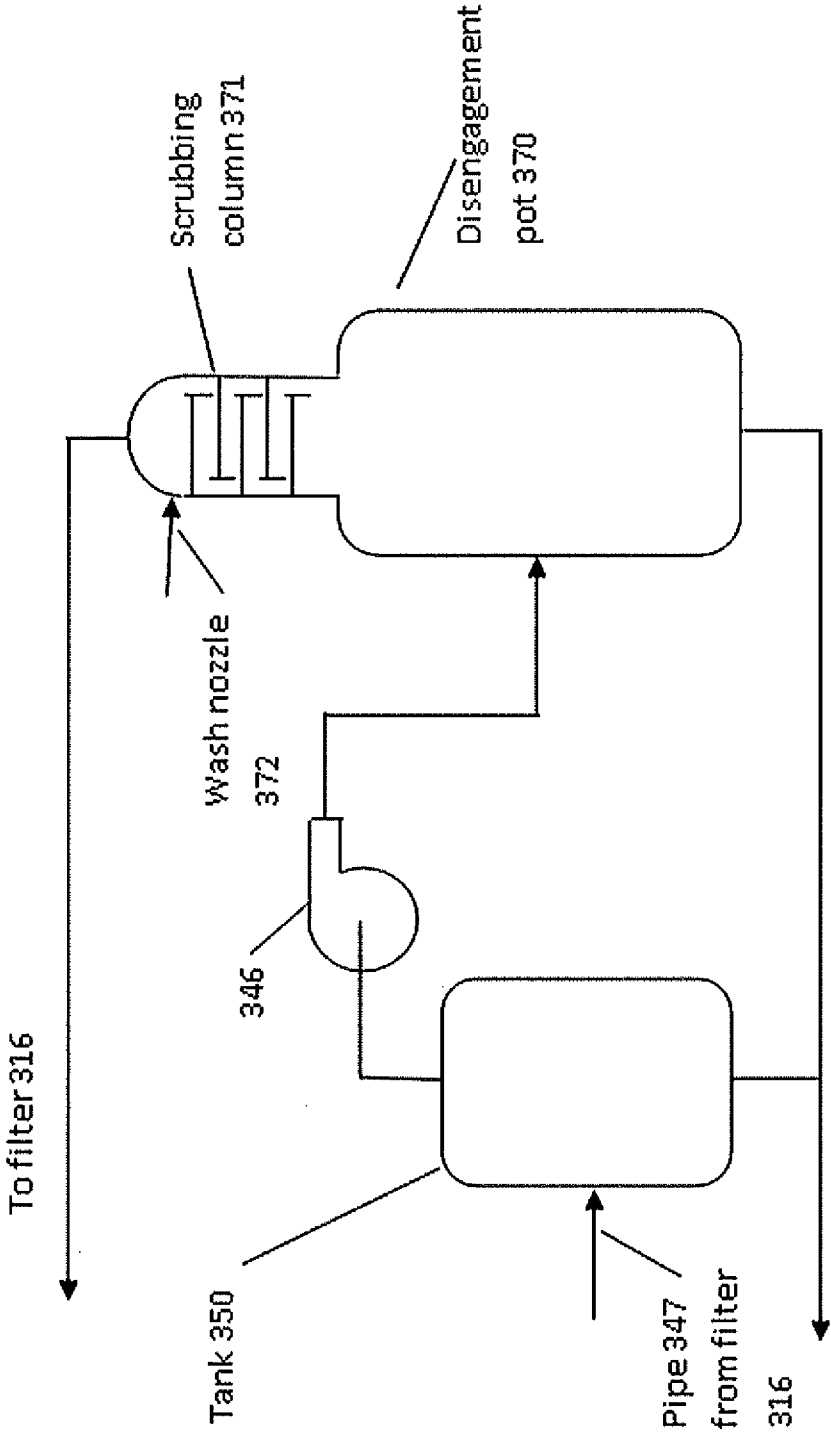


FIG. 3



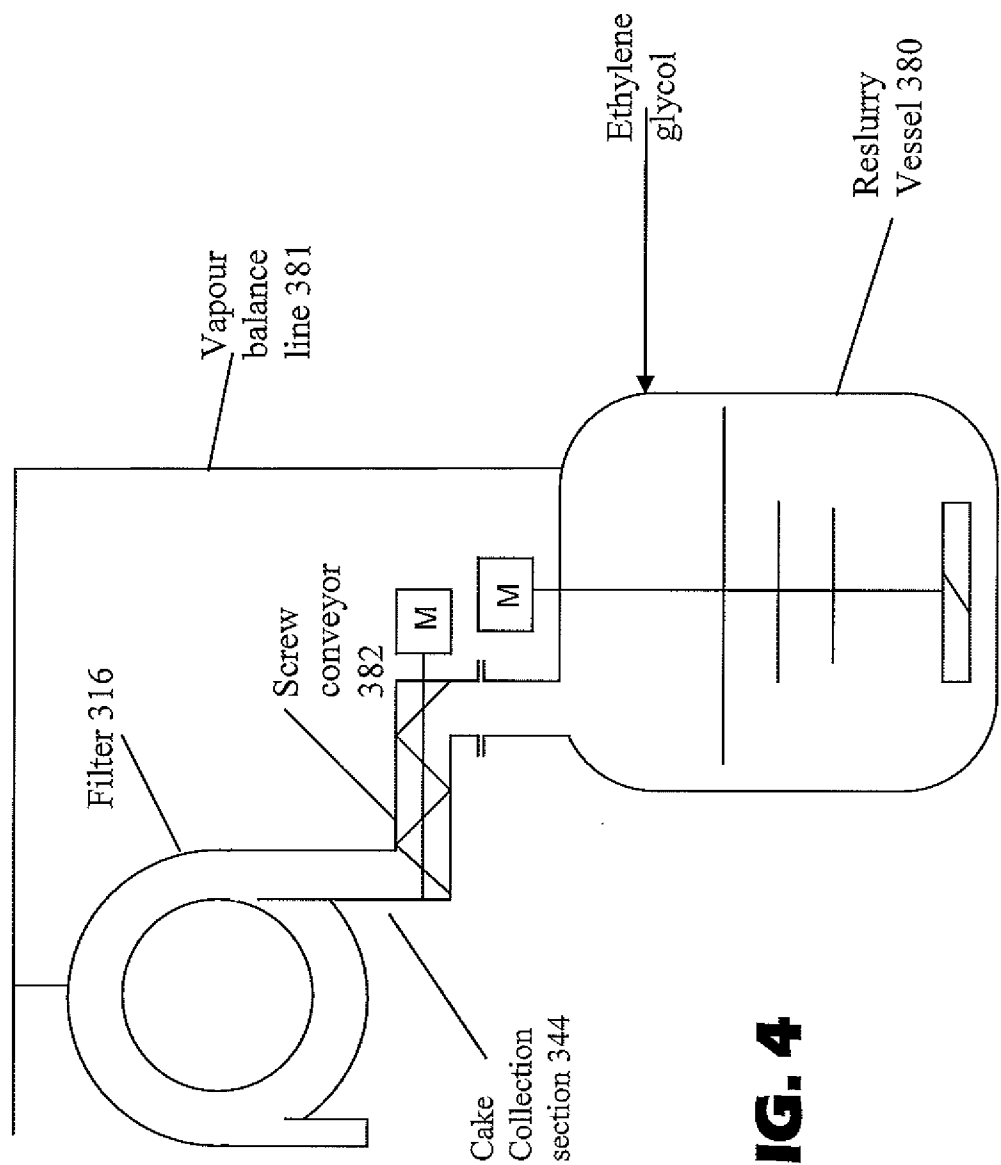
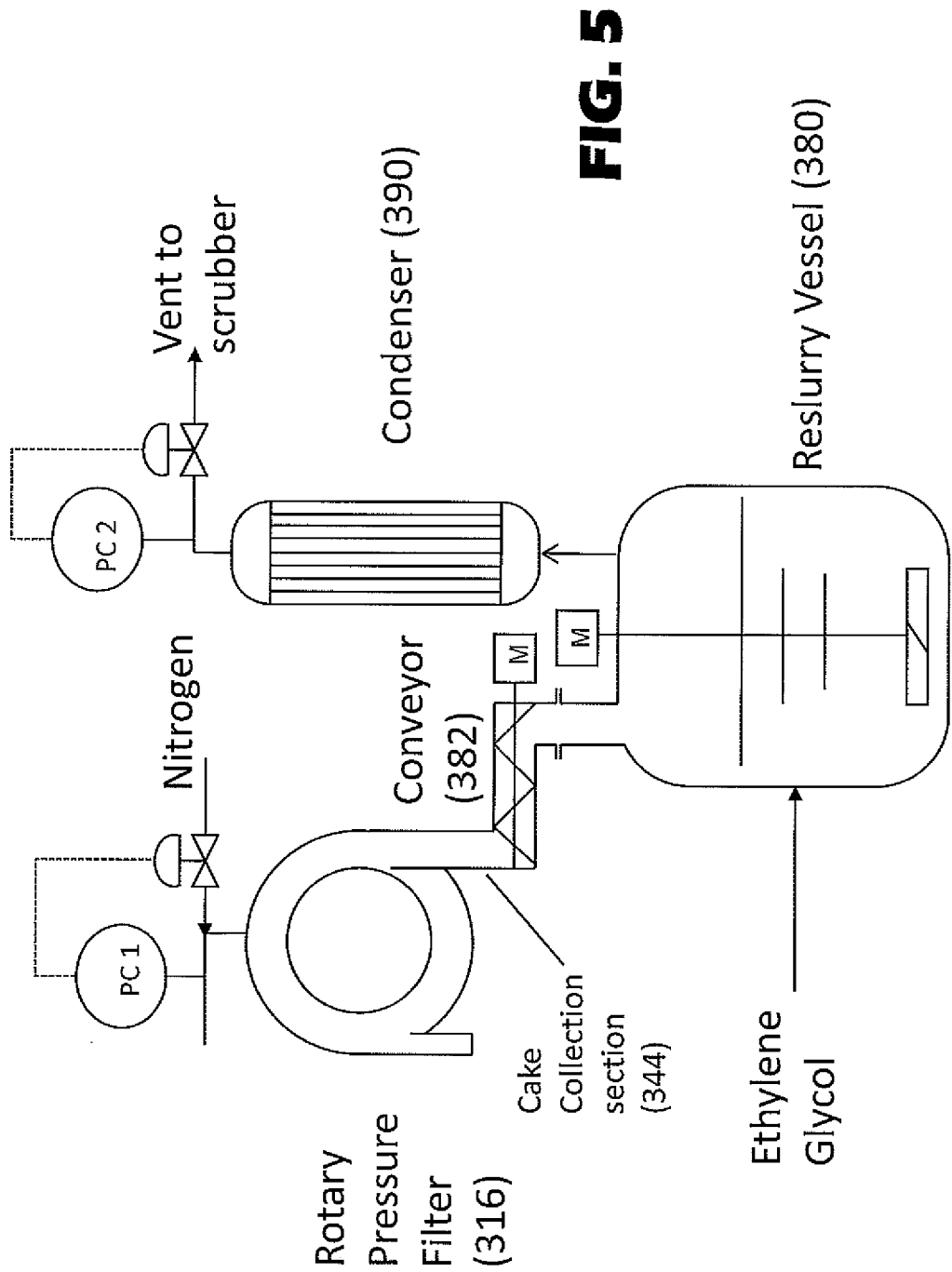


FIG. 4



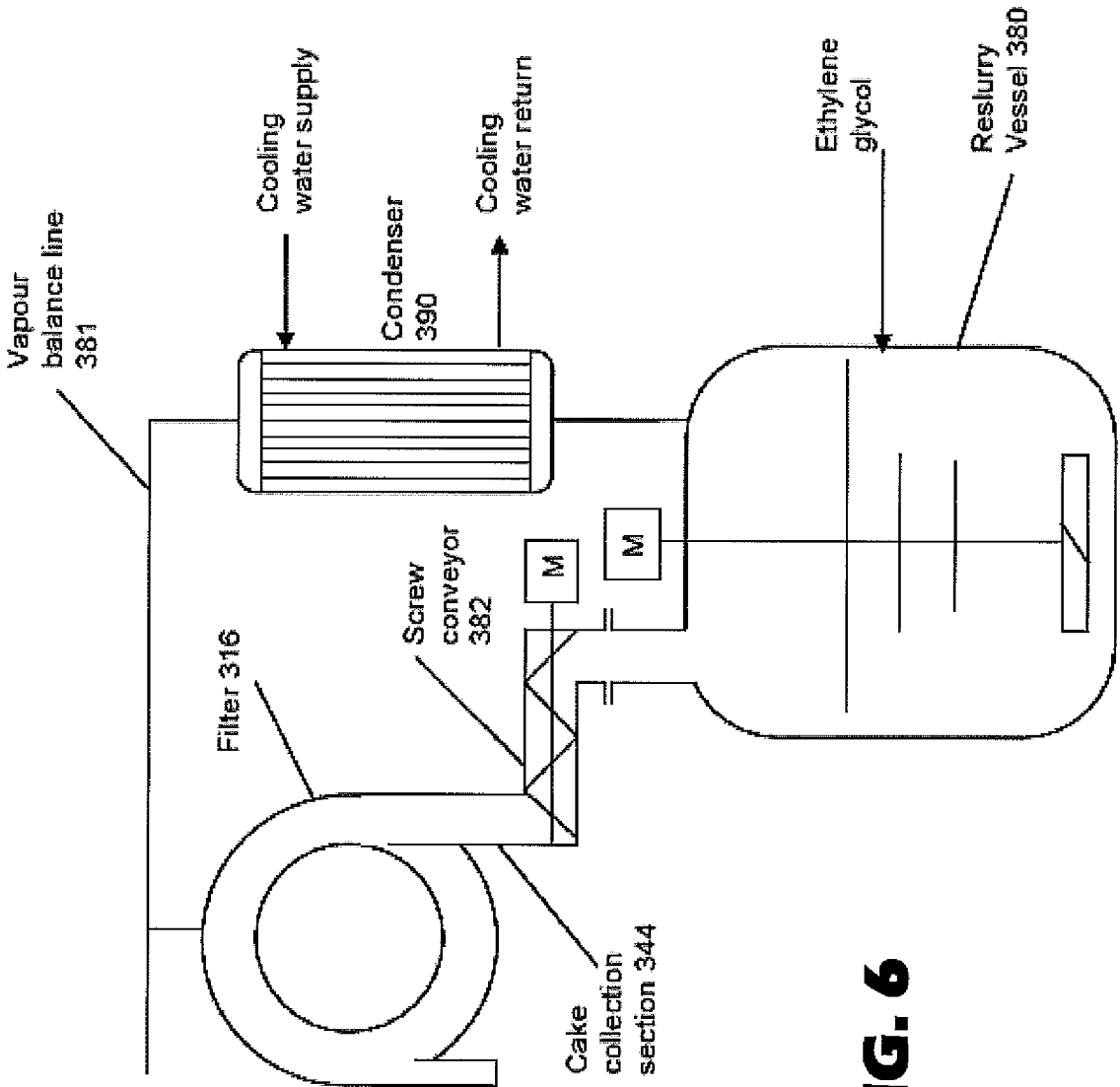


FIG. 6

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2014/066701**A. CLASSIFICATION OF SUBJECT MATTER****C07C 277/02(2006.01)i, B29B 17/02(2006.01)i, C07C 63/26(2006.01)i, C08J 11/10(2006.01)i**

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C07C 277/02; C08G 63/80; B01J 23/00; C07C 51/43; C08G 63/183; C08K 5/56; C08G 63/78; B29B 17/02; C07C 63/26; C08J 11/10

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Korean utility models and applications for utility models

Japanese utility models and applications for utility models

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

eKOMPASS(KIPO internal) & Keywords:integrated method, purified terephthalic acid, polymerization, diol, polyethylene terephthalate, catalyst, ethylene glycol

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2012-0161358 A1 (AL-MUNIF, MUNIF et al.) 28 June 2012 See abstract and claims 1-11.	1-25, 27-30
A	US 2012-0071625 A1 (RAO, MUMMANENI VENKATESWARA et al.) 22 March 2012 See abstract and claims 1-12.	1-25, 27-30
A	EP 0399799 A2 (AMOCO CORPORATION) 28 November 1990 See abstract and claims 1-21.	1-25, 27-30
A	US 2008-0033084 A1 (BASHIR, ZAHIR et al.) 07 February 2008 See abstract and claims 17-38.	1-25, 27-30
A	US 04550198 A (MYERSON, ALLAN S.) 29 October 1985 See abstract and claims 1-12.	1-25, 27-30



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

09 March 2015 (09.03.2015)

Date of mailing of the international search report

10 March 2015 (10.03.2015)

Name and mailing address of the ISA/KR

International Application Division
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INTERNATIONAL SEARCH REPORTInternational application No.
PCT/US2014/066701**Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)**

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☒ Claims Nos.: 26
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
The claim 26 relies on reference to the description or drawings instead of definite structure expressly stated in the claim.
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of any additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2014/066701

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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		KR 10-2011-0138368 A	27/12/2011
		PT 2406299 E	26/11/2013
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