

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
6 April 2006 (06.04.2006)

PCT

(10) International Publication Number
WO 2006/036168 A1

(51) International Patent Classification⁷: **C07C 51/42**,
51/47, 51/48, 63/26

(21) International Application Number:
PCT/US2004/039839

(22) International Filing Date:
29 November 2004 (29.11.2004)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
10/948,678 23 September 2004 (23.09.2004) US

(71) Applicant: **EASTMAN CHEMICAL COMPANY**
[US/US]; 100 North Eastman Road, Kingsport, TN 37660
(US).

(72) Inventors: **LIN, Robert**; 4533 Palomino Drive,
Kingsport, TN 37664 (US). **DE VREEDE, Marcel**;
Boelehaven 6, NL-2993 HE Barendrecht (NL).

(74) Agent: **OWEN, Steven, A.**; P.O. Box 511, Kingsport, TN
37662-5075 (US).

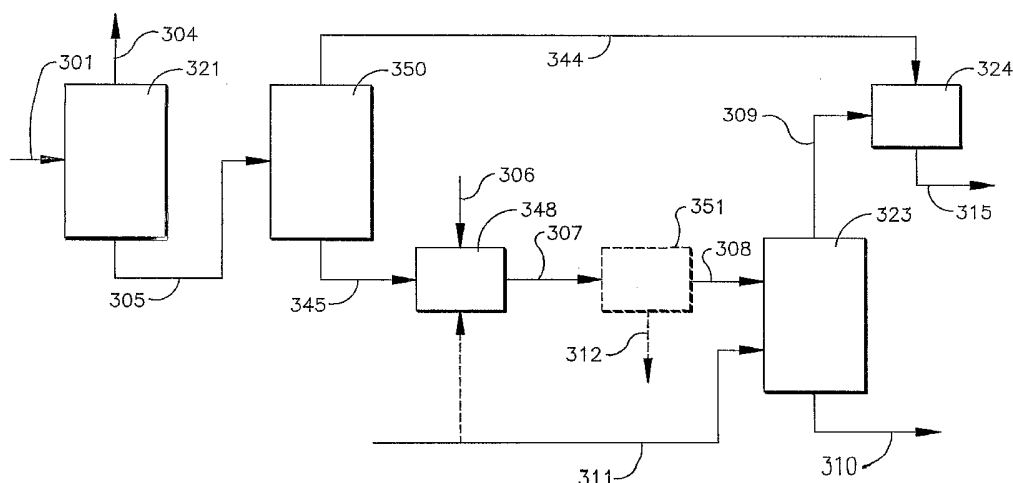
(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:
— with international search report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: EXTRACTION PROCESS FOR REMOVAL OF IMPURITIES FROM AN OXIDIZER PURGE STREAM IN THE SYNTHESIS OF CARBOXYLIC ACID



(57) Abstract: Disclosed is a process that relates to the recovery of a metal catalyst from an oxidizer purge stream produced in the synthesis of carboxylic acid, typically terephthalic acid. The process involves the addition of a wash solution to a high temperature molten dispersion to recover the metal catalyst and then subjecting an aqueous mixture or purified aqueous mixture so formed to a single stage extraction to remove organic impurities to produce an extract stream and a raffinate stream comprising the metal catalyst.

WO 2006/036168 A1

**Extraction Process for Removal of Impurities from an Oxidizer Purge
Stream in the Synthesis of Carboxylic Acid**

5

FIELD OF INVENTION

This invention relates to the recovery of a metal catalyst from an oxidizer purge stream produced in the synthesis of carboxylic acid, typically terephthalic acid. More particularly, the process involves the addition of a wash solution to a high temperature molten dispersion to recover the metal catalyst and then subjecting an aqueous mixture or purified aqueous mixture so formed to a single stage extraction to remove organic impurities to produce an extract stream and a raffinate stream comprising the metal catalyst. This invention also relates to a process to produce a high boiling point organic impurities stream from an aqueous mixture or a purified aqueous mixture.

20

BACKGROUND OF THE INVENTION

Terephthalic acid is commercially produced by oxidation of paraxylene in the presence of a catalyst, such as, for example, Co, Mn, Br and a solvent. Terephthalic acid used in the production of polyester fibers, films, and resins must be further treated to remove impurities formed as a result of the oxidation of paraxylene.

Terephthalic acid (TPA) is an intermediate in the production of polyesters for plastics and fiber applications. Commercial processes for the

manufacture of TPA are often based on the heavy-metal catalyzed oxidation of p-xylene, generally with a bromide promoter in an acetic acid solvent. Due to the limited solubility of TPA in acetic acid under practical oxidation conditions, a slurry of TPA crystals is usually formed in the oxidation reactor. Typically, the TPA oxidizer slurry is withdrawn from the reactor and TPA solids are separated from the oxidizer mother liquor using conventional solid-liquid separation techniques. The oxidizer mother liquor, which contains most of the catalyst and promoter used in the process, is recycled to the oxidation reactor. Aside from the catalyst and promoter, the oxidizer mother liquor also contains dissolved TPA and many by-products and impurities. These by-products and impurities arise partially from minor impurities present in the p-xylene feed stream. Other impurities arise due to the incomplete oxidation of p-xylene resulting in partially oxidized products. Still other by-products result from competing side reactions formed as a result of the oxidation of p-xylene to terephthalic acid. Patents disclosing the production of terephthalic acid such as U.S. patent #4,158,738 and #3,996,271 are hereby incorporated by reference in their entirety to the extent that they do not contradict statements herein.

The TPA solids undergo a solid-liquid separation wherein fresh solvent is utilized to displace a major portion of the liquid component of the oxidizer mother liquor. After drying, the TPA solids are contaminated with impurities that were present in the oxidizer mother liquor since these impurities may be incorporated into the TPA solids. Impurities are also

present due to occlusions in the TPA crystal structure and due to incomplete removal of the oxidizer mother liquor by the fresh solvent wash.

Many of the impurities in the oxidizer mother liquor stream that are recycled are relatively inert to further oxidation. Such impurities include, for example, isophthalic acid, phthalic acid and trimellitic acid. Impurities, which
5 may undergo further oxidation are also present, such as, for example, 4-carboxybenzaldehyde, p-toluic acid and p-tolualdehyde. Oxidation inert impurities tend to accumulate in the oxidizer mother liquor upon recycle. The concentration of these inert impurities will increase in the oxidizer
10 mother liquor until an equilibrium is reached whereby the rate of removal of each impurity via the TPA product balances with the rate of formation and the rate of addition to the oxidation process. The normal level of impurities in commercial crude TPA makes it unsuitable for direct use in most polymer applications.

15 Conventionally, crude TPA has been purified either by conversion to a dimethyl ester or by dissolution in water with subsequent hydrogenation over standard hydrogenation catalysts. More recently, secondary oxidative treatments have been used to produce polymer-grade TPA. It is desirable to minimize the concentration of impurities in the mother liquor and thereby
20 facilitate subsequent purification of TPA. In some cases, it is not possible to produce a purified, polymer-grade TPA unless some means for removing impurities from the oxidizer mother liquor stream is utilized.

One technique for impurity removal from a recycle stream commonly used in the chemical processing industry is to draw out or "purge" some portion of the oxidizer mother liquor that is recycled. Typically, the purge stream is simply disposed of or, if economically justified, subjected to various treatments to remove undesired impurities while recovering valuable components. One example is U.S. # 4,939,297 herein incorporated by reference in its entirety to the extent it does not contradict statements herein. The amount of purge required for control of impurities is process-dependent; however, a purge amount equal to 10-40%, hereafter known as oxidizer purge stream, of the total oxidizer mother liquor stream is usually sufficient to produce TPA adequate as feedstock for commercial polymer manufacture. In the production of TPA, the percentage purge of the oxidizer mother liquor stream necessary to maintain acceptable impurity concentrations, coupled with the economic value of the metal catalyst and solvent components in the oxidizer purge stream, make simple disposal of the oxidizer purge stream economically unattractive. Thus, there is a need for a process that recovers essentially all of the valuable metal catalysts and acetic acid contained in the oxidizer purge stream while removing a major portion of the impurities present in the oxidizer purge stream. The metal catalyst can be recovered in an active form suitable for reuse by direct recycling to the p-xylene oxidation step.

This invention is a marked improvement over a typical purge process. Some of the advantages are:

- 1) enhanced operability and reliability due to reduction in plugging potential;
- 2) reduction in overall energy usage;
- 3) reduction in the amount of water to the solvent extraction step.

5 The invention enhances the impurity removal efficacy of the process, and the operability of the process compared to the existing processes. In addition it should be noted that this invention does not just apply to the crude TPA process but any process that produces an oxidizer purge stream where recovery of metal catalyst is needed.

10

SUMMARY OF THE INVENTION

 This invention relates to removal of impurities and the recovery of a
15 metal catalyst from oxidizer purge stream produced in the synthesis of carboxylic acid, typically terephthalic acid. More particularly, the process involves the addition of wash solution to a high temperature molten dispersion to recover the metal catalyst and then subjecting an aqueous mixture or purified aqueous mixture so formed to a single stage extraction
20 to remove organic impurities to produce an extract stream and a raffinate stream. This invention also relates to a process to produce a high boiling point organic impurities stream from an aqueous mixture or a purified aqueous mixture.

 It is an object of this invention to provide a process to recover a
25 metal catalyst from an oxidizer purge stream.

It is another object of this invention to provide a process for removal of impurities and the recovery of a metal catalyst from an oxidizer purge stream produced in the synthesis of carboxylic acid.

It is another object of this invention to provide a process to produce a
5 high boiling point organic impurities stream from an aqueous mixture or a purified aqueous mixture.

In a first embodiment of this invention, a process to produce a high boiling point organic impurities stream from an aqueous mixture is provided. The process comprises:

- 10 (a) adding an extraction solvent to the aqueous mixture in an extraction zone to form an extract stream and a raffinate stream; wherein the extraction zone comprises at least one extractor; and
- (b) separating the extract stream and a solvent-rich stream in a
15 separation zone to form the high boiling point organic impurities stream.

In another embodiment of this invention, a process to produce a high boiling point organic impurities stream from a purified aqueous mixture is provided. The process comprises:

- 20 (a) adding an extraction solvent to the purified aqueous mixture in an extraction zone to form an extract stream and a raffinate stream; wherein the extraction zone comprises at least one extractor; and

- (b) separating the extract stream and a solvent-rich stream in a separation zone to form the high boiling point organic impurities stream.

These objects, and other objects, will become more apparent to others with ordinary skill in the art after reading this disclosure.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 illustrates different embodiments of the invention wherein a process to recover a metal catalyst and remove impurities from an oxidizer purge stream **301** and a process to produce a high temperature molten dispersion **345** are provided.

Figure 2 illustrates different embodiments of the invention wherein a process to produce a high boiling point organic impurities stream **315** from an aqueous mixture **351** or a purified aqueous **308** mixture is provided.

DESCRIPTION OF THE INVENTION:

In one embodiment of this invention, a process to recover a metal catalyst and remove impurities from an oxidizer purge stream **301** is provided as shown in Figure 1. The process comprises the following steps.

Step (a) comprises subjecting an oxidizer purge stream **301** comprising a carboxylic acid, a metal catalyst, impurities, water and a

solvent to evaporation in a first evaporator zone **321** to produce a vapor stream **304** and a concentrated purge slurry **305**.

The oxidizer purge stream **301** is withdrawn from a carboxylic acid oxidative synthesis process. The oxidizer purge stream **301** serves as the
5 feed stream to the present process. The oxidizer purge stream **301** comprises carboxylic acid, water, a solvent, the metal catalyst and impurities. The impurities comprise organic bromides and corrosion metals. The organic bromides are used as promoters in the oxidation reaction. Examples of corrosion metals are iron and chromium compounds, which
10 inhibit, reduce or entirely destroy the activity of the metal catalyst.

Carboxylic acids include aromatic carboxylic acids produced via controlled oxidation of an organic substrate. Such aromatic carboxylic acids include compounds with at least one carboxylic acid group attached to a carbon atom that is part of an aromatic ring, preferably having at least 6
15 carbon atoms, even more preferably having only carbon atoms. Suitable examples of such aromatic rings include, but are not limited to, benzene, biphenyl, terphenyl, naphthalene, and other carbon-based fused aromatic rings. Examples of suitable carboxylic acids include, but are not limited to, terephthalic acid, benzoic acid, p-toluic, isophthalic acid, trimellitic acid,
20 naphthalene dicarboxylic acid, and 2,5-diphenyl-terephthalic acid.

Suitable solvents include, but are not limited to, aliphatic mono-carboxylic acids, preferably containing 2 to 6 carbon atoms, or benzoic acid and mixtures thereof and mixtures of these compounds with water.

Preferably the solvent is acetic acid mixed with water, in a ratio of about 5:1 to about 25:1, preferably between about 8:1 and about 20:1. Throughout the specification acetic acid will be referred to as the solvent. However, it should be appreciated that other suitable solvents, such as those disclosed
5 previously, may also be utilized.

In step (a) of the present process, the oxidizer purge stream **301** is concentrated by conventional means in a first evaporator zone **321** comprising an evaporator to produce a vapor stream **304** and a concentrated purge slurry **305**. In an embodiment of the invention, the
10 evaporator is operated at atmospheric or slightly superatmospheric conditions, generally from about 1 atmosphere to about 10 atmospheres. The vapor stream **304** comprises a majority of the water and solvent, and the concentrated purge slurry **305** comprises the remainder of the water and solvent not removed from the oxidizer purge stream **301**. In an
15 embodiment of the invention, the evaporation removes about 50 wt% to about 80 wt% of the solvent and water, typically acetic acid and water, which are present in the oxidizer purge stream **301**.

Step (b) comprises subjecting the concentrated purge slurry **305** to evaporation in a second evaporator zone **350** to produce a solvent rich
20 stream **344** and a high temperature molten dispersion **345**; wherein about 95 wt% to about 99 wt% of the solvent and water is removed from the oxidizer purge stream **301** in step (a) and step (b) combined; and wherein

the second evaporator zone **350** comprises an evaporator operated at a temperature of about 150°C to about 200°C.

The concentrated purge slurry **305** is introduced in the second evaporator zone **350**, which comprises at least one evaporator. In an embodiment of the invention, the evaporator is operated at super
5 atmospheric or pressurized conditions, generally from about 1 atmosphere to about 10 atmospheres. The evaporation is conducted at a temperature from about 150°C to about 220°C; another range is from about 180°C to about 200°C. In an embodiment of the invention the combination of
10 evaporators **321** and **350** are operated so as to concentrate the oxidizer purge stream **301** as represented by stream **301** to a condition wherein 95-99 wt% of the solvent, typically acetic acid and water, is removed from the oxidizer purge stream **301**.

In an embodiment of the present invention the condition of the high
15 temperature molten dispersion **345** has only enough remaining solvent to provide pumpability. In one embodiment, a typical composition of the the high temperature molten dispersion **345** is shown in Table 1. Generally, the mass composition of the sum total of all compounds shown in Table 1, excluding water and acetic acid, in the high temperature molten dispersion
20 **345** can vary between about 5 wt% to about 80 wt% based on the total weight of the high temperature molten dispersion **345**. Another range for the sum total of all compounds shown in Table 1, excluding acetic acid and water, in the high temperature molten dispersion **345** can be all

combinations of upper and lower ranges where the lower ranges are 5 wt%, 10 wt%, 15 wt%, 20 wt%, 25 wt%, 30 wt%, 35 wt%, 40 wt% and the upper ranges are 80 wt%, 75 wt%, 70 wt%, 65 wt%, 60 wt%, 55 wt%, 50 wt%, 45 wt% based on the total weight of the high temperature molten dispersion

5 **345**. Further, ranges stated in this disclosure and the claims that follow should be understood to disclose the entire range specifically and not just the end point(s). For example, disclosure of the range 0 to 10 should be taken to specifically disclose 2, 2.5, 3.17 and all other number subsumed and not just 0 and 10.

10 Step (c) comprises mixing in a mixing zone **348** a wash solution **306** with the high temperature molten dispersion **345** to form an aqueous mixture **307**.

 The high temperature molten dispersion **345** is then subjected to extraction of the metal catalyst in the mixing zone **348** by introduction of a
15 wash solution **306** which can contain water or a water-acetic acid or a wash solution to form an aqueous mixture in stream **307** wherein at least 80% of the metal catalyst is recovered in the aqueous phase of the aqueous mixture **307**. Typically, at least 90% of the metal catalyst is recovered in the aqueous phase of the aqueous mixture **307**. The wash solution
20 comprises water and optionally an additional solvent. The solvent can be any substance capable of dissolving the metal catalyst to form a uniformly dispersed solution at the molecular or ionic size level. Typically, the solvent

comprises acetic acid, but solvents that have been previously mentioned in step (a) can also be utilized.

The mixing zone **348** comprises a vessel and/or a device or a plurality of vessels or devices wherein there is sufficient residence time for the metal catalyst and/or halogen compounds, such as for example bromine, to dissolve into solution. Examples of such vessels are devices include, but are not limited to, a tank and a stirred or agitated tank. In this step, it is not necessary to completely dissolve the mixture. One method is to utilize only the necessary amount of water to obtain the level of the metal catalyst recovery desired. However, the addition of wash solution **306** also serves to quench the mixture to a temperature in the range of about 60°C to about 95°C, another range is about 80°C to about 90°C. In an embodiment of the invention the quenching is done for about 0.5 to about 4 hours, another range is about 1 to about 2 hours. By this treatment organic bromides are reacted to yield inorganic bromides that are for example, preferentially retained in the aqueous fraction exiting an extractor. The quantity of bromine-containing compounds purged from the system along with the unwanted impurities is thereby minimized. The heat treatment conserves bromides and simplifies disposal of the organic impurities.

The addition of wash solution **306** in the mixing zone **348** not only recovers the metal catalyst in the high temperature molten dispersion **345**, but also aids in pumping the aqueous mixture **307**. It is desirable to keep the aqueous mixture **307** circulating with an external circulation loop.

In one embodiment, a typical composition of the aqueous mixture is shown in Table 1. Generally, the mass composition of the aqueous mixture **307** in this embodiment generally can vary wherein the mass ratio of water to acetic acid is in the range of about 1:1 to 99:1 and wherein the sum
5 aggregate of isophthalic acid, benzoic acid, 4-carboxybenzaldehyde, and terephthalic acid comprises between about 1000 ppm to about 65 wt% of the total weight of the aqueous mixture **307**. Another range can be all combinations of upper and lower ranges wherein the sum aggregate of isophthalic acid, benzoic acid, 4-carboxybenzaldehyde, and terephthalic
10 have a lower range of 5 wt%, 10 wt%, 15 wt%, 20 wt%, 25 wt%, 30 wt%, 35 wt%, 40 wt% and an upper range of 65 wt%, 60 wt%, 55 wt%, 50 wt%, 45 wt% based on the total weight of the aqueous mixture **307**.

When separating in the solid-liquid separation zone **351** is performed, a small amount of extraction solvent in conduit **311**, generally
15 about 1 to about 10% by weight, preferably about 5% by weight, may be added to the mixing zone **348** to enhance slurry handling by reducing adherence of solids to the side of, for example, a slurry feed tank. This is represented by the dashed arrow from stream **311** in Figure 1.

Step (d) comprises optionally separating organic impurities **312** from
20 the aqueous mixture **307** in a solid-liquid separation zone **351** to form a purified aqueous mixture **308**.

The aqueous mixture stream **307** can be optionally fed to a solid-liquid separation zone **351** comprising a solid-liquid apparatus, wherein

organic impurities **312** may be removed from the aqueous mixture **307** to form a purified aqueous mixture **308** and organic impurities **312**. There are no limitations on the type of solid-liquid separation apparatus as long as it is sufficient to remove organic impurities **312** from the aqueous mixture **307**.

- 5 Examples of such apparatuses include, but are not limited to, filters, centrifuges, cyclones, hydroclones, etc.

The organic impurities can comprise numerous compounds typically associated with TPA production. Examples of typical organic impurities include, but are not limited to, isophthalic acid, trimellitic acid, benzoic acid, phthalic acid, fluorenone compounds, p-toluic acid, and 4-
10 carboxybenzaldehyde.

In one embodiment, a typical composition of the purified aqueous mixture **308** is shown in Table 1. The mass composition of the purified aqueous mixture **308** in this embodiment comprises acetic acid, water, isophthalic acid, benzoic acid, 4-carboxybenzaldehyde, terephthalic acid, and cobalt; wherein the sum aggregate of the isophthalic acid, benzoic acid, 4-carboxybenzaldehyde, and terephthalic acid comprise between about 1
15 wt% to 70% based on the total weight of the purified aqueous mixture **308**; wherein the sum aggregate of isophthalic acid and terephthalic acid
20 comprise no more than 10 wt% of the purified aqueous mixture **308**.

Another range can be all combinations of upper and lower ranges wherein the sum aggregate of isophthalic acid, benzoic acid, 4-carboxybenzaldehyde, and terephthalic have a lower range of 5 wt%, 10

wt%, 15 wt%, 20 wt%, 25 wt%, 30 wt%, 35 wt%, 40 wt% based on the total weight of the purified aqueous mixture **308** and a upper range of 65 wt%, 60 wt%, 55 wt%, 50 wt%, 45 wt% based on the total weight of the purified aqueous mixture **308**; and wherein the sum aggregate of isophthalic acid and terephthalic acid comprise no more than 10 wt% based on the total weight of the purified aqueous mixture **308**.

As previously stated when the solid-liquid separation zone **351** is utilized, a small amount of extraction solvent in conduit **311**, generally about 1 to about 10% by weight, preferably about 5% by weight may be added to the mixing zone **348** to enhance slurry handling by reducing adherence of solids to the side of, for example, a slurry feed tank. This is represented by the dashed arrow from stream **311** in Figure 1.

Step (e) comprises adding an extraction solvent **311** to the aqueous mixture **307** or the purified aqueous mixture **308** in an extraction zone **323** to form an extract stream **309** and the raffinate stream **310**.

The aqueous mixture **307** or the purified aqueous mixture **308** is fed to an extraction zone **323** wherein the aqueous mixture **307** or the purified aqueous mixture **308** and the extraction solvent **311** are contacted in the extraction zone **323**. The aqueous mixture **307** or the purified aqueous mixture **308** and the extraction solvent **311** are mixed to form an extract stream **309** comprising solvent, water organic impurities, and organic solvent which forms a lighter phase, and the raffinate stream **310** comprising a metal catalyst, corrosion metals, and water. The extract

stream 309 is withdrawn as an overhead stream, and the raffinate stream 310 is withdrawn from the bottom of extractor in the extraction zone 323. In this invention, one embodiment of the extraction zone 323 is a single stage extractor.

5 The extraction solvent 311 used in the extractor should be substantially water-insoluble to minimize the amount of organic solvent dissolved in the aqueous fraction. Additionally, the extraction solvent 311 is preferably an azeotropic agent which serves to assist solvent recovery from the organic extract. Solvents, which have proven to be particularly useful
10 are C1 to C6 alkyl acetates, particularly n-propyl acetate (n-PA), isopropyl acetate, isobutyl acetate, sec-butyl acetate, ethyl acetate and n-butyl acetate, although other water-insoluble organic solvents having an appropriate density and a sufficiently low boiling point may also be used, such as p-xylene. N-propyl acetate and isopropyl acetate are particularly
15 preferred due to their relatively low water solubility, excellent azeotropic behavior, and their ability to remove the remaining acetic acid as well as high-boiling organic impurities from the aqueous mixture.

 The extraction can be effected using extraction solvent ratios from about 1 to about 4 parts by weight extraction solvent per part of extractor
20 feed depending on the extractor feed composition. Space velocities of the combined feeds to the extractor generally range from about 1 to about 3 hr⁻¹. Although the extraction can be conducted at ambient temperature and pressure, heating the extraction solvent 311 and extractor to about

30° to about 70° C. Another range of about 40° C to about 60° C can be used. Although the extract stream **309** comprises small amounts of the metal catalyst and corrosion metals, essentially all of the metal catalyst and the majority of the remaining corrosion metals are contained in the heavier
5 phase, the raffinate stream **310**:

Step (f) comprises separating the extract stream **309** and the solvent rich stream **344** in a separation zone **324** to form a high boiling point organic impurities stream **315**.

The extract stream **309** comprises organic solvent and organic
10 impurities. The extract stream **309** can further comprises acetic acid and water, often in minor amounts. The extract stream **309** may be distilled in a separation zone comprising conventional distillation equipment. The distillation equipment is operated at process conditions sufficient to recover a majority of the extraction solvent, typically n-propyl acetate, from the
15 extract stream **309**. Conventional distillation equipment includes, for example, a distillation column. One key feature to this invention is the use of the solvent rich stream **344** into the separation zone **324**.

Most of the organic impurities are extracted by the organic solvent in the extraction zone **323**. This occurs because the organic impurities show
20 a high degree of solubility for the organic solvent and to a lesser extent for acetic acid. By distilling the lighter phase from the extractor, the organic solvent is evaporated allowing the organic impurities to concentrate in the column underflow. This results in a high probability for plugging and

precipitation of solids. By utilizing the solvent rich stream **344**, the organic impurities in the column underflow can be effectively diluted and thereby solubilized by acetic acid in the column underflow.

The use of the solvent rich stream **344**, from the previous
5 evaporation serves two functions. First, the loss of the organic solvent is minimized since the solvent rich stream **344** effectively displaces the organic solvent in the column underflow. Second, the use of acetic-acid rich vapor provides significant enthalpy needed for driving the distillation/separation process.

10 The separation zone **324** will need to process significantly less hydraulic load than a typical purge process due to the greater concentration of mother liquor. Recovered extraction solvent and acetic acid may be recycled to the extractor and oxidative reactor, respectively. The high-boiling point organic impurities are removed as sludge from the base of the
15 distillation column for disposal.

Although the composition of the various streams in the process varies depending on the process conditions, a typical composition of the streams are shown in Table 1. In Table 1, the components are shown in the left hand column and the amount of these components in each stream
20 in the Figure 1 are shown in the number column corresponding to the number of the stream in Figure 1. The amounts of the components shown in Table 1 can be any measurement of weight as long as it is consistent for

all components and all streams. For example, the oxidizer purge stream 301 has acetic acid in the amount of 915 pounds, 915 grams, etc.

Table 1. Material Balance

	Process Material Balance											
	Stream in Figure 1											
	301	304	305	344	345	306	307	308	309	310	311	312
Acetic Acid	915.0	534.1	380.9	335.2	45.8	-	45.8	45.3	44.1	1.2	-	0.4
Water	55.0	39.3	15.7	14.7	1.0	80.0	81.0	80.2	35.6	44.5	-	0.7
n-Propyl Acetate	-	-	-	-	-	-	-	-	399.0	1.0	400.0	-
Terephthalic Acid	0.71	-	0.71	-	0.71	-	0.71	0.70	0.70	-	-	-
Isophthalic Acid	5.83	-	5.83	-	5.83	-	5.83	5.78	5.71	0.07	-	0.05
Phthalic Acid	3.81	-	3.81	0.12	3.69	-	3.69	3.66	3.36	0.29	-	0.03
Benzoic Acid	8.12	0.06	8.06	2.27	5.79	-	5.79	5.73	5.73	-	-	0.05
4-Carboxybenzaldehyde	1.56	-	1.56	-	1.56	-	1.56	1.54	1.52	0.02	-	0.01
Trimellitic Acid	1.17	-	1.17	-	1.17	-	1.17	1.16	1.01	0.14	-	0.01
Paratoluic Acid	2.96	0.01	2.95	0.50	2.44	-	2.44	2.42	2.39	0.03	-	0.02
Paratolualdehyde	0.51	0.05	0.46	0.26	0.20	-	0.20	0.20	0.20	-	-	-
Others	2.50	-	2.50	-	2.50	-	2.50	2.38	2.14	0.24	-	0.13
Organic Bromide	1.30	-	1.30	-	1.30	-	0.90	0.86	-	0.85	-	0.05
Ionic Bromide	0.34	-	0.34	-	0.34	-	0.74	0.70	-	0.70	-	0.04
Cobalt	1.44	-	1.44	-	1.44	-	1.44	1.37	0.01	1.35	-	0.07
Manganese	0.10	-	0.10	-	0.10	-	0.10	0.10	-	0.09	-	-
Corrosion Metals	0.08	-	0.08	-	0.08	-	0.08	0.08	-	0.08	-	-
Total	1000	573	427	353	74	80	154	152	502	51	400	2

WE CLAIM:

1. A process to produce a high boiling point organic impurities stream from an aqueous mixture said process comprising :
 - (a) adding an extraction solvent to said aqueous mixture in an extraction zone to form an extract stream and a raffinate stream; wherein said extraction zone comprises at least one extractor; and
 - (b) separating said extract stream and a solvent-rich stream in a separation zone to form said high boiling point organic impurities stream.
2. The process according to claim 1 wherein said extractor is a single stage extractor.
3. A process according to claim 1 wherein said solvent rich stream comprises a solvent selected from the group consisting of n-propyl acetate, isopropyl acetate, isobutyl acetate, sec-butyl acetate, ethyl acetate and n-butyl acetate.
4. The process according to claim 1 wherein said extractor is operated at a temperature of about 40°C to about 60°C.
5. The process according to claim 2 wherein said extractor is operated at a temperature of about 40°C to about 60°C.
6. The process according to claim 3 wherein said extractor is a single stage extractor.

7. The process according to claim 1 wherein said extractor is a counter current extractor.
8. The process according to claim 7 wherein said solvent rich stream comprises a solvent selected from the group consisting of n-propyl acetate, isopropyl acetate, isobutyl acetate, sec-butyl acetate, ethyl acetate and n-butyl acetate.
9. The process according to claim 4 wherein said solvent rich stream comprises a solvent selected from the group consisting of n-propyl acetate, isopropyl acetate, isobutyl acetate, sec-butyl acetate, ethyl acetate and n-butyl acetate.
10. A process to produce a high boiling point organic impurities stream from a purified aqueous mixture said process comprising:
 - (a) adding an extraction solvent to said purified aqueous mixture in an extraction zone to form an extract stream and a raffinate stream; wherein said extraction zone comprises at least one extractor; and
 - (b) separating said extract stream and a solvent-rich stream in a separation zone to form said high boiling point organic impurities stream.
11. The process according to claim 10 wherein said extractor is a single stage extractor.
12. A process according to claim 10 wherein said solvent rich stream comprises a solvent selected from the group consisting of n-propyl acetate,

isopropyl acetate, isobutyl acetate, sec-butyl acetate, ethyl acetate and n-butyl acetate.

13. The process according to claim 10 wherein said extractor is operated at a temperature of about 40°C to about 60°C.

14. The process according to claim 11 wherein said extractor is operated at a temperature of about 40°C to about 60°C.

15. The process according to claim 12 wherein said extractor is a single stage extractor.

16. The process according to claim 10 wherein said extractor is a counter current extractor.

17. The process according to claim 16 wherein said solvent rich stream comprises a solvent selected from the group consisting of n-propyl acetate, isopropyl acetate, isobutyl acetate, sec-butyl acetate, ethyl acetate and n-butyl acetate.

18. The process according to claim 13 wherein said solvent rich stream comprises a solvent selected from the group consisting of n-propyl acetate, isopropyl acetate, isobutyl acetate, sec-butyl acetate, ethyl acetate and n-butyl acetate.

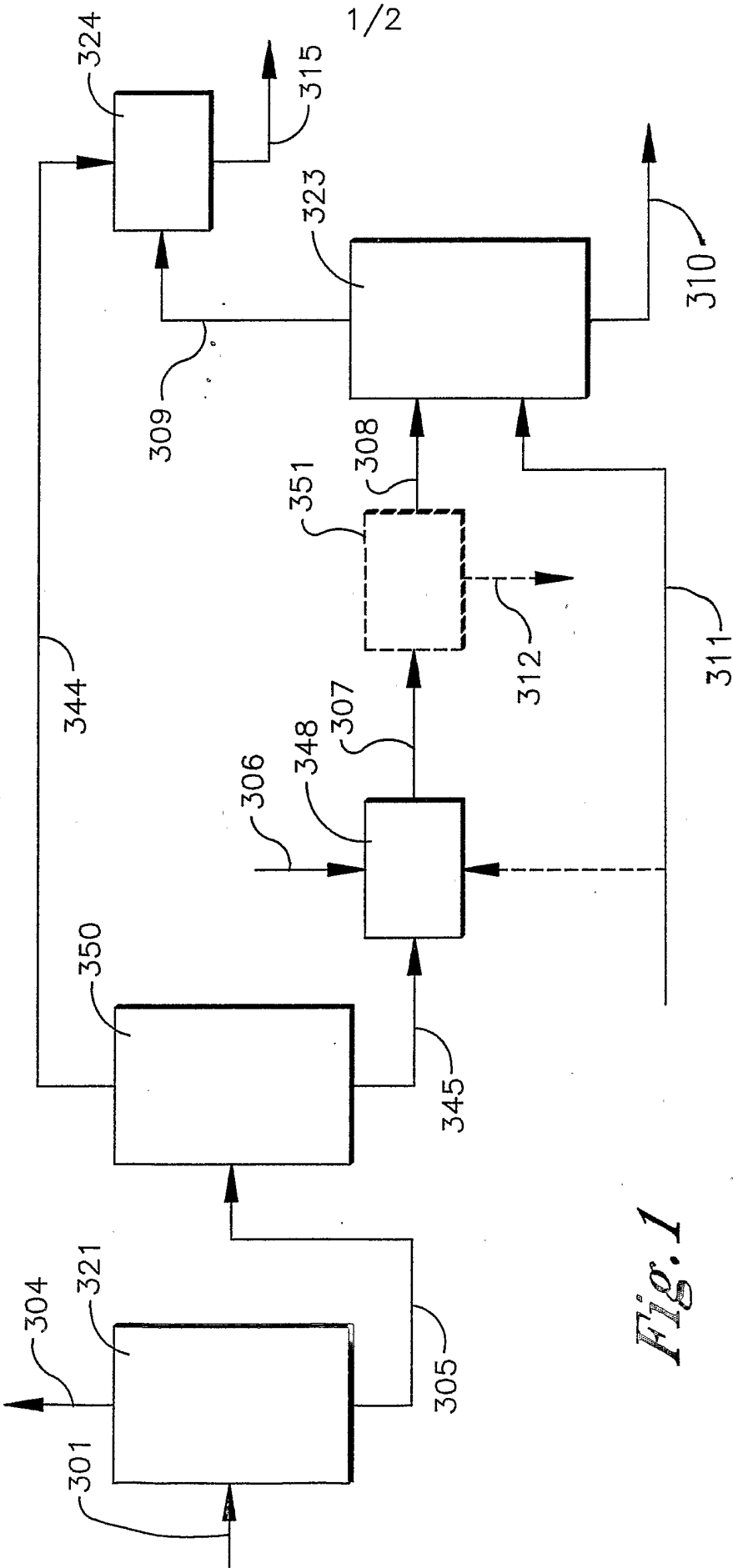


Fig. 1

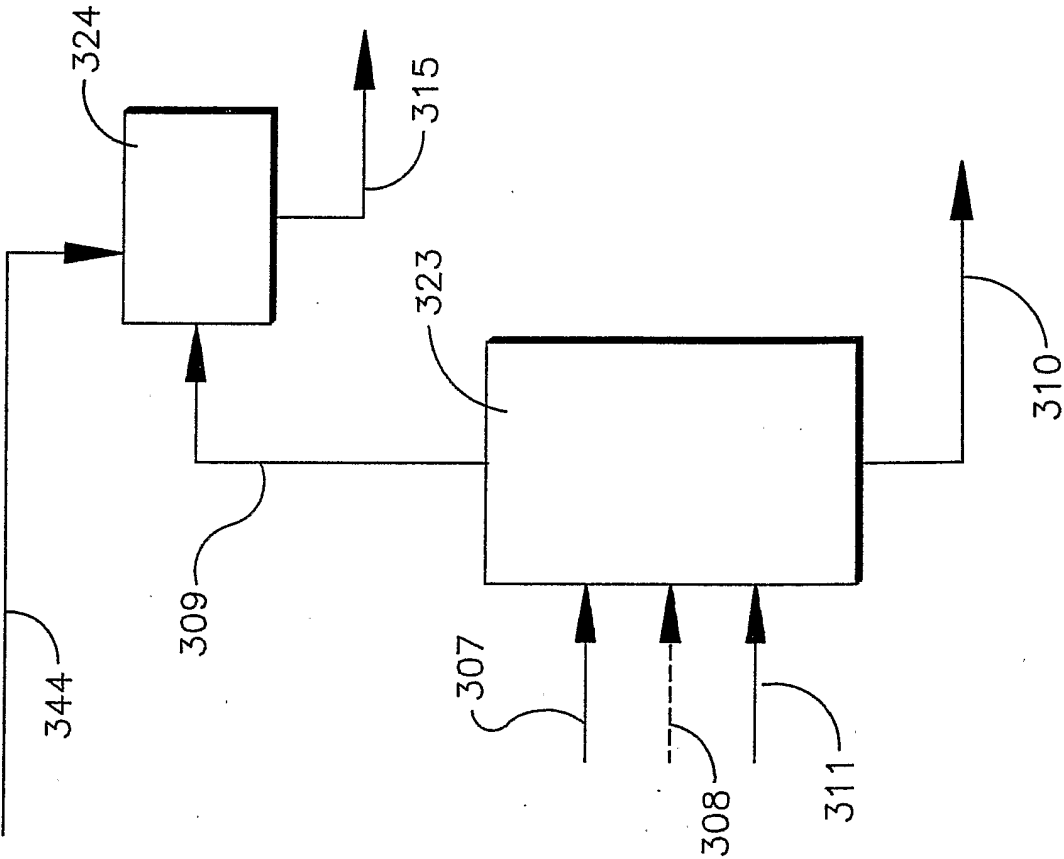


Fig. 2

INTERNATIONAL SEARCH REPORT

Application No

PCT/US2004/039839

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C07C51/42 C07C51/47 C07C51/48 C07C63/26

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)

IPC 7 C07C

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

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

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 939 297 A (BROWDER ET AL) 3 July 1990 (1990-07-03) column 3, line 24 - column 6, line 36	1-18
X	US 4 356 319 A (ROFFIA ET AL) 26 October 1982 (1982-10-26) column 1, line 45 - column 3, line 27; claims 1-3; examples 1A, 4A, 5A, 6, 7	1-18
X	EP 0 764 627 A (MITSUBISHI GAS CHEMICAL COMPANY, INC; TOYO BOSEKI KABUSHIKI KAISHA; MI) 26 March 1997 (1997-03-26) page 4, line 46 - page 5, line 14; examples 1, 2	1-9
E	EP 1 484 305 A (EASTMAN CHEMICAL COMPANY) 8 December 2004 (2004-12-08) the whole document	1-18

-/--

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in 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 document 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

9 June 2005

Date of mailing of the international search report

21/06/2005

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Cooper, S

INTERNATIONAL SEARCH REPORT

Application No
PCT/US2004/039839

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
E	EP 1 484 306 A (EASTMAN CHEMICAL COMPANY) 8 December 2004 (2004-12-08) the whole document -----	1-18

INTERNATIONAL SEARCH REPORT

Application No

PCT/US2004/039839

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 4939297	A	03-07-1990	CA 2042409 A1	06-12-1990
			DE 69010904 D1	25-08-1994
			DE 69010904 T2	16-03-1995
			DK 476009 T3	05-09-1994
			EP 0476009 A1	25-03-1992
			ES 2056469 T3	01-10-1994
			JP 2886685 B2	26-04-1999
			JP 4505620 T	01-10-1992
			KR 152534 B1	15-10-1998
			WO 9015046 A1	13-12-1990
US 4356319	A	26-10-1982	IT 1129759 B	11-06-1986
			BE 887212 A1	23-07-1981
			BR 8100324 A	11-08-1981
			CA 1152481 A1	23-08-1983
			DE 3101672 A1	26-11-1981
			ES 8203323 A1	01-07-1982
			FR 2473903 A1	24-07-1981
			GB 2067563 A ,B	30-07-1981
			JP 56113346 A	07-09-1981
			NL 8100192 A	17-08-1981
			SU 1194260 A3	23-11-1985
EP 0764627	A	26-03-1997	JP 9087230 A	31-03-1997
			CN 1149574 A ,C	14-05-1997
			EP 0764627 A1	26-03-1997
			US 5705682 A	06-01-1998
EP 1484305	A	08-12-2004	US 2004249207 A1	09-12-2004
			CA 2467002 A1	05-12-2004
			CN 1572764 A	02-02-2005
			EP 1484305 A1	08-12-2004
			JP 2004359691 A	24-12-2004
			US 2005038288 A1	17-02-2005
EP 1484306	A	08-12-2004	US 2004249208 A1	09-12-2004
			BR 0401876 A	04-01-2005
			CA 2467001 A1	05-12-2004
			CN 1572767 A	02-02-2005
			EP 1484306 A1	08-12-2004
			JP 2004358465 A	24-12-2004
			US 2005084432 A1	21-04-2005