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(54) Title: METHODS OF RECOVERING CATALYSTS

(57) Abstract: Disclosed herein are methods of separating a catalyst from a product mixture. Methods of recovering a catalyst from an epoxidized vegetable oil product mixture are further disclosed.

TITLE

METHODS OF RECOVERING CATALYSTS

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims priority to the U.S. Provisional Patent Application No. 62/281,440, filed January 21, 2016, the contents of the entirety of which are incorporated by this reference.

TECHNICAL FIELD

[0002] The present invention relates generally to catalysts. The present disclosure is further directed to methods of separating a catalyst from a product mixture. The present disclosure is also directed to methods of recovering a catalyst from an epoxidized vegetable oil product mixture.

BACKGROUND OF THE INVENTION

[0003] Methods of epoxidation of vegetable oils are well known. For example, US Patent Application US 2006/0020062 A1 to Bloom discloses that epoxidation of soybean and linseed oils is well known in the art, is performed on a commercial scale, and commonly is achieved by using a strong catalyst, oxidant, and carboxylic acid.[1]

Epoxidized vegetable oils have a wide range of utility, including uses as plasticizers and stabilizers in certain polymers.[2]

[0004] Heterogeneous systems for epoxidation are well known. For example, "Metal-catalyzed Epoxidations of Alkenes with Hydrogen Peroxide" discloses several typical heterogeneous systems, such as mineral-type catalysts including zeolites and hydrotalcites.[3] Additionally, heterogeneous systems may be constructed by attaching homogeneous catalysts to solid supports.[4] While heterogeneous systems have the advantage of easy catalyst recovery, these systems suffer from drawbacks such as limitations in the kinds of epoxides which can be produced and reduced activity relative to homogeneous catalysts.[5]

[0005] Homogeneous systems for epoxidation are also well known. For example, "Metal-catalyzed Epoxidations of Alkenes with Hydrogen Peroxide" discloses several kinds of soluble metal oxides, including the Venturello epoxidation catalyst and the Noyori epoxidation system.[6] The epoxidation of oils catalyzed by organometallic compounds is advantageous, for example being environmentally benign and efficient in both activity and selectivity.[7] However, concerns with tungsten-based systems include cost and product-impurities.[8] Additionally, catalyst recovery is more difficult relative to heterogeneous systems for epoxidation.

[0006] Overall, it would be especially advantageous to develop methods for recovering catalysts used in homogeneous systems for epoxidation.

SUMMARY OF THE INVENTION

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[2] US 2006/0020062 A1, paragraph [0005].
[3] Lane, Benjamin; Burgess, Kevin. Metal-Catalyzed Epoxidations of Alkenes with Hydrogen Peroxide. *Chem. Rev.* **2003**, *103* (7), 2458.
[4] Lane, Benjamin; Burgess, Kevin. Metal-Catalyzed Epoxidations of Alkenes with Hydrogen Peroxide. *Chem. Rev.* **2003**, *103* (7), 2459.
[5] Lane, Benjamin; Burgess, Kevin. Metal-Catalyzed Epoxidations of Alkenes with Hydrogen Peroxide. *Chem. Rev.* **2003**, *103* (7), 2458-59. ,
[6] Lane, Benjamin; Burgess, Kevin. Metal-Catalyzed Epoxidations of Alkenes with Hydrogen Peroxide. *Chem. Rev.* **2003**, *103* (7), 2459-60.
[7] Jiang, Pingping; Chen, Min; Dong, Yuming; Lu, Yun; Ye, Xia; Zhang, Weije. Novel Two-Phase Catalysis with Organometallic Compounds for Epoxidation of Vegetable Oils by Hydrogen Peroxide. J. Am. Oil Chem. Soc. **2010**, *87*, 90.
[8] Lane, Benjamin; Burgess, Kevin. Metal-Catalyzed Epoxidations of Alkenes with Hydrogen Peroxide. *Chem. Rev.* **2003**, *103* (7), 2460.

[0007] The present invention relates in one aspect to a method of separating a catalyst from a product mixture comprising diluting the product mixture with a solvent, passing the diluted product mixture through a first ion exchange resin column, and passing the diluted product mixture through a second ion exchange resin column, thus retaining the catalyst in either the first ion exchange resin column, the second ion exchange resin column, or combinations of any thereof.

[0008] The present invention relates in another aspect to a method of separating a catalyst from a product mixture comprising diluting the product mixture with a solvent, contacting the diluted product mixture with a first ion exchange resin, and contacting the diluted product mixture with a second ion exchange resin, thus retaining the catalyst in either the first ion exchange resin, the second ion exchange resin, or combinations of any thereof.

[0009] The present invention relates in yet another aspect to a method of recovering a catalyst from an epoxidized vegetable oil product mixture comprising diluting the epoxidized vegetable oil product mixture with an organic solvent, wherein the epoxidized vegetable oil product mixture comprises the catalyst, eluting the diluted epoxidized vegetable oil product mixture through a double bed resin column, wherein the double bed resin column is packed with an anion exchange resin and a cation exchange resin, and eluting a base through the double bed resin column, thus collecting the catalyst.

BRIEF DESCRIPTION OF THE DRAWINGS

[0010] Figure 1 shows a scheme for catalyst retention and recovery using a cation exchange resin followed by an anion exchange resin.

[0011] Figure 2 shows a scheme for catalyst retention and recovery using an anion exchange resin followed by a cation exchange resin.

[0012] Figure 3 shows a scheme for retention and removal of a catalyst using a single bed resin column.

[0013] Figure 4 shows results for catalyst separation using cation exchange resin followed by anion exchange resin in a mixed bed resin system, wherein the cation exchange resin is packed on top of the anion exchange resin within a single column.

[0014] Figure 5 shows results for catalyst separation using cation exchange resin followed by anion exchange resin in a single bed resin system.

[0015] Figure 6 shows a scheme for removal of Venturello catalyst components using anion exchange resin.

[0016] Figure 7 shows a scheme for calculation of catalyst absorbed/retained in resin using gravimetric method/analysis.

[0017] Figure 8 shows a breakthrough curve for absorption/retention of catalyst using Purolite® A111S (-$NR_2H^+Cl^-$ form) anion exchange resin.

[0018] Figure 9 shows results for recovered tungsten from anion exchange resin bed (Purolite® A111S, -$N^+HR_2Cl^-$ form).

[0019] Figure 10 shows results for recovered phosphorous from anion exchange resin bed (Purolite® A111S, -$N^+HR_2Cl^-$ form).

[0020] Figure 11 shows results for recovery of tungsten and phosphorous from anion exchange resin (Purolite® A111S, -$N^+HR_2Cl^-$ form).

[0021] Figure 12 shows results for recovery of tungsten and phosphorous from anion exchange resin (Purolite® A111S, -$N^+HR_2Cl^-$ form).

[0022] Figure 13 shows extent of tungsten and phosphorous recovery from anion exchange resin (Purolite® A111S, -$N^+HR_2Cl^-$ form).

[0023] Figure 14 shows a scheme for conversion of –$N^+HR_2Cl^-$ form resin to –$N^+HR_2OH^-$ form resin.

[0024] Figure 15 shows an exemplary resin bed set-up.

[0025] Figure 16 shows additional views of an exemplary resin bed set-up.

[0026] Figure 17 shows an additional view of an exemplary resin bed set-up.

[0027] Figure 18 shows an additional view of an exemplary resin bed set-up.

[0028] Figure 19 shows results of a calibration of flow rate using a Masterflex L/S pump.

[0029] Figure 20 shows results of a calibration of flow rate using a Masterflex L/S pump.

DETAILED DESCRIPTION OF ILLUSTRATIVE EMBODIMENTS OF THE INVENTION

[0030] In an illustrative embodiment, a method of the present invention includes separating a catalyst from a product mixture comprising diluting the product mixture with a solvent, passing the diluted product mixture through a first ion exchange resin column, and passing the diluted product mixture through a second ion exchange resin column, thus retaining the catalyst in either the first ion exchange resin column, the second ion exchange resin column, or combinations of any thereof.

[0031] In another illustrative embodiment, a method of the present invention includes separating a catalyst from a product mixture comprising diluting the product mixture with a solvent, contacting the diluted product mixture with a first ion exchange resin, and contacting the diluted product mixture with a second ion exchange resin, thus retaining the catalyst in either the first ion exchange resin, the second ion exchange resin, or combinations of any thereof.

[0032] In yet another illustrative embodiment, a method of the present invention includes recovering a catalyst from an epoxidized vegetable oil product mixture comprising diluting the epoxidized vegetable oil product mixture with an organic solvent, wherein the epoxidized vegetable oil product mixture comprises the catalyst, eluting the diluted epoxidized vegetable oil product mixture through a double bed resin column, wherein the double bed resin column is packed with an anion exchange resin and a cation exchange resin, and eluting a base through the double bed resin column, thus collecting the catalyst.

[0033] In a further embodiment, the product mixture comprises an epoxidized vegetable oil. In one embodiment, the product mixture consists of a substance selected from the group consisting of an epoxidized vegetable oil, a catalyst, and combinations of any thereof.

[0034] The present invention contemplates many catalysts, including a catalyst comprising tungsten and phosphorous, as well as a catalyst comprising a Venturello catalyst.

[0035] The present invention contemplates many solvents, including an organic solvent, as well as a solvent selected from the group consisting of ethanol, toluene, and combinations of any thereof. In one embodiment, the solvent is combined with the product mixture in a ratio of 3:1 volume/volume.

[0036] In a further embodiment, the first ion exchange resin column is a cation exchange resin column and the second ion exchange resin column is an anion exchange resin column.

[0037] In a further embodiment, the first ion exchange resin is an anion exchange resin and the second ion exchange resin is a cation exchange resin.

[0038] In a further embodiment, the first ion exchange resin is a cation exchange resin and the second ion exchange resin is an anion exchange resin.

[0039] In one embodiment, the anion exchange resin comprises an $N^{+}R_2HCl^{-}$ group. In another embodiment, the anion exchange resin comprises Lewatit® S 4528 resin.

[0040] In one embodiment, the cation exchange resin comprises Lewatit® TP 207 resin.

[0041] In a further embodiment, the contacting the diluted product with the first ion exchange resin is achieved by a method selected from the group consisting of shaking the first ion exchange resin with the diluted product mixture, stirring the first ion exchange resin with the diluted product mixture, and passing the diluted product mixture through a column packed with the first ion exchange resin.

[0042] In a further embodiment, the contacting the diluted product mixture with the second ion exchange resin is achieved by a method selected from the group consisting on shaking the second ion exchange resin with the dilute product mixture, stirring the second ion exchange resin with the diluted product mixture, and passing the diluted product mixture through a column packed with the second ion exchange resin.

[0043] In a further embodiment, the passing the diluted product mixture through a column packed with the first ion exchange resin and the passing the diluted product mixture through a column packed with the second ion exchange resin is at a rate of from about 2 bed volumes (BV)/hour to about 4 bed volumes (BV)/hour.

[0044] In a further embodiment, the first ion exchange resin and the second ion exchange resin are contained in two, successive single bed resin columns.

[0045] In a further embodiment, the first ion exchange resin and the second ion exchange resin are contained in a double bed resin column.

[0046] In a further embodiment, the catalyst is recovered from the first ion exchange resin, the second ion exchange resin, or combinations of any thereof. In one

embodiment, the recovering the catalyst from the first ion exchange resin, the second ion exchange resin, or combinations of any thereof comprises contacting the first ion exchange resin, the second ion exchange resin, or combinations of any thereof with a base.

[0047] The present invention contemplates many bases, including a base selected from the group consisting of sodium hydroxide, ammonium hydroxide, sodium bicarbonate, ammonium bicarbonate, and combinations of any thereof. In one embodiment, the base has a concentration of at least 1 Normal. In another embodiment, the base has a concentration of between about 1 Normal and about 8 Normal.

[0048] In a further embodiment, the first ion exchange resin and the second ion exchange resin are present in equal amounts. In one embodiment, the first ion exchange resin and the second ion exchange resin ranges from a total combined weight of about 4 grams to about 80 grams.

[0049] In a further embodiment, the anion exchange resin is packed on top of the cation exchange resin.

[0050] In a further embodiment, the anion exchange resin and the cation exchange resin are present in equal amounts. In one embodiment, the anion exchange resin and the cation exchange resin are present in a total amount of from about 4 grams to about 80 grams.

[0051] Referring now to the drawings, various schema are provided for carrying out the above illustrative embodiments. Thus, in Figure 1, a general scheme for catalyst retention and recovery using a cation exchange resin followed by an anion exchange resin is shown. The Venturello catalyst can be viewed as a salt of an anion (of a soft Lewis base) and a cation (of a soft Lewis acid). The Venturello catalyst is composed of a tri-negatively charged peroxophosphotungsten moiety $[PO_4\{WO(O_2)_2\}_4]^{3-}$ and a mono-positively charged suitable phase transfer cation. In certain preferred embodiments, the phase transfer cation is the methyltrioctylammonium cation $[\{(C_8H_{17})_3N(CH_3)\}^+]$. Therefore, the cation exchange resin may include various functional groups including monocarboxylic acid and iminodiacetic acid as weak acid cations, as well as sulfonic acid and phosphonic acid as strong acid cations. The functional group of the weak anion exchange resin may be a primary, secondary, or tertiary amine group. The resin matrix is preferably composed of styrene divinyl

benzene copolymer. When a pure catalyst solution or an organic phase of an epoxidation reaction mixture comprising soybean oil, soybean oil epoxide, an insignificant amount of by-products (from about 1% to about 3%), and primarily diols and Venturello catalyst is passed through the cation exchange resin first, a proton is exchanged with the phase transfer cation of the catalyst, giving rise to an ester reacting with the acid group. A pronated form of the Venturello catalyst which comes from the cation exchange resin bed is then passed through the anion exchange resin bed where it forms a salt upon reacting with the amine group. (Figure 1, Steps 1 and 2). In certain preferred embodiments, the cation exchange resin comprises a group represented by X in the diagram, wherein X is preferably an anion of acetic acid, iminodiacetic acid, sulfonic acid, or phosphonic acid. In certain preferred embodiments, the anion exchange resin comprises a group represented by R' in the scheme, wherein R' is preferably an H group, a CH_3 group, or a CH_2CH group. In certain preferred embodiments, for catalyst retention, the cation exchange resin comprises Lewatit® TP 207 and the anion exchange resin comprises Lewatit® S 4528. For catalyst recovery, a solution of any organic acid, including CH_3COOH, HCOOH, $(COOH)_2$, $HO_2CCH(OH)CH(OH)CO_2H$, and $pCH_3(C_6H_4)SO_3H$, in a suitable organic solvent, including toluene, heptane, acetonitrile, and ethyl acetate, may be passed through the cation exchange resin to recover the phase transfer reagent, represented as RA in Figure 1. (Figure 1, Step 3). In certain preferred embodiments, RA represents Aliquat® 336 (*N*-methyl-*N*,*N*,*N*-trioctyloctan-1-ammonium chloride) as a salt of an anionic part of the acid used. In certain embodiments, an inorganic acid solution in an organic solvent may be used instead of an organic acid in a suitable organic solvent, with preferred inorganic acids including HCl, HNO_3, H_2SO_4, and H_2SO_3. In certain preferred embodiments, the solvent is ethanol. In order to recover the anionic portion of the Venturello catalyst (the portion containing tungsten and phosphorous), an aqueous solution of a suitable salt is passed through the anion exchange resin. (Figure 1, Step 4). The suitable salt is represented as M'A', wherein M' is preferably K^+, Na^+, NH_4^+, Ca^{2+}, and Mg^{2+} and wherein A' is preferably I^-, Br^-, Cl^-, OH^-, NO_3^-, HCO_3^-, HSO_4^-, and CH_3COO^-. This allows the anionic portion of the Venturello catalyst to be separated as a salt of M' or in an alternative form when the peroxophosphotungsten moiety cannot retain its structural integrity due to the highly basic conditions.

[0052] In Figure 1a, the general scheme for catalyst retention and recovery described above (Figure 1) is modified to show a specified cation exchange resin followed by a specified anion exchange resin. The cation exchange resin used for catalyst retention is Lewatit® TP 207 and the anion exchange resin used for catalyst retention is Lewatit® S 4528.

[0053] In Figure 2, a general scheme for catalyst retention and recovery using an anion exchange resin followed by a cation exchange resin is shown. In certain embodiments, the cation exchange resin used may comprise a quaternary ammonium group. For catalyst retention, the anion exchange resin shown in step 1 may comprise a compound represented by $[N(R')_3]^+Cl^-$, wherein R' preferably represents an H group, a CH_3 group, or a CH_2CH_3 group. For catalyst retention, the cation exchange resin shown in step 2 may comprise a compound represented by XH, wherein X preferably represents an anion of acetic acid, iminodiacetic acid, sulfonic acid, or phosphonic acid. For catalyst recovery shown in step 3, M'A' is used as an eluent in an aqueous solution, wherein M' preferably represents K^+, Na^+, NH_4^+, Ca^{2+}, or Mg^{2+} and A' preferably represents I^-, Br^-, Cl^-, OH^-, NO_3^-, HCO_3^-, HSO_4^-, or CH_3COO^-. For catalyst recovery shown in step 4, HA is used as an acid, wherein HA preferably represents CH_3COOH, HCOOH, $(COOH)_2$, $HO_2CCH(OH)CH(OH)CO_2H$, $pCH_3(C_6H_4)SO_3H$, HCl, HNO_3, H_2SO_4, or H_2SO_3.

[0054] In Figure 2a, the general scheme for catalyst retention and recovery using an anion exchange resin followed by a cation exchange resin described above (Figure 2) is modified to show a specified anion exchange resin followed by a specified cation exchange resin. The anion exchange resin used for catalyst retention is chemically modified Lewatit® S 4528 and the cation exchange resin used for catalyst retention is Lewatit® TP 207.

[0055] In Figure 3, a scheme for retention and removal of a catalyst using a single bed resin column is shown. An anion exchange resin, for example Lewatit® S 4528, comprising an $-NR_2$ group, is modified with HCl, giving an anion exchange resin with an $N^+HR_2Cl^-$ group. A catalyst or a product mixture comprising a catalyst is diluted with toluene or ethanol and passed through the modified anion exchange resin, retaining the catalyst in the anion exchange resin represented as $(-N^+HR_2)_3M$, and giving the phase transfer reagent represented as RCl in the eluate. An aqueous solution of NH_4OH

or NH_4HCO_3 is passed through the anion exchange resin, removing the catalyst represented as $(NH_4)_3M$ from the anion exchange resin, now with an $(-N^+HR_2)_3OH$ group. The phase transfer reagent represented as RCl in the eluate is passed through a cation exchange resin, such as Dowex™ Mac 3, comprising a –COOH group, retaining the phase transfer reagent in the cation exchange resin. AcOH in toluene or in ethanol is passed through the cation exchange resin, removing the phase transfer reagent represented as AcOR from the cation exchange resin. Generally, MR_3 represents a Venturello catalyst, wherein M represents a peroxophosphotungstate anion and R represents a phase transfer cation. For this scheme, the anion exchange resin bed is used first, followed by the cation exchange resin bed. A flow rate of around 4 bed volumes (BV, wet)/hour under gravity is maintained. Double bed resin may be used following the same sequence. Alternatively, this scheme is applicable for removing catalyst under a stirring/shaking condition.

[0056] In Figure 4, results for catalyst separation using cation exchange resin followed by anion exchange resin in a mixed bed system, wherein the cation exchange resin is packed on top of the anion exchange resin within a single column, is shown. Overall, 97.5% retention of total tungsten is achieved.

[0057] In Figure 5, results for catalyst separation using cation exchange resin followed by anion exchange resin in a single bed resin system is shown. Overall, 98.14% retention of total tungsten is achieved.

[0058] In Figure 6, a scheme for removal of Venturello catalyst components using anion exchange resin is shown. In the first step, the anion resin is modified to convert tertiary amine functional groups to corresponding quaternary amine groups. In the second step, a solution comprising the Venturello catalyst is contacted with the modified anion resin and the Venturello catalyst along with phase transfer reagent are extracted in the eluent. In this scheme, M = peroxophosphotungstate anion and RCl = the phase transfer reagent Aliquat® 336 (chloride form).

[0059] In Figure 7, a scheme for the calculation of catalyst absorbed/retained in resin by a gravimetric method/analaysis is shown. The catalyst absorbed/retained may be calculated using the equation: $(x) = \frac{(1-\frac{y}{z})}{0.463} \times 100\%$, wherein y represents the total mass removed and z represents the total mass of catalyst.

[0060] In Figure 8, a breakthrough curve for the absorption/retention of catalyst using the anion exchange resin Purolite® A111S (-$NR_2H^+Cl^-$ form) is shown. The catalyst absorption (percent, with respect to maximum capacity of resin) is plotted on the y-axis and the mass of the eluate (grams) is plotted on the x-axis. The curve plateaus at around 28.62% catalyst absorption with respect to maximum capacity of the resin.

[0061] In Figure 9, results for recovered tungsten from an anion exchange resin bed (Purolite® A111S, -$N^+HR_2Cl^-$ form) are shown. The total recovery of tungsten was found to be 102%

[0062] In Figure 10, results for recovered phosphorous from an anion exchange resin bed (Purolite® A111S, -$N^+HR_2Cl^-$ form) are shown. The total phosphorous recovery (~224%) was erroneous, and the first point in the graph shows a tungsten/phosphorous (W/P) ratio of 10.5 instead of the theoretically expected 23.4.

[0063] In Figure 11, results for recovery of tungsten and phosphorous from an anion exchange resin column (Purolite® A111S, -$N^+HR_2Cl^-$ form) are shown. The extent of catalyst absorption was 92.8%. The extent of tungsten recovery was 39.7%. The phosphorous recovery results were found to be erroneous

[0064] In Figure 12, results for recovery of tungsten and phosphorous from an anion exchange column (Purolite® A111S, -$N^+HR_2Cl^-$ form) are shown. The extent of catalyst absorption was 78.6%. The extent of tungsten recovery was 38%. The phosphorous recovery results were found to be erroneous.

[0065] In Figure 13, results for the extent of tungsten and phosphorous recovery from an anion exchange resin (Purolite® A111S, -$N^+HR_2Cl^-$ form) under stirring condition are shown. Overall, the lower the charge ratio of catalyst:resin, the higher the extent of catalyst recovery.

[0066] In Figure 14, a scheme for conversion of the –$N^+HR_2Cl^-$ form of an anion exchange resin to the –$N^+HR_2OH^-$ form using an NH_4OH solution is shown. In step 1, the anion exchange resin Purolite® A111S is chemically modified using HCl. In step 2, the modified anion exchange resin resultant from step 1 is chemically modified with 2N NH_4OH. The –$N^+HR_2OH^-$ form of the anion exchange resin is obtained after using a solution of NaCl in step 3.

[0067] In Figure 15, a resin bed system optimized to facilitate separation of Venturello catalyst from a scaled-up soybean oil epoxidation reaction is shown. Two columns, each 24 inches long with 1400 mL capacity, were used in a series. The anion exchange column was set up first in the series, followed by the cation exchange column. To deliver a feed solution to the columns, a Master flex L/S pump (peristaltic pump) with detachable pump head was used. To check the pressure within the columns, a pressure gauge was set up before the columns in the series. To regulate the eluate flow rate, valves were placed after each column.

[0068] In Figure 16, an additional view of the resin bed system optimized to facilitate separation of Venturello catalyst from a scaled-up soybean oil epoxidation reaction is shown.

[0069] In Figure 17, additional views of the resin bed system optimized to facilitate separation of Venturello catalyst from a scaled-up soybean oil epoxidation reaction are shown.

[0070] In Figure 18, an additional view of the resin bed system optimized to facilitate separation of Venturello catalyst from a scaled-up soybean oil epoxidation reaction is shown.

[0071] In Figure 19, results of calibration of the flow rate of a Master flex L/S pump are shown.

[0072] In Figure 20, results of calibration of the flow rate of a Master flex L/S pump using two columns are shown.

[0073] The present invention is more particularly illustrated by the following non-limiting examples:

[0074] The term single bed resin as used herein means a column packed with a single resin. In certain preferred embodiments, the single bed resin may comprise only cation exchange resin, or alternatively only anion exchange resin.

[0075] The term double bed resin as used herein means a column packed with two kinds of resin. In certain preferred embodiments, the double bed resin may comprise cation exchange resin on top of anion exchange resin, or alternatively anion exchange resin on top of cation exchange resin.

[0076] The term mixed bed resin as used herein is synonymous with double bed resin.

[0077] Table 1: Resins Used in the Examples

Resin Name	Description	CAS Number	Company
Lewatit® TP 207	Weakly acidic, macroporous cation exchange resin with chelating iminodiacetate groups	135620-93-8	LANXESS AG, Cologne, Germany
Lewatit® S 4528	Weakly basic, macroporous anion exchange resin	113114-05-9	LANXESS
Diaion™ WA 30	Weakly basic anion exchange resin	69011-17-2	Mitsubishi Chemical, Japan
Diaion™ WK 60L	Weakly acidic cation exchange resin	9052-45-3	Mitsubishi Chemical, Japan
Dowex™ Mac-3	Macroporous, weak acid cation exchange resin	9052-45-3	The Dow Chemical Company
Dowex™ 99 Ca	Strongly acidic cation exchange resin		The Dow Chemical Company
Diaion™ WK 100	Weakly acidic cation exchange resin	111559-80-9	Mitsubishi Chemical
Diaion™ WK 40	Weakly acidic cation exchange resin		Mitsubishi Chemical
Diaion™ WT01S	Weakly acidic cation exchange resin	11159-80-9	Mitsubishi Chemical
Lewatit® S 8528	Weakly acidic cation exchange resin	130353-60-5	LANXESS
Dowex™ 99CA/2010	Strongly acidic cation exchange resin		The Dow Chemical Company
Purolite® A111S	Macroporous, weak base anion exchange resin	68441-29-2	Purolite

[0078] Examples 1-4: Catalyst separation using single bed resin column – cation exchange resin followed by anion exchange resin. A solution of toluene and Venturello catalyst, wherein the Venturello catalyst comprises a tri-negatively charged peroxophosphotunsten moiety and a mono-positively charged methyltrioctylammonium cation as a phase transfer reagent (PTR) was processed in a single bed resin column according to the scheme in Figure 1. The solution of toluene and Venturello catalyst was passed through a column packed with the cation exchange resin Lewatit® TP 207. The average flow rate of the eluate was maintained at around 4 bed volumes (BV, wet)/hour (Fig. 1, step 1). The eluate was collected and passed through a column packed with the anion exchange resin Lewatit® S 4528 (Fig. 1, step 2). A solution of 1 normal (N) acetic acid (AcOH) in toluene was passed through the cation exchange resin to recover the phase transfer reagent (PTR) as an acetate salt (Fig. 1, step 3). A solution of 1N ammonium hydroxide (NH_4OH) was passed through the anion exchange resin to recover the tungsten and phosphorous (Fig. 1, step 4). This procedure was repeated, using the following combinations of cation exchange resins and anion exchange resins: cation exchange resin (Lewatit® TP 207) followed by anion exchange resin (Diaion™ WA 30); cation exchange resin (Diaion™ WK 60L) followed by anion exchange resin (Lewatit® S 4528); cation exchange resin (Dianion™ WK 60L) followed by anion exchange resin (Dianion™ WA 30). While the quantities of reagents varied based on the amounts of resin used, in one specific example, 0.38 g of Venturello catalyst was dissolved in 100 mL of toluene and passed through a single bed resin column packed with cation exchange resin (Lewatit® TP 207). The eluate was collected and passed through a single bed resin column packed with anion exchange resin (Lewatit® S 4528). A solution of 1N acetic acid in toluene (100 mL) was passed through the cation exchange resin to recover the PTR as an acetate salt. A solution of 1N NH_4OH/NH_4HCO_3 (100 mL) was passed through the anion exchange resin to recover the tungsten and phosphorous. Table 4, entry 1 represents tungsten and phosphorous recovery results. Table 6, entry 4 represents catalyst retention in the resin bed results.

[0079] Example 5: Catalyst separation using shaking/stirring condition – anion exchange resin followed by cation exchange resin. The $–NR_2$ group of the anion exchange resin Lewatit® S 4528 was converted to the $–N^+R_2HCl^-$ group by shaking the

anion exchange resin with a solution of 1N HCl (ethanol/water = 1:1, volume/volume) for 24 hours (Fig. 2, step 1). The resin was filtered, washed thoroughly with an ethanol/water 1:1, volume/volume solution, and air dried. The objective of this chemical modification of the anion exchange resin was to convert the tertiary amine group to the corresponding quaternary amine group. Alternatively, commercially available anion exchange resins with quaternary amine groups may be used. The quaternary amine group is advantageous compared to primary, secondary, or tertiary amine groups for at least two reasons. First, the anionic portion of the Venturello catalyst containing tungsten and phosphorous is more expensive than the phase transfer reagent Aliquat® 336. Therefore, a method to recover the anionic portion of the Venturello catalyst without a required step to recover the Aliquat® 336 (which does not contribute to epoxidized soybean oil decomposition) is cost-effective and less time consuming compared to a method using primary, secondary, or tertiary amine groups. Second, only one column packed with anion exchange resin is used to recover the anionic portion of the Venturello catalyst when using a quaternary amine, and therefore increased recovery of the anionic portion of the Venturello catalyst is expected compared to use of primary, secondary, or tertiary amine groups, which would require use of two successive columns.

[0080] A product mixture comprising an organic phase and a reaction mixture from an epoxidation of soybean oil was diluted with an ethanol/toluene solution (product mixture:ethanol/toluene = 1:3, volume/volume) and shaken/stirred in the presence of the anion exchange resin containing the $-N^{+}R_2HCl^{-}$ group for 18 hours (Fig. 2, step 2). The organic phase comprised soybean oil, epoxidized soybean oil, toluene (about 10%), by-products (diols, about 1-3%), and Venturello catalyst (about 1.9% by weight). The product mixture in all examples was from an epoxidation of soybean oil (ADM feedstock) conducted in a 50 mL autoclave reactor under N_2 atmosphere in semi-batch mode using Venturello catalyst comprising a tri-negatively charged peroxophosphotungsten moiety and a mono-positively charged methytrioctylammonium cation as a phase transfer cation, with 50% aqueous H_2O_2 added slowly with a syringe pump. In all iterations, the product mixture was obtained from a fresh batch and compositionally the same. The anion exchange resin was removed, washed, and shaken in a solution of 1N ammonium hydroxide for 20 hours (Fig. 2, step 3). The eluate from

the diluted product mixture shaken/stirred in the presence of the anion exchange resin was collected and stirred with the cation exchange resin Dowex™ Mac-3, H^+ form, for 20 hours (Fig. 2, step 4) and then stirred in a solution of 1N acetic acid in ethanol/toluene for 20 hours (Fig. 2, step 5). The cation exchange resin was filtered off and the ethanol/toluene was evaporated to yield the phase transfer reagent (PTR) Aliquat® 336 (trioctylmethylammonium chloride, CAS 5137-55-3, Sigma-Aldrich) as a viscous liquid (identified by proton (1H) NMR).

[0081] Example 6: Catalyst separation using single bed resin column – anion exchange resin followed by cation exchange resin. The $–NR_2$ group of the anion exchange resin Lewatit® S 4528 was converted to the $–N^+R_2HCl^-$ group by shaking the anion exchange resin with a solution of 1N HCl (ethanol/water = 1:1, volume/volume) for 24 hours (Fig. 3, step 1). The resin was filtered, washed thoroughly with an ethanol/water 1:1, volume/volume solution, and air dried. A product mixture comprising an organic phase [soybean oil, epoxidized soybean oil, toluene (about 10%), by-products (diols, about 1-3%), Venturello catalyst $[PO_4\{WO(O_2)_2\}_4]$ $[\{(C_8H_{17})_3N(CH_3)\}_3]$ (about 1.9% by weight)] was diluted with an ethanol/toluene solution (product mixture:ethanol/toluene = 1:3, volume/volume) and passed through a column packed with the anion exchange resin containing the $–N^+R_2HCl^-$ group (Fig. 3, step 2). A basic solution (1N ammonium hydroxide or ammonium bicarbonate) was passed through the anion exchange resin to recover the peroxophosphotungstate anion as an ammonium salt (Fig. 3, step 3). The eluate from step 2 was collected and passed through a column packed with the cation exchange resin Dowex™ Mac-3, containing the -COOH group (Fig. 3, step 4). A solution of 1 normal (N) acetic acid (AcOH) in toluene or ethanol was passed through the cation exchange resin to recover the phase transfer reagent (PTR) as an acetate salt (Fig. 3, step 5).

[0082] Example 7: Catalyst retention and recovery. A heptane solution of the Venturello catalyst (1.93 g of Venturello catalyst in 300 mL of heptane) was passed through a resin column at a flow rate of about 35 mL/hour under gravity. Both a mixed bed resin column (double bed resin column) and a single bed anion exchange resin column were tested. For the mixed bed resin system, a cation exchange resin was packed at the top of the column and an anion exchange resin was packed at the bottom of the column. For the single bed resin system, the eluent was passed through the cation

exchange resin first, followed by the anion exchange resin. The Venturello catalyst contained 28.42% tungsten and 1.44% phosphorous.

[0083] A solution of p-toluene sulfonic acid in acetonitrile was passed through the resin column but catalyst recovery was negligible (0.54%). A solution of acetic acid (3.1 equivalents with respect to tungsten) was passed through the resin column but did not improve catalyst recovery.

[0084] A solution of ammonium hydroxide and a solution of ammonium bicarbonate were passed through the resin column separately to recover tungsten either as NH_4WO_4 (water-soluble) or as an ammonium salt of the phosphotungsten moiety. A total of 100 mL of either solution (ammonium hydroxide, ammonium bicarbonate) was passed through the resin column at a flow rate of about 15 mL/hour (about 4 bed volumes (BV)/hour).

[0085] Regarding the solution of ammonium bicarbonate (1N), results for recovery of the catalyst from both the single bed anion exchange resin and the mixed bed resin system were compared. Around 43% of the tungsten and around 94% of the phosphorous was recovered from the mixed bed resin system. However, only around 8.1% of the tungsten and around 16.7% of the phosphorous was recovered from two successive single bed anion resins.

[0086] Regarding the solution of ammonium hydroxide, results for the recovery of the catalyst from both the single bed anion exchange resin and the mixed bed resin were compared using different concentrations of the solution of ammonium hydroxide. Around 8% of the tungsten and around 4.4% of the phosphorous was recovered from the single bed anion exchange resin when using 1N ammonium hydroxide. Around 15.8% of the tungsten and around 21.5% of the phosphorous was recovered from the single bed anion exchange resin when using 8N ammonium hydroxide. When the amount of catalyst was doubled in the heptane solution before passing through the resin column, the recovery of the tungsten and the phosphorous using a solution of ammonium hydroxide (8N) decreased to about 12.1% of the tungsten and 10% of the phosphorous. When the amount of resin was doubled in the column, the recovery of the tungsten and phosphorous using a solution of 1N ammonium hydroxide decreased to about 4.6% of the tungsten and about 2.4% of the phosphorous.

[0087] The details of the results obtained from Example 7 are summarized below in Table 2.

[0088] Table 2: Evaluation of Catalyst Recovery (Tungsten and Phosphorous) Varying Different Parameters

Entry	Column Type (m = mixed bed resin; s = single bed anion exchange resin)	Amount of resin used (g, each for single)	Amount of catalyst (g)	Solvent used for retention of catalyst	Volume of solvent (mL)	Eluent used for retention of catalyst	Volume of eluent (mL)	Recovered tungsten (weight %)	Recovered phosphorus (weight %)
1	m	10	1.93	heptane	140	8N NH_4OH	140	72.4	-
2	s	2	0.38	heptane	80	8N NH_4OH	80	16.3	-
3	s	2	0.76	heptane	90	8N NH_4OH	90	10.8 (12.1)	-
4	m	20	1.93	toluene	100	8N NH_4OH	100	36.2	42.6
5	m	4	0.38	toluene	100	8N NH_4OH	100	24.2	17.8
6	m	4	0.38	toluene	100	1N NH_4OH	100	22.8	12.6
7	s	2	0.38	toluene	100	8N NH_4OH	100	15.8	21.4
8	s	2	0.76	toluene	100	8N NH_4OH	100	12.1	10.0
9	s	2	0.38	toluene	100	1N NH_4OH	100	8.1	4.4
10	s	4	0.38	toluene	100	1N NH_4OH	100	4.6	2.4
11	m	4	0.38	toluene	100	1N NH_4HCO_3	100	40.7	65.4
12	m	4	0.38	toluene	100	1N NH_4OH	100	21.8	8.8
13	s	2	0.38	toluene	100	1N NH_4HCO_3	100	7.8	11.6
14	s	2	0.38	toluene	100	1N NH_4OH	100	7.7	3.1

[0089] Example 8: Catalyst recovery. Solutions of ammonium hydroxide and ammonium bicarbonate were used to recover tungsten and phosphorous from columns packed with a mixed bed resin system and a single bed resin. The flow rate was maintained at around 4 bed volumes (BV)/hour for the single bed resin column and around 2 BV/hour for the mixed bed resin system.

[0090] The recovery of catalyst (tungsten and phosphorous) was compared varying the amounts of resins in the mixed bed resin column. The total amount of resin was tested using 4 grams (g), 20g, and 80g, with the amount of cation exchange resin and anion exchange resin present in equal amounts. The amount of the tungsten recovered increased from about 41% when 4g of resin was used, to about 61% when 20g of resin was used, to about 100% when 80g of resin was used. The Venturello catalyst contained 28.42% tungsten and 1.44% phosphorous.

[0091] The details of the results obtained from this portion of Example 8 are summarized below in Table 3.

[0092] Table 3: Evaluation of Catalyst Recovery (Tungsten and Phosphorous) Using Mixed Bed Resin with Varied Amounts of Resin

Entry	Column Type (m = mixed bed resin)	Total amount of resin used (g)	Type of resin	Amount of catalyst (g)	Volume of catalyst solution (mL) in toluene	Name & Volume (mL) of eluent to remove 'W' and 'P'	Recovered tungsten (weight %)	Recovered phosphorus (weight %)
1	m	4	Lewatit® TP 207 (cation), Lewatit® S 4528 (anion)	0.38	100	1N NH_4HCO_3 100	40.7	65.4
2	m	20	Lewatit® TP 207 (cation), Lewatit® S 4528 (antion)	1.93	120	1N NH_4HCO_3 120	61.1	86.9
3	m	80	Dianion™ WK 60L (cation), Lewatit® S 4528 (anion)	7.72	600	1N NH_4HCO_3 660	99.9	88.9

[0093] The recovery of catalyst (tungsten and phosphorous) was compared for different anion exchange resins. To improve recovery of the tungsten and phosphorous, the resin in the column was removed after passing the eluent through the resin, stirred with the eluent for about 4 to about 5 hours, filtered and washed with deionized water. This additional stirring with the eluent yielded an additional recovery of about 9% to about 25% of the tungsten and an additional recovery of about 12% to about 28% of the phosphorous. The numbers reported in parentheses in Table 3 below represent the total amount of the element collected after removing the resin from the column after elution and stirring the resin with 50 mL of a 1N solution of ammonium bicarbonate for 40 hours followed by washing with deionized water.

[0094] The details of the results obtained from this portion of Example 8 are summarized below in Table 4.

[0095] Table 4: Evaluation of Catalyst Recovery (Tungsten and Phosphorous) Using Mixed Bed Resin with Different Types of Anion Resin

Entry	Column Type (s = single bed resin)	Total amount of resin used (g)	Type of resin	Amount of catalyst (g)	Volume of catalyst solution (mL) in toluene	Name & Volume (mL) of eluent to remove 'W' and 'P'	Recovered tungsten in weight %	Recovered phosphorus in weight
1	s	20 (10 +10)	Dianion ™ WK 60L (cation), Dianion ™ WA 30 (anion)	1.89	120	1N NH_4HCO_3 320	40.4 (51.9)	83.8 (108.0)
2	s	20 (10 +10)	Dianion ™ WK 60L (cation), Lewatit® S 4528 (anion)	1.89	120	1N NH_4HCO_3 320	67.6 (73.3)	96.0 (108.1)

[0096] The eluent was passed through the mixed bed twice to improve recovery of the tungsten and the phosphorous. The resin beds were activated with a 1N

solution of acetic acid in toluene. The Venturello catalyst contained 28.42% tungsten and 1.44% phosphorous. The details of the results obtained from this portion of Example 8 are summarized below in Table 5.

[0097] Table 5: Evaluation of Catalyst Recovery (Tungsten and Phosphorous) Passing the Eluent through the Mixed Bed Resin System Twice

Entry	Column Type (m = mixed bed resin)	Total amount of resin used (g)	Type of resin	Amount of catalyst (g)	Volume of catalyst solution (mL) in toluene	Name & Volume (mL) of eluent to remove 'W' and 'P'	Recovered tungsten (weight %)	Recovered Phosphor-us (weight %)
1st time use	m	20 (10+ 10)	Lewatit ® TP 207 (cation), Lewatit ® S 4528 (anion)	1.93	120	8N NH_4OH 120	34.6	29.6
2nd time use	m	20 (10+ 10	Lewatit ® TP 207 (cation), Lewatit ® S 4528 (anion)	1.89	120	1N NH_4OH 120	101.1	79.8

[0098] The retention of catalyst (tungsten and phosphorous) in the resin bed was compared. For the mixed bed resin column, the cation resin Lewatit® TP 207 yielded better retention than the cation resin Dianion™ WK 60L. Passing the solution containing the catalyst through the same column multiple times increased the catalyst retention. The solvent used was toluene. The Venturello catalyst contained 28.42% tungsten and 1.44% phosphorous. To retain the catalyst, 100 mL of the catalyst solution in toluene was passed through the resin.

[0099] The details of the results obtained from this portion of Example 8 are summarized below in Table 6 and Table 7.

[00100] Table 6: Evaluation of Catalyst Retention (Tungsten and Phosphorous) Varying Combinations of Resin in Single Bed Resin and Mixed Bed Resin Systems

Entry	Column Type (m = mixed bed resin; s = single bed resin)	Amount of resin used (g, each for single)	Amount of catalyst (g)	Type of resin	Volume of solvent (mL)	Recovered tungsten (weight %)	Recovered phosphorus (weight %)
1	m	20	1.93	Lewatit® TP 207 (cation), Lewatit® S 4528 (anion)	100	99.9	99.9
2	m	80	7.72	Dianion™ WK 60L (cation), Lewatit® S 4528 (anion)	400	76.1	81.8
3	s	20	1.93	Dianion™ WK 60L (cation), Lewatit® S 4528 (anion)	100	78.9	91.6
4	s	20	1.93	Dianion™ WK 60L (cation), Dianion™ WA 30 (anion)	100	86.7	80.6

[00101] Table 7: Evaluation of Catalyst Retention (Tungsten and Phosphorous) Reusing the Mixed Bed Resin System

Entry	Column Type (m = mixed bed resin)	Amount of resin used	Amount of catalyst (g)	Type of resin	Eluent to remove 'W' and 'P' prior to reuse	Recovered tungsten (weight %)	Recovered phosphorus (weight %)
1 1st use	m	20	1.93	Lewatit® TP 207 (cation), Lewatit® S 4528 (anion)	-	99.9	99.9
2 Re-use	m	20	1.93	Lewatit® TP 207 (cation), Lewatit® S 4528 (anion)	1N NH_4OH (100 mL)	98.5	98.3

3 Re-use	m	20	1.93	Lewatit® TP 207 (cation), Lewatit® S 4528 (anion)	1N NH_4HCO_3 100 mL	99.7	99.3

[00102] Example 9: Catalyst and Phase Transfer Reagent (PTR) Recovery. Solutions containing catalyst and phase transfer reagent were shaken with different resins and eluents for several hours. Anion exchange resin was used first, followed by cation exchange resin. The $-NR_2$ group of the anion exchange resin Lewatit® S 4528 was converted to the $-NR_2HCl$ group by shaking the resin with a 50mL solution of 1N HCl (methanol/water = 1:1) for 24 hours. The modified anion exchange resin was filtered off and washed with a 1:1 methanol/water solution. A solution of 40 mL of acetonitrile and 1g Venturello catalyst was shaken with the modified anion exchange resin for 25 hours. The modified anion exchange resin was filtered off and washed with a 1:1 methanol/water solution. The PTR was Aliquat® 336. A total of 1g of the Venturello catalyst was used in each entry, along with 8g of Lewatit® S 4528. The Venturello catalyst contained 28.42% tungsten and 1.44% phosphorous.

[00103] The amount of phase transfer reagent (PTR) was greater than 100%. The details of the results obtained from this portion of Example 9 are summarized below in Table 8.

[00104] Table 8: Evaluation of Phase Transfer Reagent (PTR) Recovery Using Anion Exchange Resin

Entry	Volume of catalyst solution in acetonitrile (mL)	Time of shaking in a mechanical shaker (h)	calculated mass of PTR (g) in the catalyst	Recovered PTR (%)
1	40	25	0.607	110
2 (repeat)	40	25	0.576	105
3 (repeat)	40	25	0.589	107

[00105] Resin was shaken in various eluents with 80mL of a methanol/water 1:1 (volume/volume) solution for 40 hours to recover the catalyst (tungsten and

phosphorous). The eluents tested were 1N ammonium bicarbonate, 1N sodium hydroxide, and 1N ammonium hydroxide. The three eluents had similar efficiency for recovering the tungsten. A total of 1g of catalyst was used in each entry, along with 8g of Lewatit® S 4528. The catalyst was loaded with 28.42% tungsten and 1.44% phosphorous. The retention of the catalyst in the resin bed was considered to be 100%.

[00106] The details of the results obtained from this portion of Example 9 are summarized below in Table 9.

[00107] Table 9: Evaluation of Neat Catalyst (Tungsten and Phosphorous) Recovery Using Anion Exchange Resin and Different Eluents

Entry	Eluent	Recovered phosphorus (wt. %)	Recovered tungsten (wt. %)
1	1N NH_4HCO_3 in 80 mL methanol+water (1:1, w/w)	58.3	79.6
2	1N NaOH 80 mL methanol+water (1:1, w/w)	44.5	81.9
3	1N NH_4OH in 80 mL methanol+water (1:1, w/w)	52.2	77.7

[00108] Example 10: Catalyst Recovery Using Solutions Containing Catalyst and a Product Mixture. An isolated product mixture containing epoxidized soybean oil (ESO) and catalyst was shaken with the anion exchange resin Lewatit® S 4528 and various eluents for 22 hours to determine amounts of tungsten and phosphorous recovered. A total of 10g of epoxidized soybean oil containing 0.27g of catalyst was used in each entry, along with 8g of Lewatit® S 4528. The catalyst was loaded with 28.42% tungsten and 1.44% phosphorous. The retention of the catalyst in the resin bed was considered to be 100%.

[00109] The details of the results obtained from Example 10 are summarized below in Table 10.

[00110] Table 10: Evaluation of Catalyst (Tungsten and Phosphorous) Recovery Using a Product Mixture, Anion Exchange Resin, and Different Eluents

Entry	Eluent	Recovered phosphorus (wt.%)	Recovered tungsten (wt.%)
1	1N NH_4HCO_3 in 80 mL methanol+water (1:1, w/w)	58.3	79.6
2	1N NH_4OH 80 mL methanol+water (1:1, w/w)	44.5	81.9

[00111] Example 11: Phase Transfer Reagent (PTR) Recovery. Various microporous weak acid cation exchange resins were screened to compare recovery of the phase transfer reagent (PTR) Aliquat® 336 under shaking conditions. Improved retention and recovery of the PTR was observed using a macroporous weak acid resin (Dowex™ Mac-3) and a microporous strong acid resin (Dowex™ 99 CA, H^+ form). These resins which provided improved retention and recovery of the PTR were also tested by packing in columns.

[00112] The details of the results obtained from Example 11 are summarized below in Table 11 and Table 12. For Table 10, 6g of dry cation exchange resin was shaken with solutions of PTR in a mechanical shaker for 24 hours. To retain the PTR, 0.4g of Aliquat® (the PTR) in 20 mL of toluene and 30 mL of acetonitrile was used (entries 1-4). To recover the PTR, 20 mL of 2N acetic acid in toluene was used. For Tables 11 and 12, for the shaking conditions, 6g of dry cation exchange resin was shaken with solutions of PTR in a mechanical shaker for 24 hours. To retain the PTR, 0.4g of Aliquat® (PTR) in 20 mL of toluene was used. To recover the PTR, 20 mL of 2N acetic acid in toluene was used. For Table 12, for the resin column, 6g of dry cation exchange resin was packed in the column. A solution containing 0.4g of Aliquat® (PTR) in 50 mL of toluene was eluted at a flow rate of 10 mL/hour to retain the PTR in the resin bed. A 50 mL solution of 2N acetic acid was eluted at a flow rate of 10 mL/hour to recover the PTR.

[00113] Table 11: Evaluation of Phase Transfer Reagent (PTR) Retention and Recovery Using Different Cation Exchange Resins under Shaking Conditions

Entry	Cation exchange resin	Retained PTR (wt. %)	Recovered PTR (%), w.r.t retained PTR
1	Diaion™ WK100 (NH_4^+ form)	8.0	-
2	Diaion™ WK100 (Na^+ form)	11.7	-
3	Lewatit® TP 207 (NH_4^+ form)	11.1	-
4	Lewatit® TP 207 (Na^+ form)	11.9	-
5	Dianion™ WK40	29.9	25.1

6	Dianion™ WT01S	30.0	56.2
7	Lewatit® S8528	16.1	78.9
8	Dowex™ Mac–3, Macroporous	75.9	94.8
9	Dowex™ 99CA/210, (H^+ form)	89.0	66.3
10	Dowex™ 99CA/210, (Ca^{2+} form)	34.3	75.8

[00114] Table 12: Evaluation of Phase Transfer Reagent (PTR) Retention and Recovery Using Different Cation Exchange Resins under Shaking Conditions and Resin Column

Entry	Cation exchange resin	Under shaking condition (wt. %)		Using resin column (wt. %)	
		Retained PTR	Recovered PTR (w.r.t. retained PTR)	Retained PTR	Recovered PTR (w.r.t. retained PTR)
1	Dowex™ Mac–3, Macroporous	75.9	94.8	80.3	90.2
2	Dowex™ 99CA, (H^+ form)	89.0	66.3	97.4	71.1

[00115] Example 12: Phase Transfer Reagent (PTR) Recovery Using Solutions Containing PTR, Catalyst, and a Product Mixture. A product mixture containing epoxidized soybean oil (ESO), catalyst, and PTR was passed through a resin bed to retain the catalyst, followed by passing an ethanol/ammonium hydroxide solution through the resin bed to recover the catalyst. Using Lewatit® S 4528 as the anion exchange resin and Dowex™ Mac 3, H+ form, as the cation exchange resin, 71.3% of the PTR (Aliquat® 336) was recovered from the single bed resin column. Using the same reagents but substituting shaking conditions instead of using the single bed resin columns, 73.3% of the PTR (Aliquat® 336) was recovered. For the single bed resin column entry, 12.3g of epoxidized soybean oil (ESO, ER-74) in 50 mL of ethanol was passed through 5g of Lewatit® S 4528, HCl salt form, at a flow rate of 15 mL/minute, and the eluate was then passed through 5g of Dowex™ Mac-3, H+ form, and then eluted with a solution of 1N acetic acid in 50 mL of ethanol at a flow rate of about 15 mL/minute. Calculations were done considering 100% retention of the catalyst in the resin bed.

[00116] The details of the results obtained from Example 12 are summarized below in Table 13.

[00117] Table 13: Evaluation of Phase Transfer Reagent (PTR) Recovery Using a Product Mixture, Shaking Conditions, and a Single Bed Resin Column

Entry	Description	Content of PTR (calculated for Cl form)	Content of PTR (calculated for AcO form)	Calculated mass of recovered PTR (AcO form)	Recovered PTR (%)
1	Stirring condition	0.184 g	0.195g	0.143 g	73.3
2	Using resin column	0.184 g	0.195 g	0.139 g	71.3

[00118] Example 13: Catalyst separation using cation exchange resin followed by anion exchange resin. Both single bed resin and mixed bed resin systems were evaluated. For the single bed resin system, the cation exchange resin was used first, followed by the anion exchange resin. For the mixed bed resin system, the cation exchange resin was packed at the top of the column and the anion exchange resin was packed in the lower part of the column. For all of the columns, 5g of epoxidized soybean oil product mixture was loaded onto 10g of resin (cation resin = Lewatit® TP 207; anion resin = Lewatit® S 4528), with a wet bed volume of about 17 mL. For the single bed resin system, the flow rate was about 45 mL/hour (about 2.5 bed volumes (BV)/hour). For the mixed bed resin system, the flow rate was about 40 mL/hour. Toluene was used as the eluent (about 100 to about 130 mL).

[00119] The results of Example 13 are shown in Fig. 4 and Fig. 5. For the mixed bed resin system, retention of total tungsten was 97.5%. For the single bed resin system, retention of total tungsten was 98.14%.

[00120] Examples 14-18: Absorption capacity of anion exchange resin under stirring condition. In order to determine the optimal charge ratio of catalyst to resin (catalyst:resin) to get maximum retention of the Venturello catalyst in the resin, five experiments were done using a fixed amount of dry resin (3.5 g) and different equivalents of charge of catalyst (catalyst:resin ranging from 1:1 to 1:12). A macroporous, weak base anion exchange resin (Purolite® A111S) was used for all

experiments. The resin was modified to convert the tertiary amine functional groups to the corresponding quaternary amine group. (Figure 6). The resin was stirred with a 40g Venturello catalyst solution in toluene at a mild agitation speed (300 rpm) for 12 hours. After 12 hours of stirring, 4g of solution was removed and dried. Gravimetric analysis was performed to obtain qualitative results. (Figure 7). The total amount of catalyst retained was calculated from the isolated mass of catalyst and/or catalyst components. Results, summarized below in Table 14, showed that the extent of Venturello catalyst absorbed varied dramatically with charge ratio.

[00121] Table 14: Qualitative Estimation of Catalyst Absorbed/Retained Using Purolite® A111S Anion Exchange Resin by Gravimetric Method, Stirring Condition

Entry	ID	Catalyst used (g)	Charge of catalyst: resin	Isolated mass (g)	Catalyst absorbed (%)
1	E62-1	0.5	1:12	0.28	95.0
2	E62-2	1	1:6	0.57	92.8
3	E62-3	2	1:3	1.50	54.0
4	E62-4	4	1:1.5	3.05	51.3
5	E62-5	6	1:1	4.85	41.4

[00122] Example 19: Breakthrough point of anion exchange resin used for Venturello catalyst absorption. The breakthrough point corresponds to how many times a resin column may be used to absorb catalyst before saturation. In order to determine the breakthrough point, a single bed resin column was filled with 3.5 g of dry Purolite® A111S anion exchange resin. Twelve catalyst solutions were prepared using 0.5 g of Venturello catalyst and 19.5 g of toluene (20g catalyst solution, total) used as eluent. The resin column contained a charge equivalent to 6 g of Venturello catalyst (catalyst:resin charge ratio = 1:12), with the wet volume of resin totaling about 7 mL. Each catalyst solution was passed through the resin column with an average eluate flow rate of 15 mL/hour (2 BV/hour) under gravity. The content of catalyst or catalyst components was analyzed from each set of eluate (20 g) by gravimetric method to

estimate the extent of catalyst absorption in each run. It was expected that at some point, there would be no catalyst absorption, which would correspond to the breakthrough point. The results are summarized below in Table 15. After the 6th run onward, catalyst absorption dropped significantly. After the 11th run onward, no Venturello catalyst absorption was noted. Therefore, the resin bed became saturated after the 11th run and the maximum catalyst absorption at the breakthrough point was 28.62% with respect to the catalyst absorption measured by gravimetric method. These results are summarized in Table 16 below and Figure 8.

[00123] Table 15: Qualitative Estimation of Catalyst Absorbed/Retained Using Purolite® A111S (-NR_2·HCl form) Anion Exchange Resin by Gravimetric Method, Resin Column

Run	ID	Catalyst used (g)	Isolated mass (g)	Catalyst retained (%)
1	E63-1	0.5	0.27	99.4
2	E63-2	0.5	0.35	64.8
3	E63-3	0.5	0.40	43.2
4	E63-4	0.5	0.42	34.6
5	E63-5	0.5	0.43	30.2
6	E63-6	0.5	0.41	38.9
7	E63-7	0.5	0.47	13.0
8	E63-8	0.5	0.48	4.3
9	E63-9	0.5	0.48	4.3
10	E63-10	0.5	0.47	13.0

[00124] Table 16: Qualitative Estimation of Catalyst Absorbed/Retained Using Purolite® A111S Anion Exchange Resin by Gravimetric Method, Resin Column

Run	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**
ID	E63-1	E63-2	E63-3	E63-4	E63-5	E63-6	E63-7	E63-8	E63-9	E63-10	E63-11	E63-12
Isolated mass (g)	0.27	0.35	0.40	0.42	0.43	0.41	0.47	0.48	0.48	0.47	0.496	0.503
Catalyst absorbed in each run (%)	99.4	64.8	43.2	34.6	30.2	38.9	13.0	4.3	4.3	13.0	1.7	0

Total catalyst (%) absorbed w.r.t. charge	8.23	13.63	16.96	19.84	22.36	25.6	26.68	27.04	27.4	28.48	28.62	28.62

[00125] Examples 20-24: Optimization of the catalyst:resin charge ratio for effective absorption of Venturello catalyst. In order to determine the optimal charge ratio of catalyst:resin to obtain maximum retention of Venturello catalyst, as well as to determine the maximum absorption capacity of resin for a particular catalyst:resin charge ratio, five different experiments were conducted using a fixed amount of dry resin (3.5 g) and different equivalents of charge ratio of catalyst:resin (from 1:3 to 1:12). A 20g solution of Venturello catalyst in toluene was prepared using different amounts of catalyst for the different catalyst:resin charge ratios. Each catalyst solution was passed through a resin column at an average eluate flow rate of 15 mL/hour (2 BV/hour) under gravity. The content of catalyst or catalyst components was analyzed for each set of eluate (20 g) by gravimetric method to estimate the extent of catalyst absorption. Using the gravimetric method, total catalyst absorbed/retained was calculated from the isolated mass of catalyst and/or catalyst components. The results are summarized below in Table 17. The higher the charge ratio of catalyst:resin, the greater the extent of catalyst absorption/retention. Based on these results, a catalyst:resin charge ratio of about 1:12 may be considered as an optimum ratio for effective absorption of Venturello catalyst for a one-time run.

[00126] Table 17: Optimization of Catalyst:Resin Charge Ratio for Effective Absorption/Retention of Catalyst, One Time Run, Gravimetric Method

Entry	**ID**	**Catalyst used (g)**	**Charge of catalyst: resin**	**Isolated mass (g)**	**Catalyst absorbed (%)**
1	E68-1	0.5	1:12	0.272	98.5
	E63-1	0.5	1:12	0.270	99.4
2	E64-1	1.1	1:6	0.63	92.3

3	E64-2	1.65	1:4	1.10	72.0
4	E64-3	2.2	1:3	1.56	62.8

[00127] Examples 25-27: Optimization of eluate flow rate for effective absorption of Venturello catalyst. The flow rate of eluate plays an important role in effective absorption/retention of catalyst. Generally, the greater the flow rate, the lower the absorption capacity. From literature, a flow rate of about 2-3 BV (wet/swelled)/hour was determined to be desirable. To validate this for the present invention, three separate catalyst separation experiments were conducted using 0.5 g Venturello catalyst in 34.5 g toluene and a catalyst:resin ratio of 1:12. The catalyst solutions were passed through the resin bed with different flow rates. The applied eluate flow rates were about 14 mL/min (2 BV/hour), about 21 mL/min (3 BV/hour), and 28 mL/min (4 BV/hour), respectively. Based on gravimetric estimation, the lowest flow rate (2 BV/hour) gave the maximum absorption of Venturello catalyst (98.5%) whereas the highest flow rate (4 BV/hour) gave the lowest absorption (78.6%) and the intermediate flow rate (3 BV/hour) gave mediocre absorption (92.8%). The results are summarized below in Figure 18. Therefore, an eluate flow rate of about 2-3 BV/hour may be considered an optimum flow rate.

[00128] Table 18: Optimization of Eluate Flow Rate for Effective Absorption of Catalyst, Anion Exchange Resin Bed [Purolite® A111S, $-N^{+}HR_2Cl^{-}$ form], Gravimetric Method

Entry	**ID**	**Flow rate of eluate**	**Catalyst used (g)**	**Charge of catalyst: resin**	**Isolated mass (g)**	**Catalyst absorbed (%)**
1	E68-1	~14 mL/h (2 BV/h)	0.5	1:12	0.272	98.5
2	E68-2	~21 mL/h (3 BV/h)	0.5	1:12	0.285	92.8
3	E68-3	~28 mL/h (4 BV/h)	0.5	1:12	1.318	78.6

[00129] Examples 28-31: Combined effect of catalyst concentration and eluate flow rate on catalyst absorption capacity using anion exchange resin. The combined effect of catalyst concentration and eluate flow rate was studied in four experiments. In the first two experiments (Table 19, entries 1 and 2), catalyst concentration was varied (2.5% by weight and 1.4% by weight), while the eluate flow rate was maintained at 2 BV (swelled)/hour. In the last experiments (Table 19, entries 3 and 4), the eluate flow rate was varied (2 BV/hour and 3 BV/hour), while the catalyst concentration was maintained at 1.4% by weight. From these results, it was determined that almost similar absorption of catalyst could be achieved (~99%) by varying catalyst concentration from 2.5% by weight to 1.4% by weight, while the extent of catalyst absorption decreased slightly (from 98.5% to 92.8%) when the eluate flow rate was increased from 2 BV/hour to 3 BV/hour. If the catalyst concentration is decreased further (to 1% by weight) while the eluate flow rate is increased to 4 BV/hour, the extent of catalyst absorption decreases further (from 92.8% to 78.6%). Under current scaled-up epoxidation reaction conditions, the organic layer contains about 2.6% by weight catalyst. Therefore, the reaction mixture containing catalyst may be diluted 2-3 times for effective absorption of catalyst.

[00130] Table 19: Combined Effect of Catalyst Concentration and Eluate Flow Rate on Catalyst Absorption/Retention Capacity of Anion Exchange Resin, Gravimetric Method

Entry	ID	Flow rate of eluate	Mass of solution (g)	Catalyst concentration (wt. %)	Isolated mass (g)	Catalyst absorbed (%)
1	E63-1	~14 mL/h (2 BV/h)	20	2.5	0.270	99.4
2	E68-1	~14 mL/h (2 BV/h)	35	1.4	0.272	98.5
3	E68-2	~21 mL/h (3 BV/h)	35	1.4	0.285	92.8
4	E69-2	~21 mL/h (3 BV/h)	50	1.0	1.318	78.6

[00131] Example 32: Determination of Extent of Catalyst Recovery from Saturated Resin Column. In this experiment, catalyst was removed from a saturated resin column used for the breakthrough experiments. The extent of catalyst recovered was calculated with respect to the absorbed/retained catalyst measured by the gravimetric method. Samples of eluate were collected, warmed to expel NH_3 from residual NH_4OH, and analyzed by ICP. After eluting 280 g of 1N aqueous NH_4OH solution, the total recovery of tungsten was found to be 102%. (Figure 9).

[00132] Conditions for obtaining the saturated resin column were: 3.5 g dry Purolite® A111S anion exchange resin; 0.5 g Venturello catalyst dissolved in 19.5 g toluene (20 g total solution) as eluent; 0.5 g of catalyst in each run (total of 12 runs); catalyst:resin charge ratio = 1:12; wet volume of resin = approximately 7 mL; and eluate flow rate = approximately 15 mL/minute (2 BV/hour). The total absorption was 28.62% (at breakthrough point) with respect to the total charge of resin, and 26.95% with respect to the total mass of catalyst run (6 g).

[00133] Conditions for catalyst removal/recovery from the saturated column were: 1N NH_4OH as eluent; flow rate = 3 BV/hour (wet resin); 280 g eluent total; sodium tungstate dehydrate ($Na_2WO_4 \cdot 2H_2O$) as ICP standard.

[00134] The first 35 g of eluate contained the maximum extent (~98%) of tungsten, meaning that only a small amount of eluent is required for maximum recovery of catalyst when using a resin column saturated with catalyst. The phosphorous recovery results showed a trend similar to that of tungsten, but the total recovery (~224%) was erroneous, and the first point in Figure 10 shows a tungsten/phosphorous (W/P) ratio of 10.5 instead of the theoretically expected 23.4. (Figure 10). Therefore, it would be preferred to dilute the eluate (especially the first amount of eluate obtained) before using the eluate for ICP analysis.

[00135] Examples 33 and 34: Determination of Extent of Catalyst Recovery from an Unsaturated Resin Column. Two similar experiments were conducted in which 0.5 g of Venturello catalyst was used for a catalyst absorption study (catalyst:resin charge ratio = 1:12). The extent of catalyst absorption was 92.8% (Figure 11) and 78.6% (Figure 12). The extent of tungsten recovery was 39.7% (Figure 11) and 38% (Figure 12). The phosphorous recovery results were found to be erroneous.

[00136] The conditions for the experiment represented by Figure 11 (Example 33) were: 1N NH_4OH as eluent; flow rate = 3 BV/hour (wet resin) (21 mL/hour); 57 mL eluent total; sodium tungstate dehydrate ($Na_2WO_4 \cdot 2H_2O$) as ICP standard. Total absorption of catalyst was 92.8% with respect to the total catalyst used (0.5 g Venturello catalyst, absorbed/retained using 35 g toluene at a flow rate of 3 BV/hour).

[00137] The conditions for the experiment represented by Figure 12 (Example 34) were: 1N NH_4OH as eluent; flow rate = 3 BV/hour (wet resin) (21 mL/hour); 57 mL eluent total; sodium tungstate dehydrate ($Na_2WO_4 \cdot 2H_2O$) as ICP standard. Total absorption of catalyst was 78.6% with respect to the total catalyst used (0.5 g Venturello catalyst, absorbed/retained using 35 g toluene at a flow rate of 4 BV/hour).

[00138] Examples 35-39: Determination of Extent of Catalyst Recovery from Resin under Stirring Condition. Five different experiments were conducted using a fixed amount of dry resin (3.5 g, Purolite® A111S anion exchange resin, $-N^+HR_2Cl^-$ form) and different amounts of catalyst (catalyst:resin ratio varying from 1:12 to 1:1). The resin was stirred in NH_4OH (40 g, aqueous solution) for 12 hours at an agitation speed of 300 rpm. The loading of tungsten and phosphorous in the catalyst is 32.6% and 1.374%, respectively. For each experiment, a slight white precipitate was noticed at the bottom of the samples, and therefore erroneous results may have been obtained as the concentration may have been outside the ICP range. The extent of recovered tungsten is summarized in Table 20 and Figure 13. The tungsten recovery of 67% for catalyst:resin ratio of 1:1 seemed to be erroneous as the concentration of this sample was out of the ICP range. Overall, the lower the charge ratio of catalyst:resin, the higher the extent of catalyst recovery.

[00139] Table 20: Recovery of Tungsten from Anion Exchange Resin under Stirring Condition.

Entry	ID	Catalyst Used (g)	Catalyst:Resin Charge Ratio	Catalyst Absorbed (%)	Tungsten Absorbed (mg)	Tungsten Recovered (mg)	Tungsten Recovered (%)
1	E62-1	0.5	1:12	95.0	154.8	67.4	43.5
2	E62-2	1	1:6	92.8	302.5	141.8	46.9

3	E62-3	2	1:3	54.0	352.1	253.2	71.9
4	E62-4	4	1:1.5	51.3	668.9	529.4	79.1
5	E62-5	6	1:1	41.4	809.8	543.4 (may be erroneous because concentration out of ICP range)	67.1 (may be erroneous because concentration out of ICP range)

[00140] Example 40: Effect of Chemical Modification of Purolite® A111S Anion Exchange Resin. The use of anion exchange resin with $-N^+HR_2OH^-$ form instead of $-N^+HR_2Cl^-$ form can possibly reduce the acid content in epoxidized soybean oil. Therefore, in this experiment, the $N^+HR_2OH^-$ form was attempted to be prepared from the $N^+HR_2Cl^-$ form using a 2N aqueous NH_4OH solution. Use of a relatively strong base, such as NH_4OH, creates a high chance of formation of the $-NR_2$ form instead of the $-N^+HR_2OH^-$ form. (Figure 14). In this experiment, 30 g of Purolite® A111S ($-N^+HR_2Cl^-$ form) was stirred in 50 mL of a 2N aqueous NH_4OH solution for 3 hours. The resin was washed with deionized water several times, followed by a solution of acetone and water, and finally with acetone. After filtration, the resin was dried. Approximately 23 g of resin was collected. Reduction of weight of the resin indirectly proved formation of the $-NR_2$ form, the $-N^+HR_2OH^-$ form, or both. The resin (5 g) was stirred with deionized water (50 mL) for 30 minutes. After filtration, the filtrate was preserved in order to check for hydroxyl content. Addition of phenolphthalein solution did not show any pink coloration, indicating that the filtrate did not contain any OH^- groups that might have come from residual NH_4OH. The washed resin was stirred in 50 mL of an aqueous NaCl (4 g) solution for 6 hours. The resin was filtered off and the filtrate was collected to check for hydroxyl content. The filtrate was titrated with a 0.68 N aqueous HCl solution (titrated by a standard NaOH solution). The measured hydroxyl content was 41 milli-equivalents per kilogram (at least 20 times less than commercially available resin). Therefore, this process was not effective for converting anion exchange resin with the $-N^+HR_2Cl^-$ form to the $-N^+HR_2OH^-$ form.

[00141] Example 41: Large scale separation of Venturello catalyst. In order to separate the Venturello catalyst form the scaled-up (518 g soybean oil) epoxidation reaction, an adequate resin bed system was optimized. Two columns 24 inches long with 1400 mL capacity were used. The anion exchange column was set up first, followed by the cation exchange column. To deliver the feed, a Master flex L/S pump (peristaltic pump) with detachable pump head was used. To check the pressure within the columns, a pressure gauge was set up before the columns. To regulate the eluate flow rate, valves were placed after each column. Figures 15-18 show the set up. The flow rate was calibrated using water as the solvent. (Figures 19-20).

[00142] After the scaled-up epoxidation of soybean oil, about 500 g of toluene and 500 g of double-distilled water were added to the reaction mixture and stirred for 1 minute to quench the reaction and facilitate the separation of the aqueous and organic phases. After 30 minutes, the organic phase was separated from the aqueous phase and treated with anhydrous Na_2SO_4 (50 g) to remove the residual H_2O/H_2O_2 from the organic phase. The organic phase was further diluted with toluene (from about 350 g to about 500 g) to reduce the viscosity.

[00143] The resins used were Purolite A111s ($-NR_2H^+Cl^-$ form) [anion exchange resin] and Dowex Mac 3 (H^+ form) [cation exchange resin]. The anion exchange resin column was placed first, followed by the cation exchange resin column. Each resin column was filled with 480 g of dry resin in an adequate amount of toluene. The wet volume of the anion and cation exchange resin columns were 960 mL and 580 mL, respectively. The anion exchange resin column was prepared using 500 mL of toluene, whereas the cation exchange resin column was prepared using 400 mL of toluene and 700 mL of acetone. These resin columns were used to separate Venturello catalyst (7.6 g in each batch) from the scaled-up (518 g soybean oil) epoxidation reaction mixtures of three different batches. The diluted reaction mixture (1620 g) of the first batch (ER-102) was run through the columns one time at a flow rate of 20 mL/min (about 1.2-2 BV/hour). The diluted reaction mixtures (1420 g) of the second (ER-103) and third (ER-104) batches were run through the resin columns two times each with set flow rates of 20 mL/min (1st run) and 30 mL/min (2nd run). In order to collect residual product from inside the resin column, 400 mL of toluene was passed through each column at the end of the catalyst separation for each batch. The total charges of resin

(480 g) in each column compared to the catalyst present (about 7.6 g) in the reaction mixture of each batch was about 70:1. The results are summarized in Table 21 and Table 22 below.

[00144] Table 21: Details about Purification of Epoxidized Soybean Oil (ESO) using Ion Exchange Resin Column – Resin Column Set-up

Column	**Nature of Resin**	**Resin Used**	**Amount**	**Column Height**	**Wet Volume**	**Solvent Used for Filling the Resin**
1	Anion exchange	Purolite A111S (-NR3+Cl- form)	480 g	16.5 feet	960 mL	Toluene (500 mL)
2	Cation exchange	Dowex Mac 3 (H+ form)	480 g	10 feet	580 mL	1. Acetone (500 mL) 2. Acetone + toluene (400 mL; 1:1 volume/volume) 3. Toluene (200 mL)

[00145] Table 22: Details about Purification of Epoxidized Soybean Oil (ESO) using Ion Exchange Resin Column – Product Purification

Product (to be purified)	**Amount**	**Toluene used (to dilute)**	**Anhydrous Na2SO4 used (to remove residual water)**	**Set flow rate (mL/minute)**	**Toluene used at end of run**
ER-102	Approximately 580 g	1620 g	50 g	20	400 mL
ER-103	Approximately 580 g	1420 g	50 g	1st run: 20 2nd run: 30	400 mL
ER-104	Approximately 580 g	1420 g	50 g	1st run: 20 2nd run: 30	400 mL

[00146] In order to remove toluene from the epoxdized soybean oil product, the diluted product was roto-evaporated two times for about 40-45 minutes at 70°C and about 40 minutes at 80°C, respectively. After the first time, the color of the product remained similar to the color of the diluted product. However, after the second time, the color of the product noticeably changed.

[00147] The present invention has been described with reference to certain examples. However, it will be recognized by those of ordinary skill in the art that various substitutions, modifications, or combinations of any of the examples may be made without departing from the spirit and scope of the invention. Thus, the invention is not limited by the description of the examples, but rather by the appended claims as originally filed.

CLAIMS

What is claimed is:

1. A method of separating a catalyst from a product mixture comprising:

diluting the product mixture with a solvent;

passing the diluted product mixture through a first ion exchange resin column; and

passing the diluted product mixture through a second ion exchange resin column;

thus retaining the catalyst in either the first ion exchange resin column, the second ion exchange resin column, or combinations of any thereof.

2. The method of claim 1, wherein the product mixture comprises an epoxidized vegetable oil.

3. The method of claim 1 or claim 2, wherein the catalyst comprises tungsten and phosphorous.

4. The method of claim 1 or claim 2, wherein the catalyst comprises a Venturello catalyst composed of a tri-negatively charged peroxophosphotungsten moiety and mono-positively charged phase transfer cation.

5. The method of claim 1 or claim 2, wherein the mono-positively charged phase transfer cation is a methyltrioctylammonium cation.

6. The method of claim 1 or claim 2, wherein the solvent comprises an organic solvent.

7. The method of claim 1 or claim 2, wherein the solvent comprises toluene.

8. The method of claim 1 or claim 2, wherein the first ion exchange resin column is a cation exchange resin column and the second ion exchange resin column is an anion exchange resin column.

9. The method of claim 8, wherein the cation exchange resin comprises a functional group selected from the group consisting of a monocarboxylic acid group, an acetic acid group, an iminodiacetic acid group, a sulfonic acid group, a phosphonic acid group, and combinations of any thereof.

10. The method of claim 8, wherein the anion exchange resin comprises a weak anion exchange resin.

11. The method of claim 10, wherein the weak anion exchange resin comprises a group selected from the group consisting of a primary amine group, a secondary amine group, a tertiary amine group, and combinations of any thereof.

12. The method of claim 8, wherein the anion exchange resin comprises a functional group selected from the group consisting of an H group, a CH_3 group, a CH_2CH group, and combinations of any thereof.

13. A method of separating a catalyst from a product mixture comprising:

diluting the product mixture with a solvent;

contacting the diluted product mixture with a first ion exchange resin; and

contacting the diluted product mixture with a second ion exchange resin;

thus retaining the catalyst in either the first ion exchange resin, the second ion exchange resin, or combinations of any thereof.

14. The method of claim 13, wherein the product mixture comprises an epoxidized vegetable oil, a catalyst, and combinations of any thereof.

15. The method of claim 13 or claim 14, wherein the catalyst comprises a Venturello catalyst.

16. The method of claim 13 or claim 14, wherein the solvent comprises an organic solvent.

17. The method of claim 13 or claim 14, wherein the solvent is selected from the group consisting of ethanol, toluene, and combinations of any thereof.

18. The method of claim 13 or claim 14, wherein the solvent is combined with the product mixture in a ratio of 3:1 volume/volume.

19. The method of claim 13, wherein the first ion exchange resin is an anion exchange resin and the second ion exchange resin is a cation exchange resin.

20. The method of claim 13, wherein the first ion exchange resin is a cation exchange resin and the second ion exchange resin is an anion exchange resin.

21. The method of claim 19 or claim 20, wherein the anion exchange resin comprises an $N^+R_2HCl^-$ group.

22. The method of claim 13, wherein the contacting the diluted product with the first ion exchange resin is achieved by a method selected from the group consisting of shaking the first ion exchange resin with the diluted product mixture, stirring the first ion exchange resin with the diluted product mixture, and passing the diluted product mixture through a column packed with the first ion exchange resin.

23. The method of claim 13, wherein the contacting the diluted product mixture with the second ion exchange resin is achieved by a method selected from the group consisting of shaking the second ion exchange resin with the diluted product mixture, stirring the second ion exchange resin with the diluted product mixture, and passing the diluted product mixture through a column packed with the second ion exchange resin.

24. The method of claim 22 or claim 23, wherein the passing the diluted product mixture through a column packed with the first ion exchange resin and the passing the diluted product mixture through a column packed with the second ion exchange resin is at a rate of from about 2 bed volumes (BV)/hour to about 4 bed volumes (BV)/hour.

25. The method of claim 13 or claim 14, wherein the first ion exchange resin and the second ion exchange resin are contained in two, successive single bed resin columns.

26. The method of claim 13 or claim 14, wherein the first ion exchange resin and second ion exchange resin are contained in a double bed resin column.

27. The method of claim 13 or claim 14, further comprising recovering the catalyst from the first ion exchange resin, the second ion exchange resin, or combinations of any thereof.

28. The method of claim 27, wherein the recovering the catalyst from the first ion exchange resin, the second ion exchange resin, or combinations of any thereof comprises contacting the first ion exchange resin, the second ion exchange resin, or combinations of any thereof with a base.

29. The method of claim 28, wherein the base is selected from the group consisting of sodium hydroxide, ammonium hydroxide, sodium bicarbonate, ammonium bicarbonate, and combinations of any thereof.

30. The method of claim 28 or claim 29, wherein the base has a concentration of at least 1 Normal.

31. The method of claim 28, wherein the base has a concentration of between about 1 Normal and about 8 Normal.

32. The method of claim 13 or claim 14, wherein the first ion exchange resin and the second ion exchange resin are present in equal amounts.

33. The method of claim 13 or claim 14, wherein the first ion exchange resin and the second ion exchange resin ranges from a total combined weight of about 4 grams to about 80 grams.

34. A method of recovering a catalyst from an epoxidized vegetable oil product mixture comprising:

diluting the epoxidized vegetable oil product mixture with an organic solvent;

wherein the epoxidized vegetable oil product mixture comprises the catalyst;

eluting the diluted epoxidized vegetable oil product mixture through a double bed resin column;

wherein the double bed resin column is packed with an anion exchange resin and a cation exchange resin; and

eluting a solution through the double bed resin column;

thus collecting the catalyst.

35. The method of claim 34, wherein the catalyst comprises tungsten and phosphorous.

36. The method of claim 34 or claim 35, wherein the catalyst comprises a Venturello catalyst.

37. The method of claim 34 or claim 35, wherein the anion exchange resin comprises a weakly basic, macroporous anion exchange resin.

38. The method of claim 34 or claim 35, wherein the cation exchange resin comprises a weakly acidic, macroporous cation exchange resin with chelating iminodiacetate groups.

39. The method of claim 34 or claim 35, wherein the solution comprises a base selected from the group consisting of sodium hydroxide, ammonium hydroxide, sodium bicarbonate, ammonium bicarbonate, and combinations of any thereof.

40. The method of claim 34 or claim 35, wherein the solution comprises ammonium bicarbonate.

41. The method of claim 34 or claim 35, wherein the solution comprises an aqueous solution of a salt selected from the group consisting of KI, KBr, KCl, KOH, KNO_3, $KHCO_3$, $KHSO_4$, KCH_3COO, NaI, NaBr, NaCl, NaOH, $NaNO_3$, $NaHCO_3$,

$NaHSO_4$, $NaCH_3COO$, NH_4I, NH_4Br, NH_4Cl, NH_4OH, NH_4HCO_3, NH_4HSO_4, NH_4CH_3COO, CaI, CaBr, CaCl, CaOH, $CaNO_3$, $CaHCO_3$, $CaHSO_4$, $CaCH_3COO$, MgI, MgBr, MgCl, MgOH, $MgNO_3$, $MgHCO_3$, $MgHSO_4$, $MgCH_3COO$, and combinations of any thereof.

42. The method of claim 34 or claim 35, wherein the anion exchange resin is packed on top of the cation exchange resin.

43. The method of claim 34 or claim 35, wherein the anion exchange resin and the cation exchange resin are present in equal amounts.

44. The method of claim 34 or claim 35, wherein the anion exchange resin and the cation exchange resin are present in a total amount of from about 4 grams to about 80 grams.

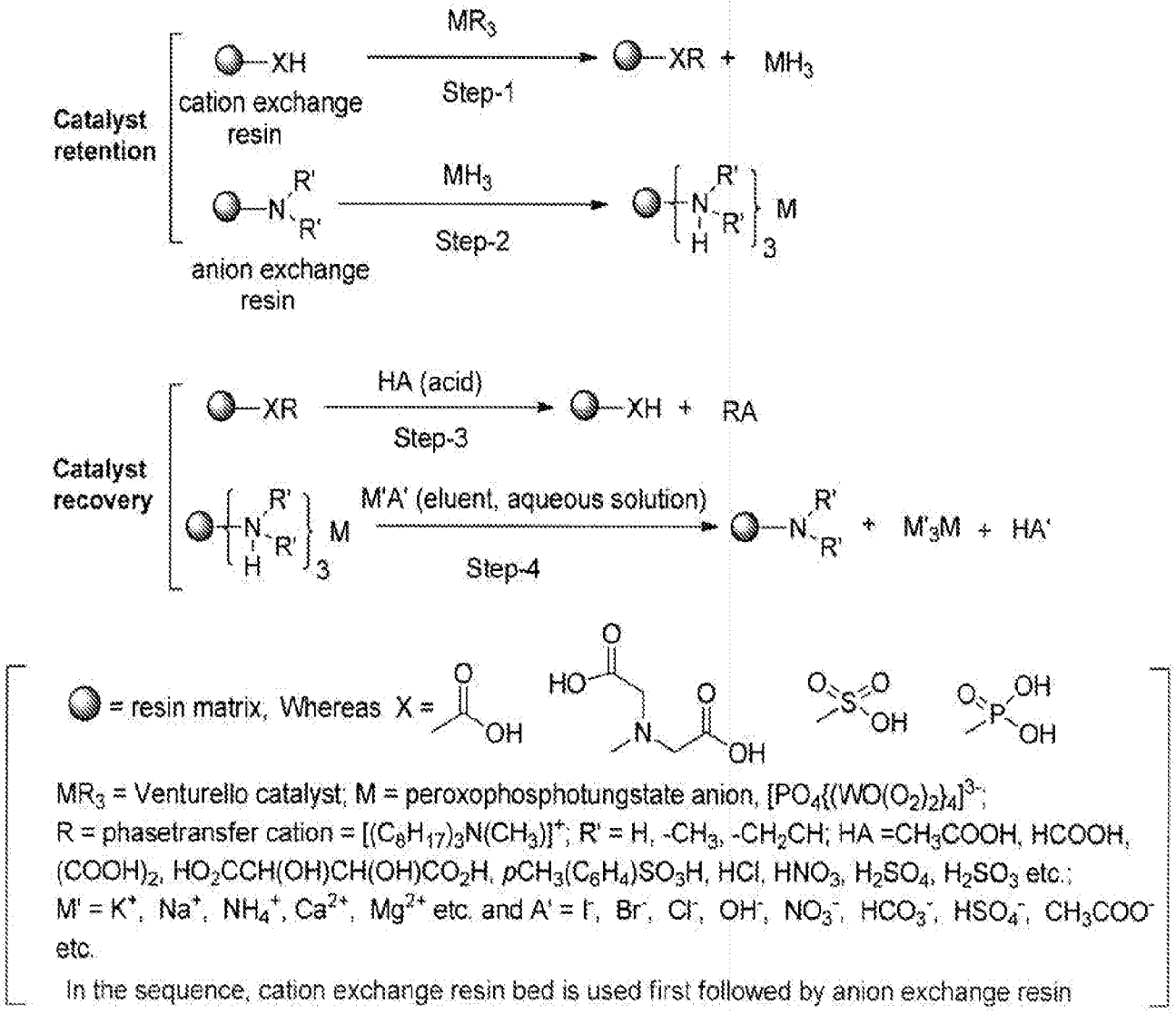
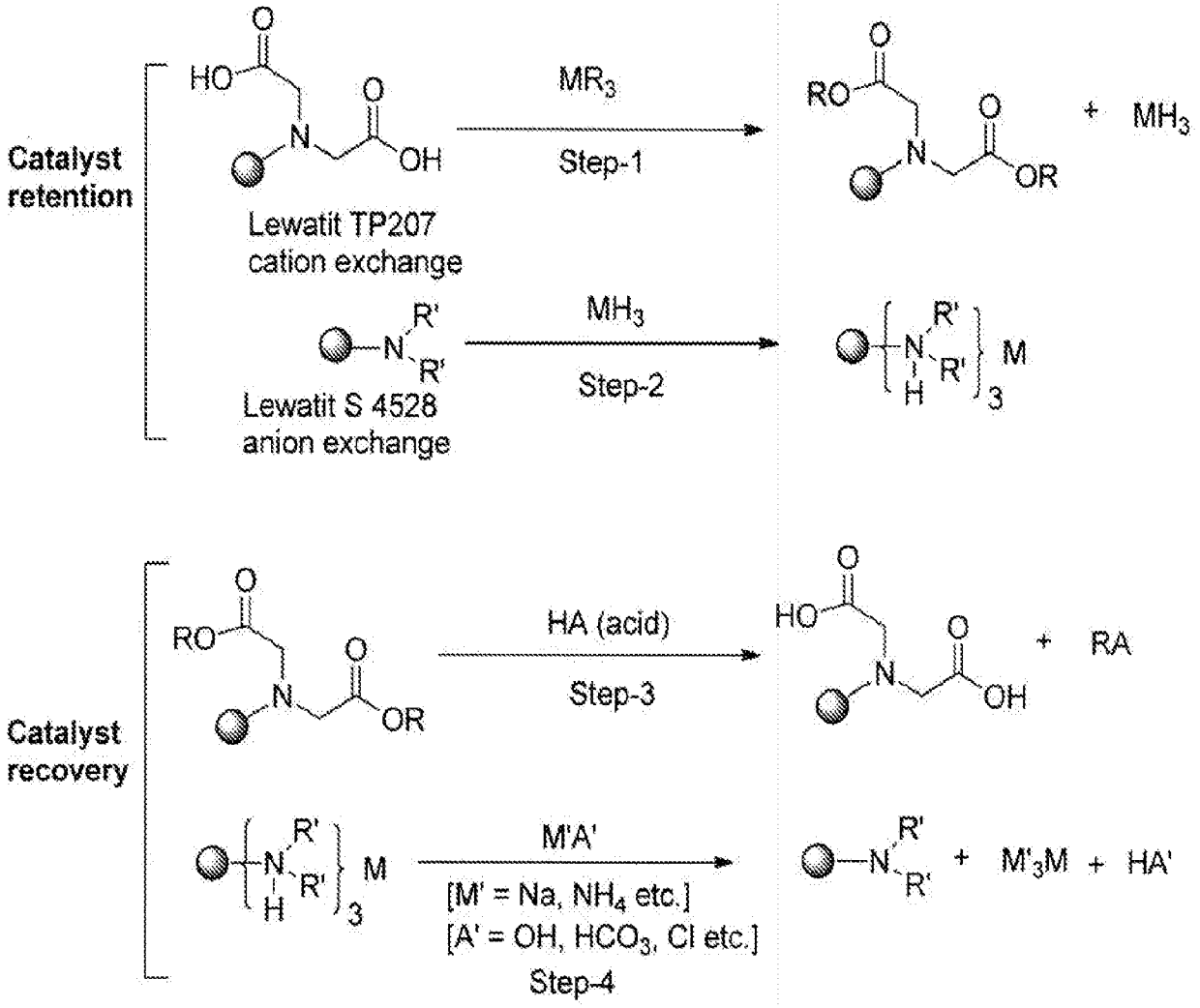


Fig. 1: General Scheme for Catalyst Retention and Recovery Using a Cation Exchange Resin Followed by an Anion Exchange Resin When Functional Group of Anion Exchange Resin is Either Primary, Secondary or Tertiary Amine Group



MR_3 = Venturello catalyst; M = peroxophosphotungstate anion, $[PO_4\{(WO(O_2)_2\}_4]^{3-}$;
R = phasetransfer cation = $[(C_8H_{17})_3N(CH_3)]^+$; R' = H, $-CH_3$, $-CH_2CH_3$; HA = CH_3COOH
In the sequence, cation exchange resin bed is used first followed by anion exchange resin

Fig. 1a: Scheme for Catalyst Retention and Recovery Using a Specific Cation Exchange Resin Followed by an Anion Exchange Resin

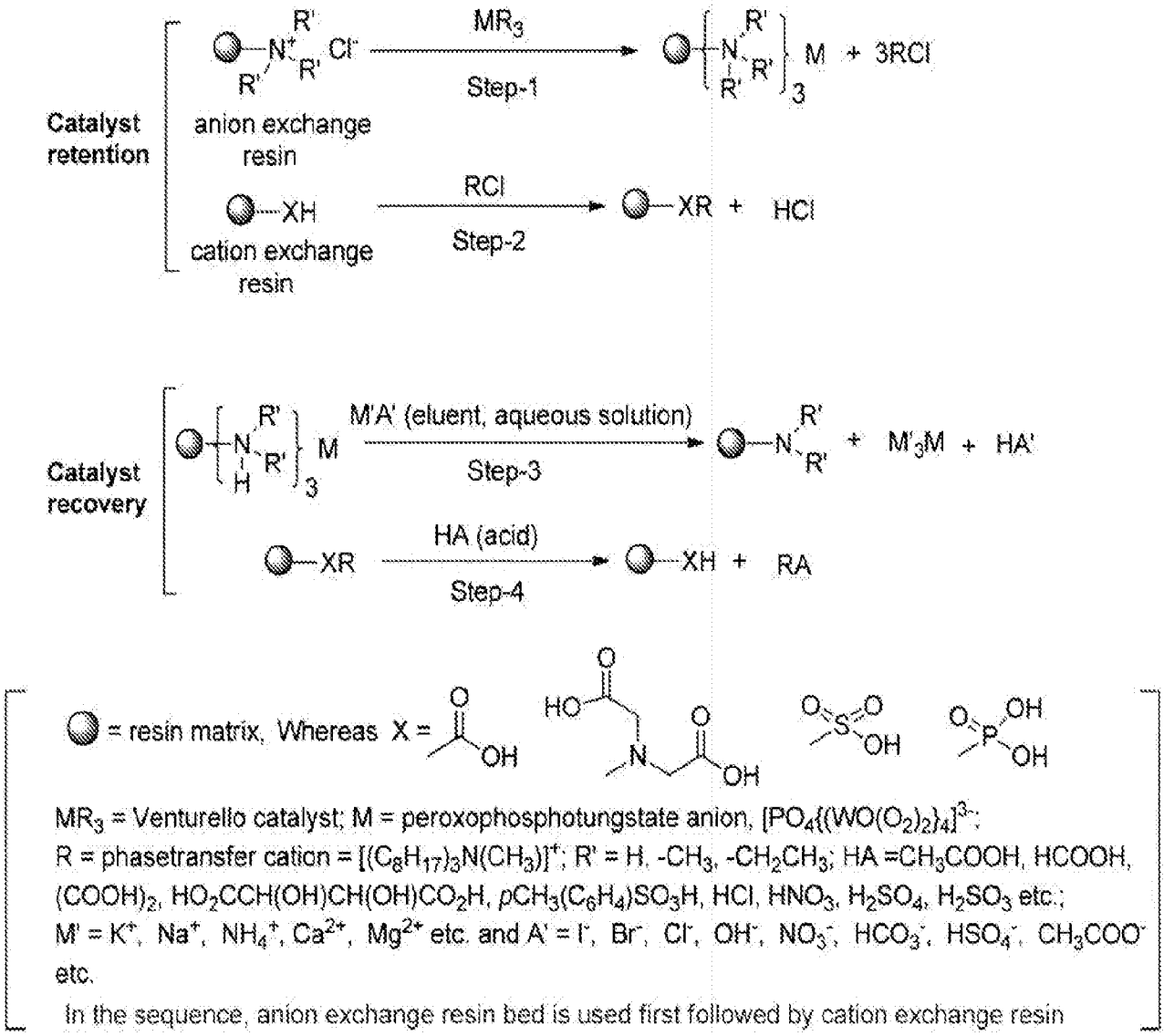


Fig. 2: General Scheme for Catalyst Retention and Recovery Using a Anion Exchange Resin Followed by a Cation Exchange Resin When Functional Group of Anion Exchange Resin is a Quaternary Ammonium Group

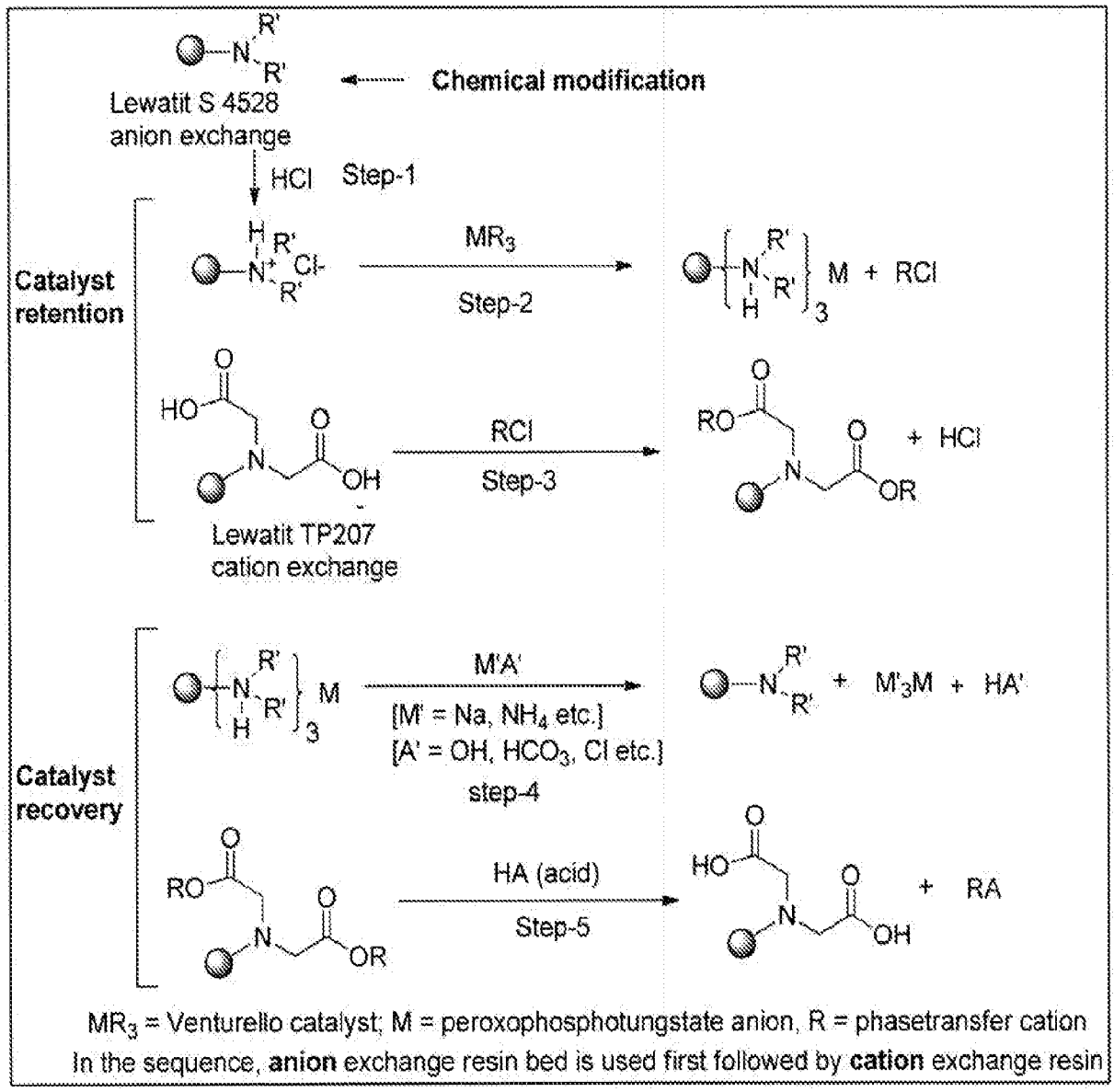
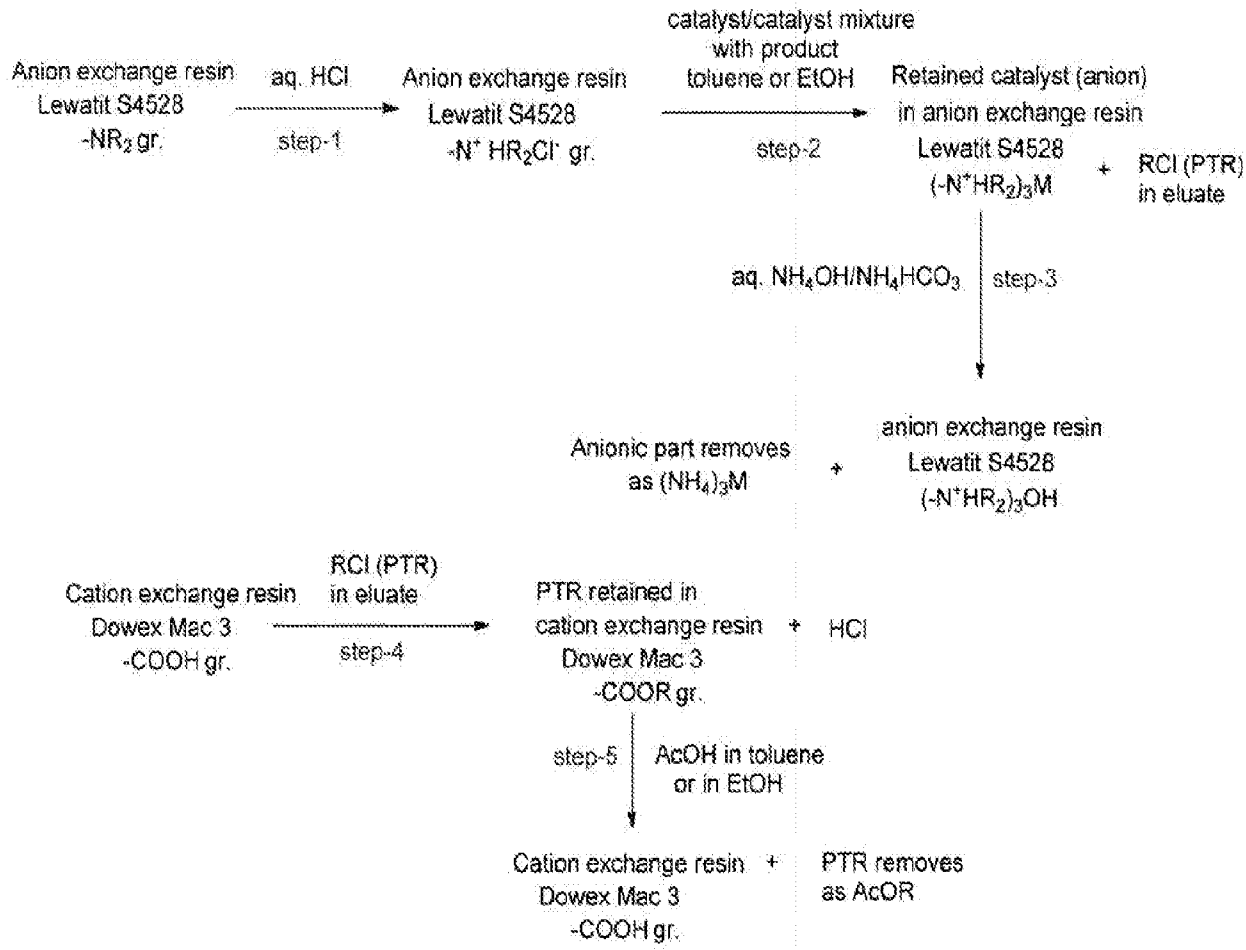


Fig. 2a: Scheme for Catalyst Retention and Recovery Using an Anion Exchange Resin Followed by a Cation Exchange Resin



MR_3 = Venturello catalyst; M = peroxophosphotungstate anion, R = phasetransfer cation
In the sequence, anion exchange resin bed is used first followed by cation exchange resin
Flow rate was maintained around 4 bed volume (wet)/h under gravity. Double bed resin
can be used following same sequence. This scheme is also applicable for removing catalyst
under stirring /shaking condition.

Fig. 3: Scheme for Retention and Removal of Catalyst Using a Single Bed Resin Column

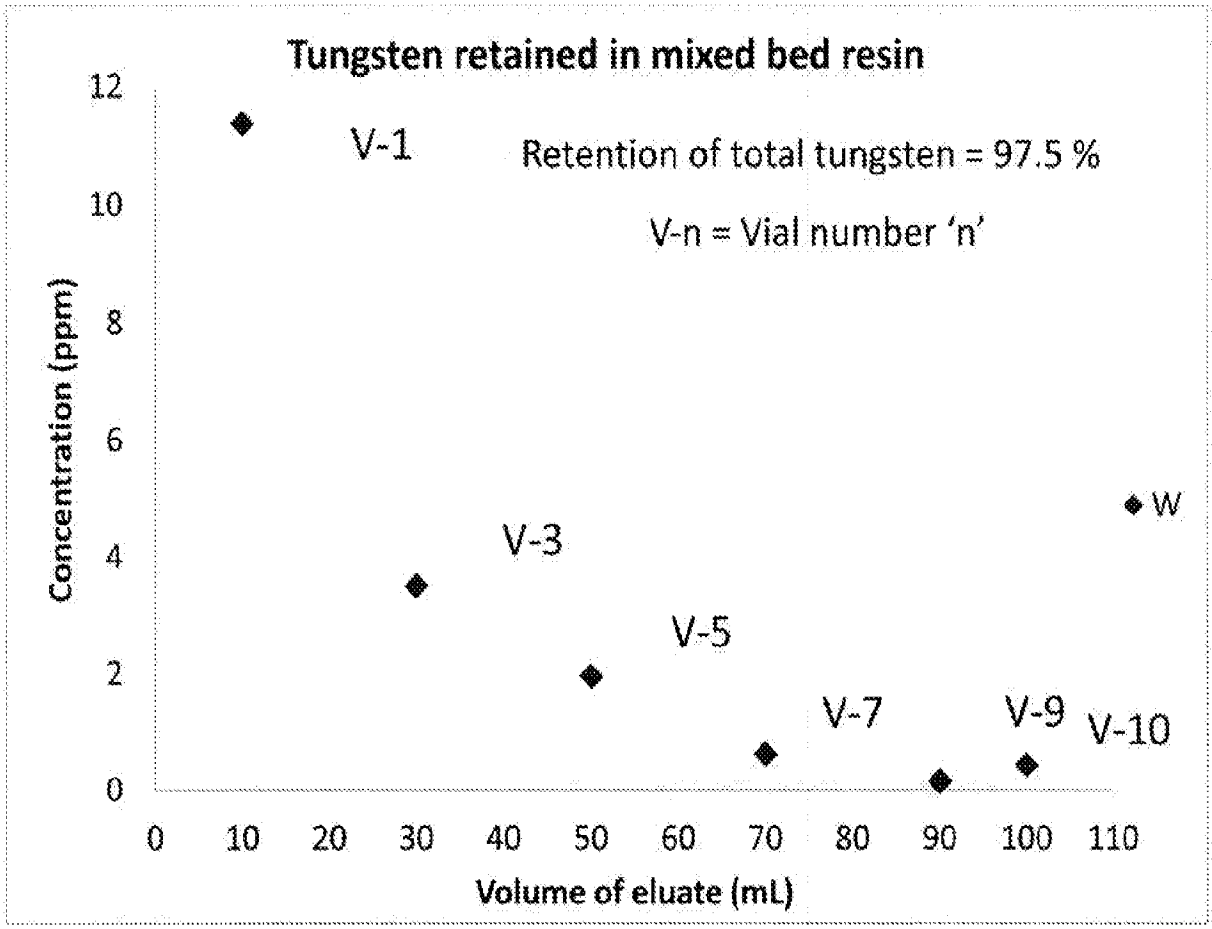


Fig. 4: Catalyst Separation Using Cation Exchange Resin Followed by Anion Exchange resin – Mixed Bed Resin System

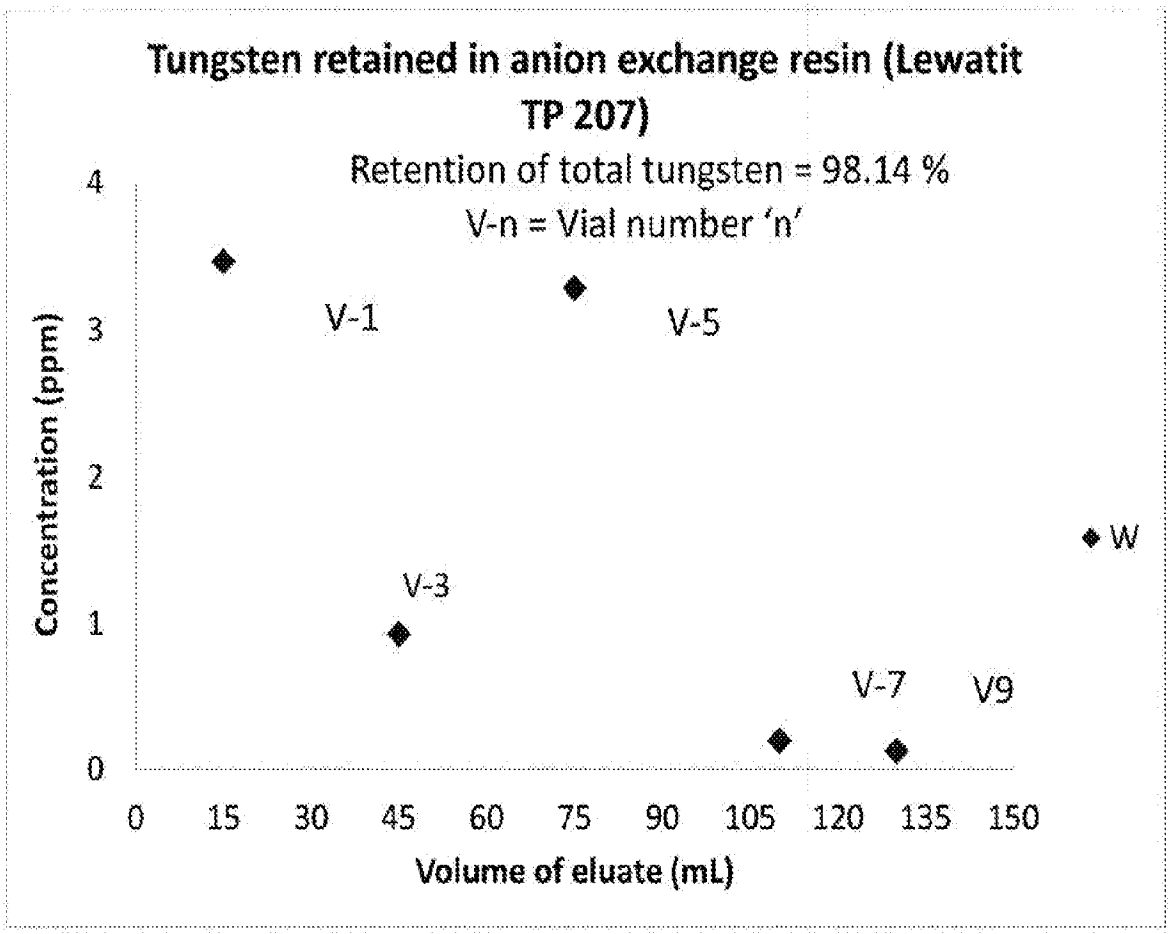


Fig. 5: Catalyst Separation Using Cation Exchange Resin Followed by Anion Exchange resin – Single Bed Resin System

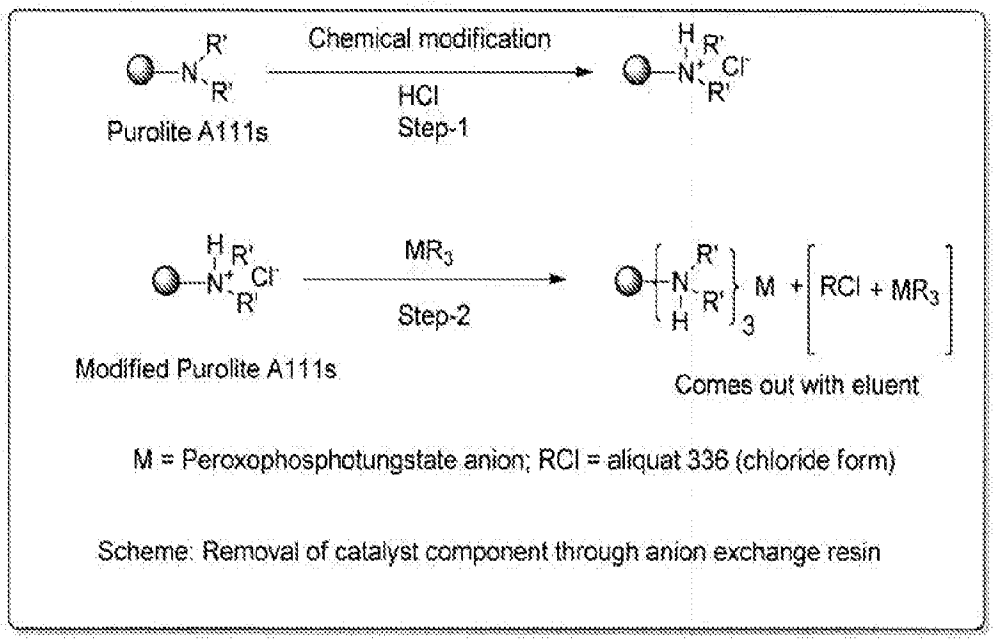


Fig. 6: Scheme for removal of Venturello catalyst component using anion exchange resin

Calculation:

Let, absorbed catalyst = x %, so, isolated catalyst = (1-x) %, isolated PTR (aliquat 336) = x %

y = total mass removed, z = mass of total catalyst taken, Mol. wt. of catalyst = 2256.4 g/mol.

Mol. wt. of PTR = 404 g/mol, PTR/cat. = 0.537

[PTR = Phase transfer reagent, cat = catalyst (Venturello)]

So, $0.537xz + (1-x) = y$

Catalyst absorbed/retained (x) = $\{[1-(y/z)]/0.463\}\times 100$ %

Fig. 7: Scheme for calculation of catalyst absorbed/retained in the resin (Gravimetric Method/Analysis)

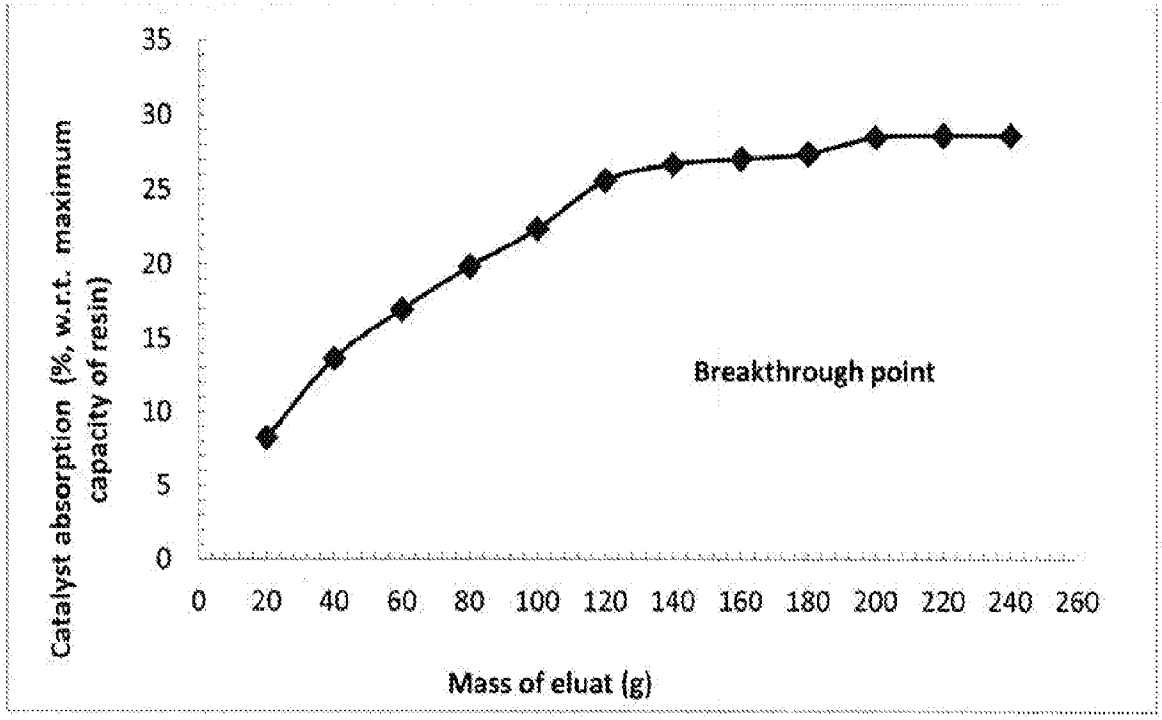


Fig. 8: Breakthrough Curve for Absorption/Retention of Catalyst Using Purolite® A111S (-$NR_3H^+Cl^-$ form) Anion Exchange Resin

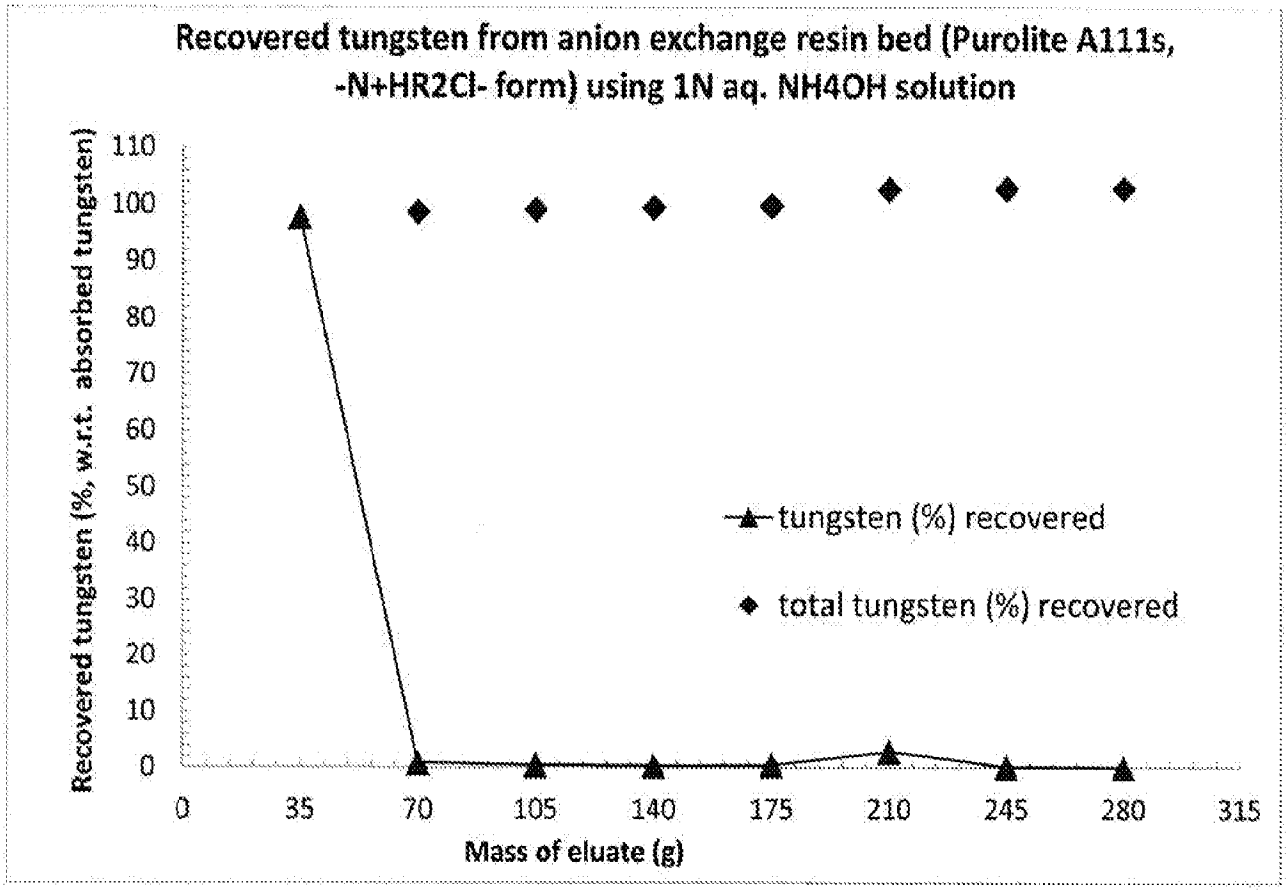


Fig. 9: Recovered Tungsten from Anion Exchange Resin Bed (Purolite® A111S, -$N^+HR_2Cl^-$ form)

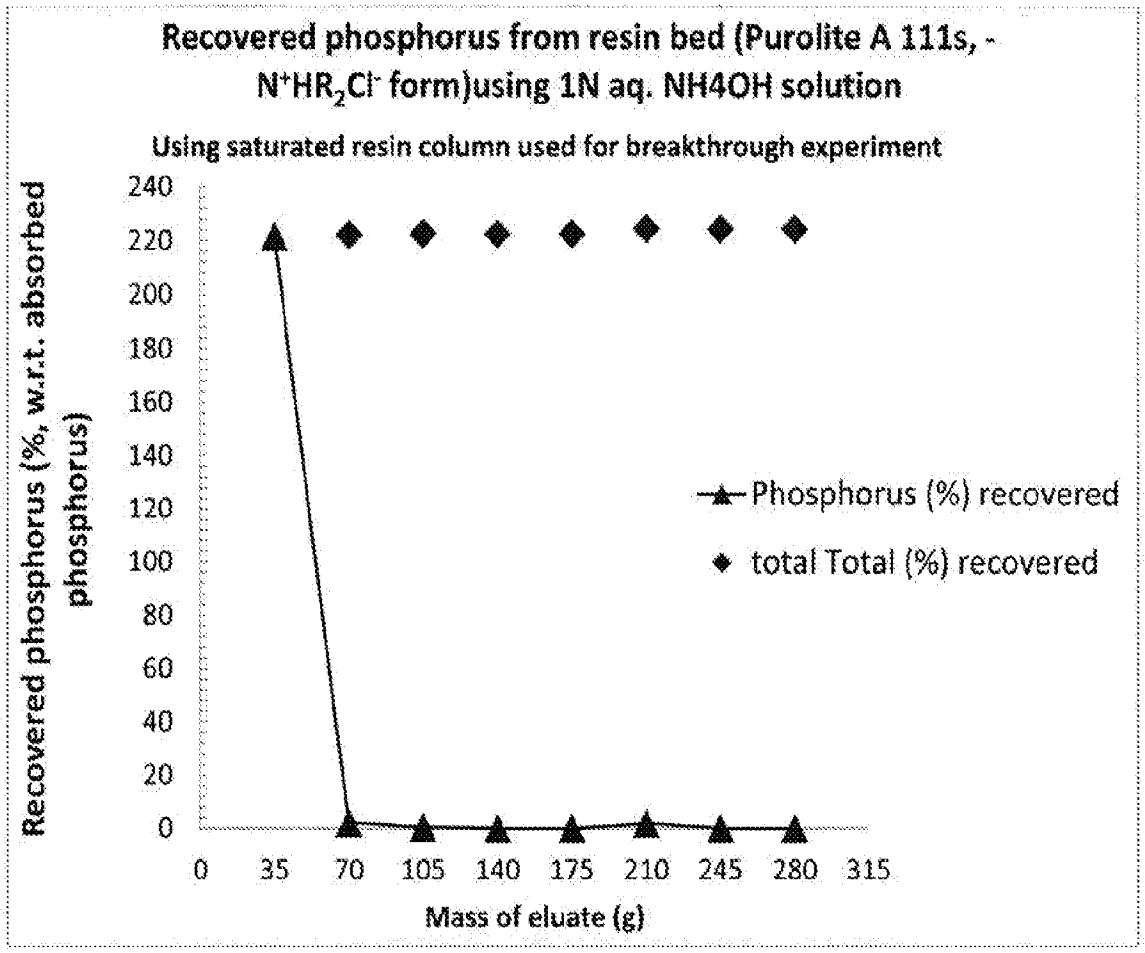
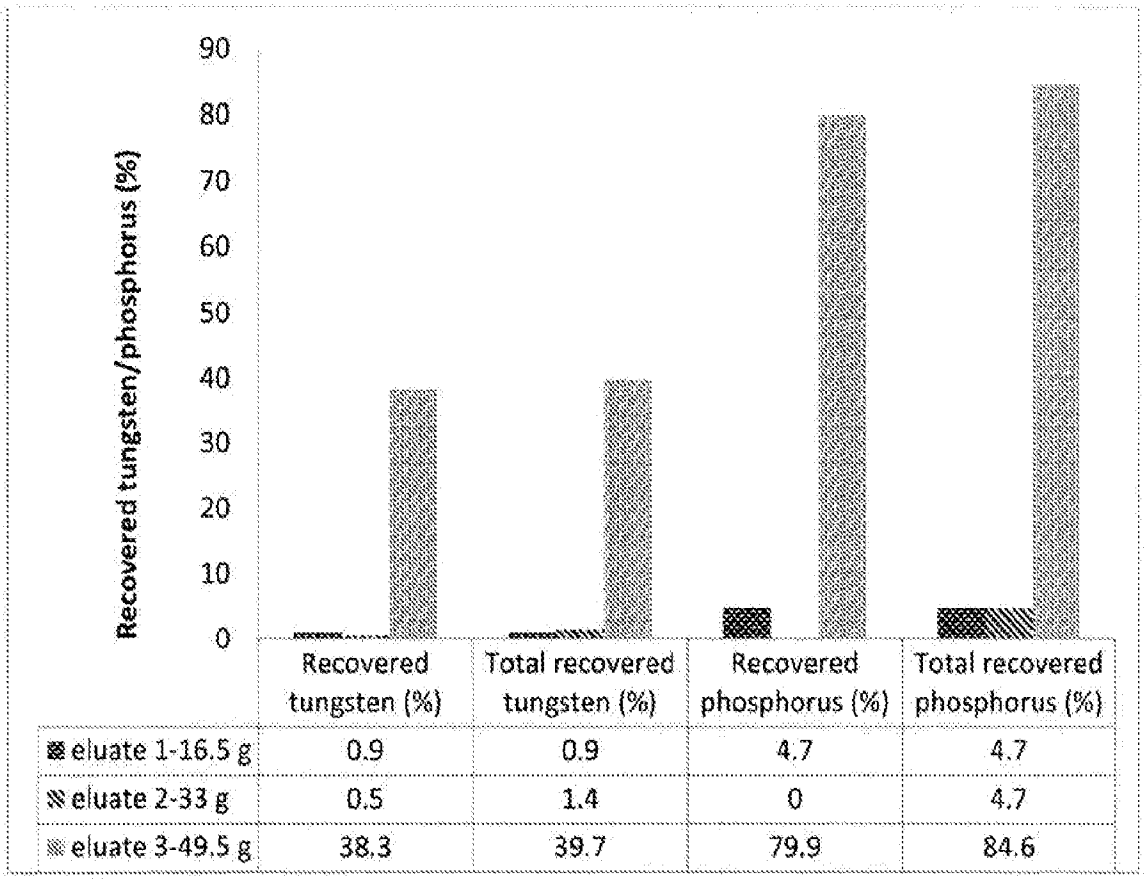
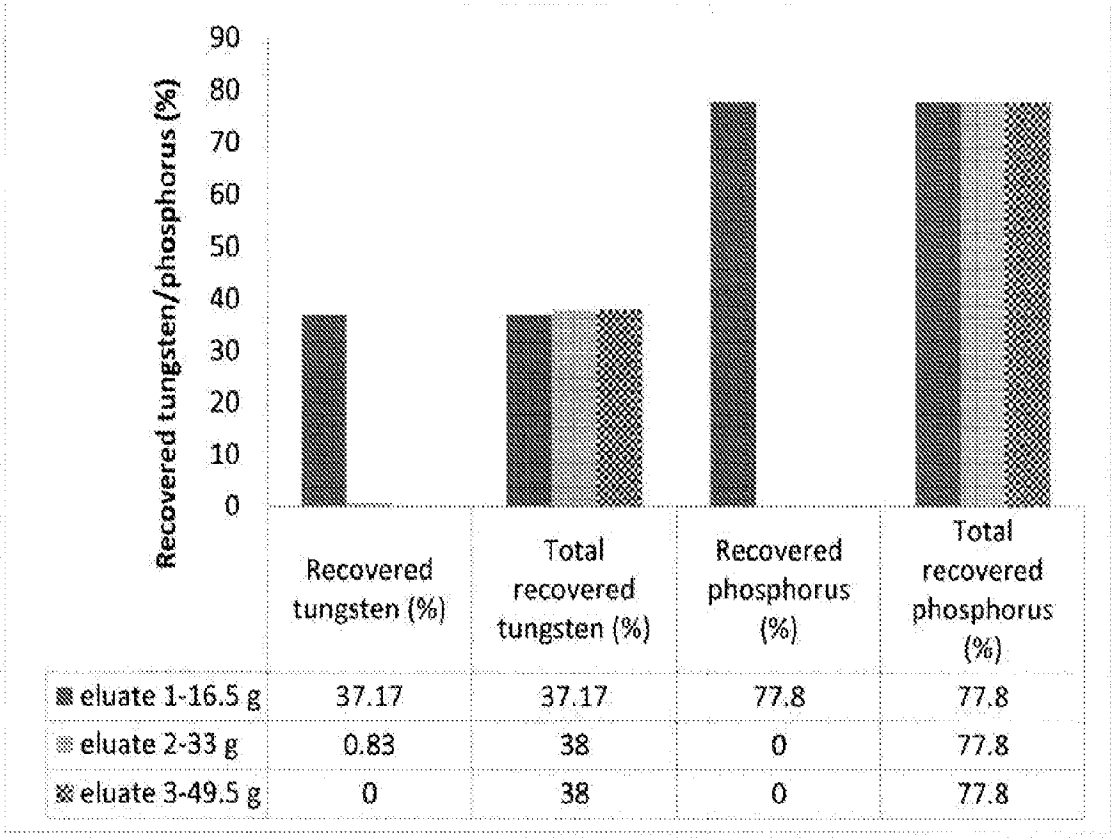


Fig. 10: Recovered Phosphorous from Anion Exchange Resin Bed (Purolite® A111S, - $N^+HR_2Cl^-$ form)



	Recovered tungsten (%)	Total recovered tungsten (%)	Recovered phosphorus (%)	Total recovered phosphorus (%)
eluate 1-16.5 g	0.9	0.9	4.7	4.7
eluate 2-33 g	0.5	1.4	0	4.7
eluate 3-49.5 g	38.3	39.7	79.9	84.6

Fig. 11: Recovery of Tungsten and Phosphorous from Anion Exchange Resin (Purolite® A111S, $-N^{+}HR_2Cl^{-}$ form)



	Recovered tungsten (%)	Total recovered tungsten (%)	Recovered phosphorus (%)	Total recovered phosphorus (%)
eluate 1-16.5 g	37.17	37.17	77.8	77.8
eluate 2-33 g	0.83	38	0	77.8
eluate 3-49.5 g	0	38	0	77.8

Fig. 12: Recovery of Tungsten and Phosphorous from Anion Exchange Resin (Purolite® A111S, $-N^+HR_2Cl^-$ form)

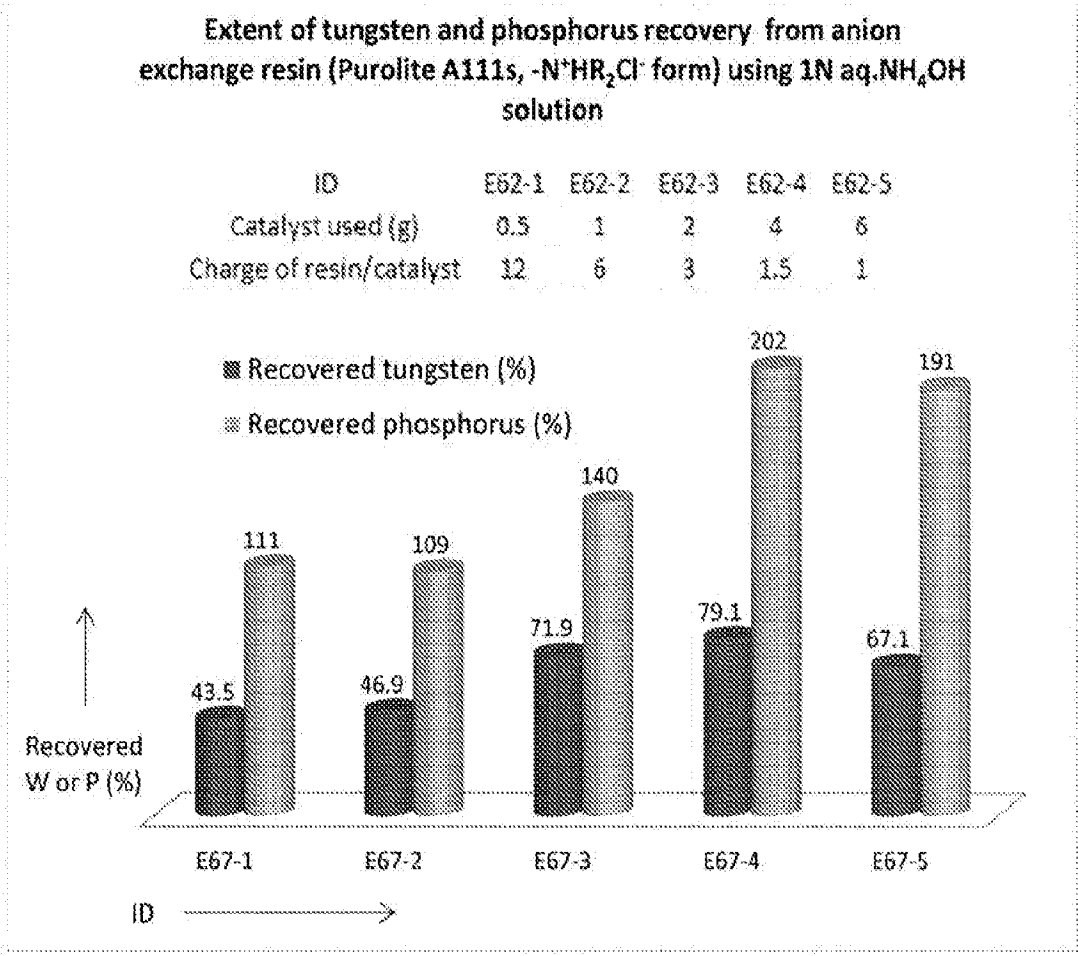


Fig. 13: Extent of Tungsten and Phosphorous Recovery from Anion Exchange Resin (Purolite® A111S, -$N^+HR_2Cl^-$ form)

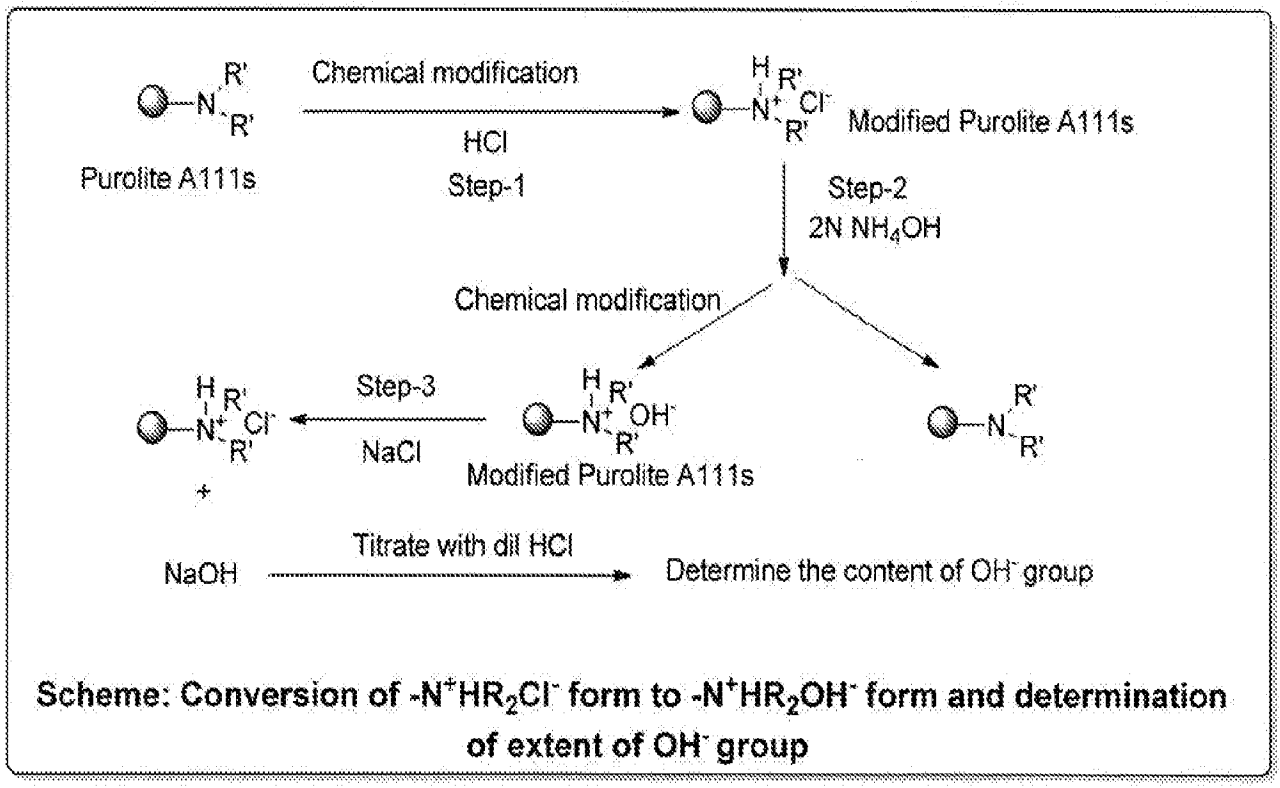


Fig. 14: Scheme for Conversion of $-N^{+}HR_2Cl^{-}$ form to $-N^{+}HR_2OH^{-}$ form

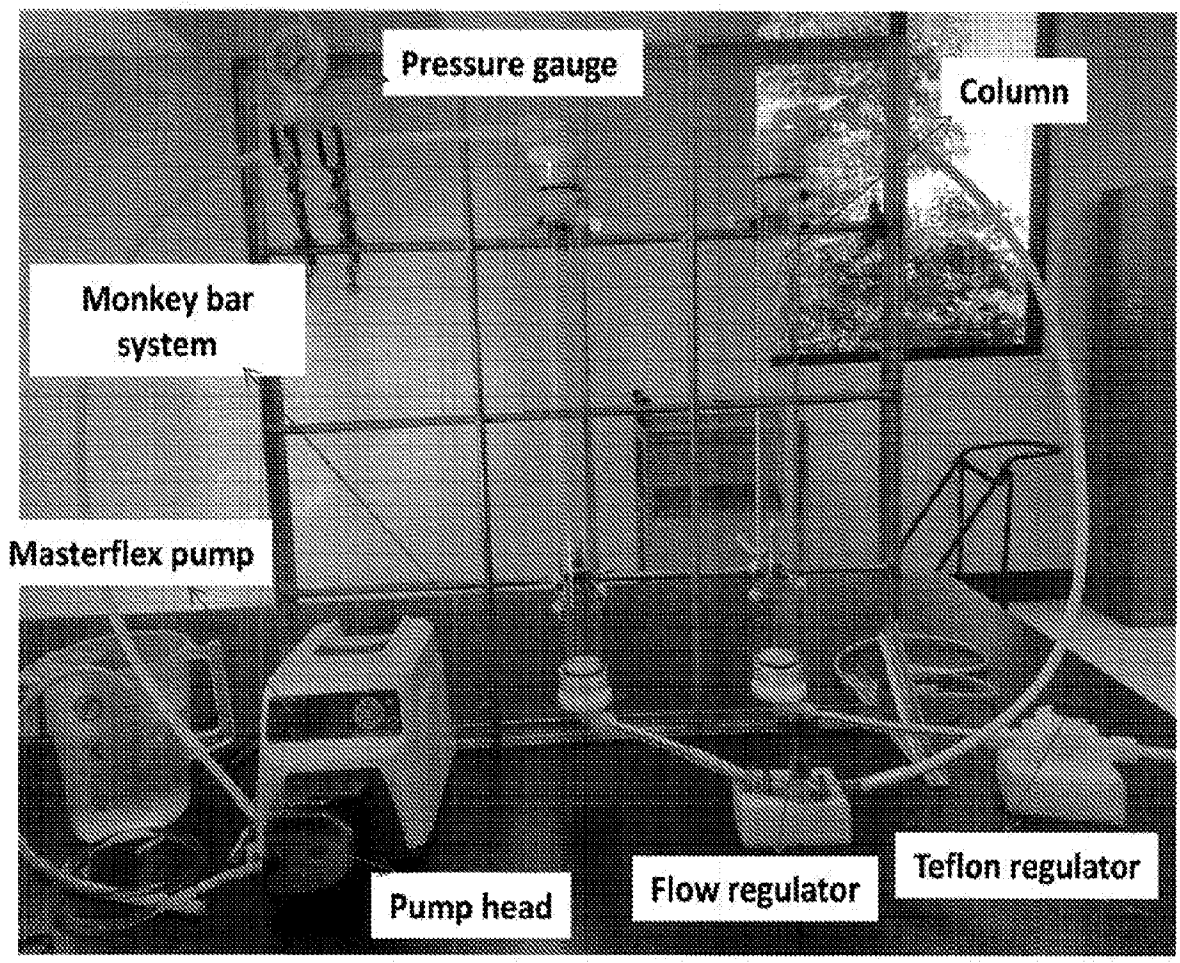


Fig. 15: Resin Bed Set-up

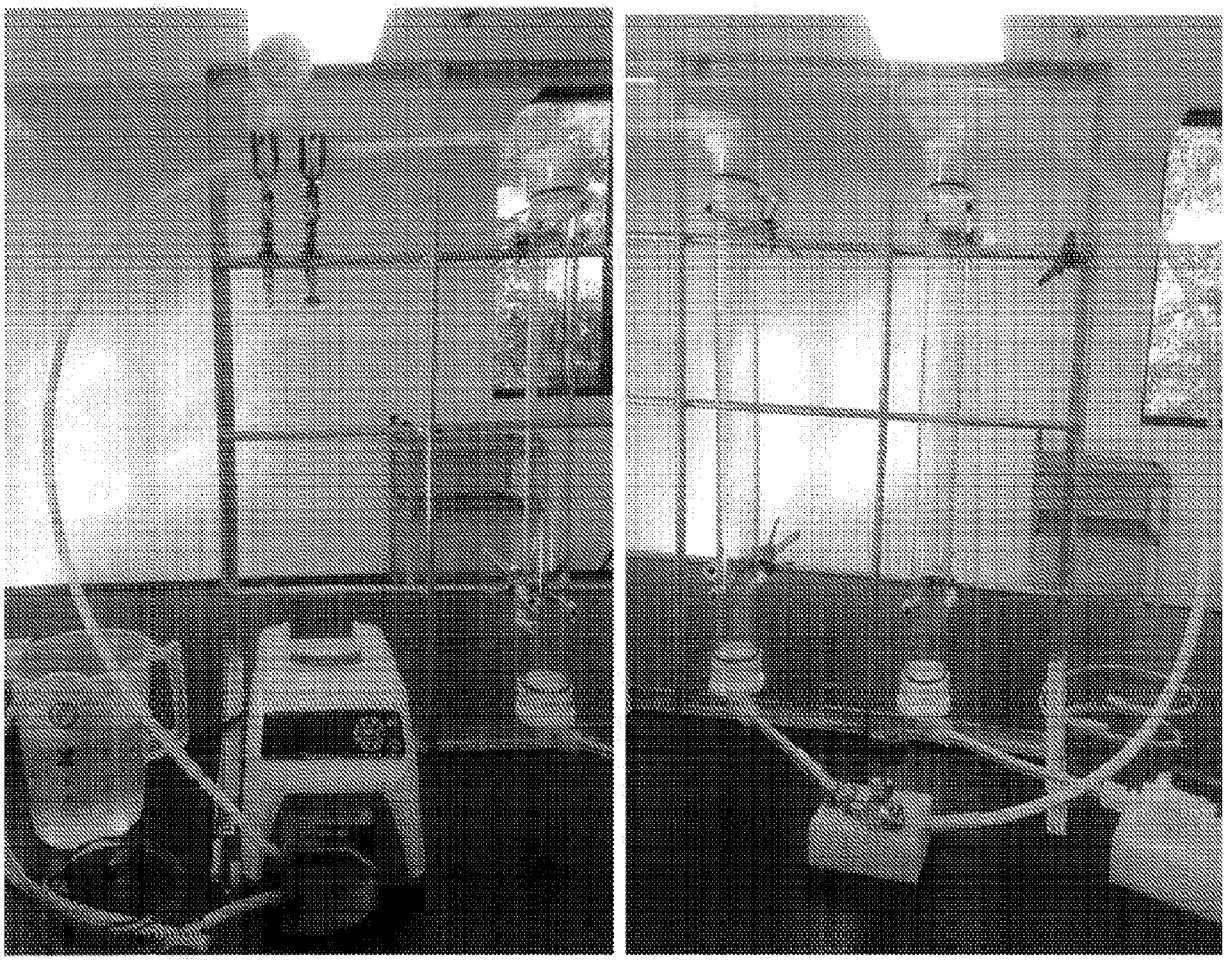


Fig. 16: Additional Views of Resin Bed Set-up

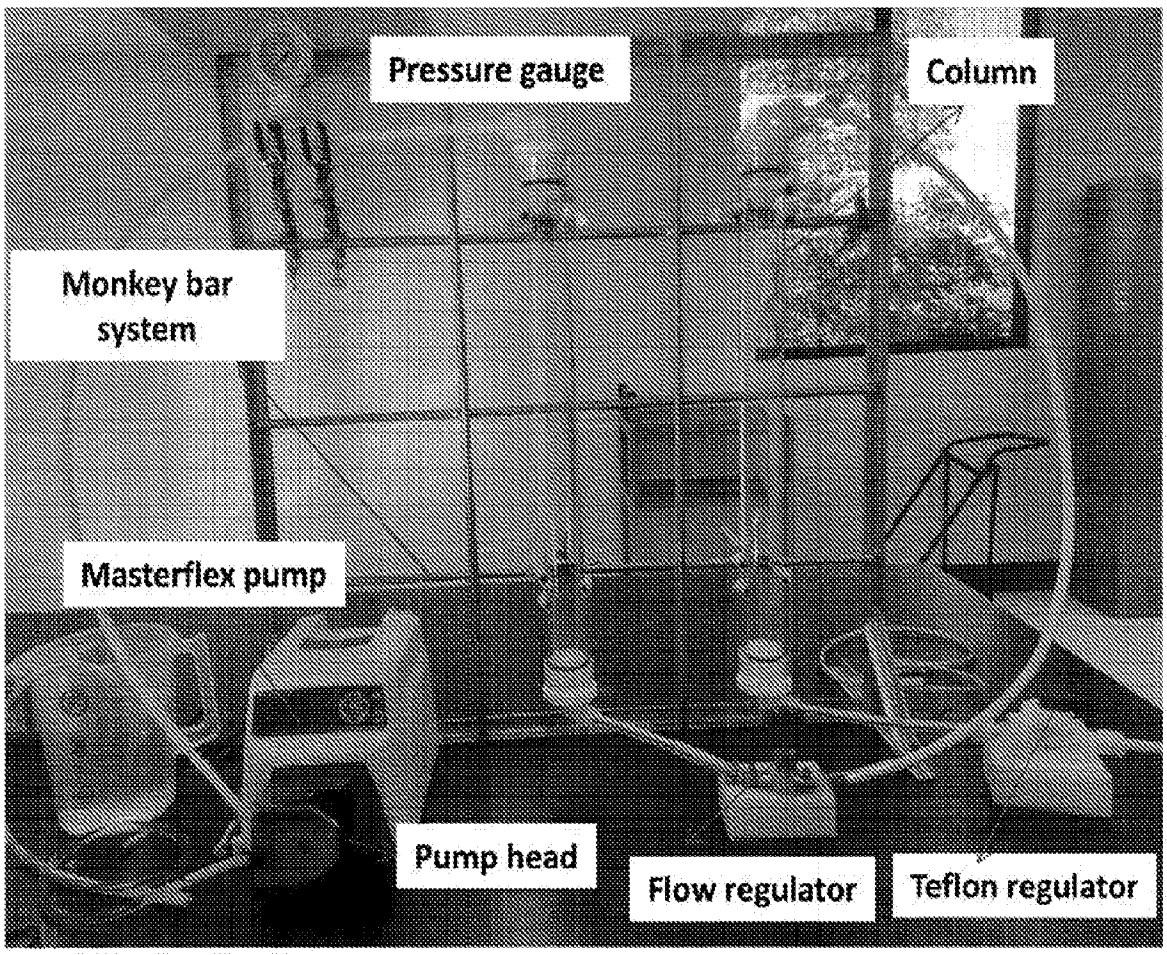


Fig. 17: Additional View of Resin Bed Set-Up

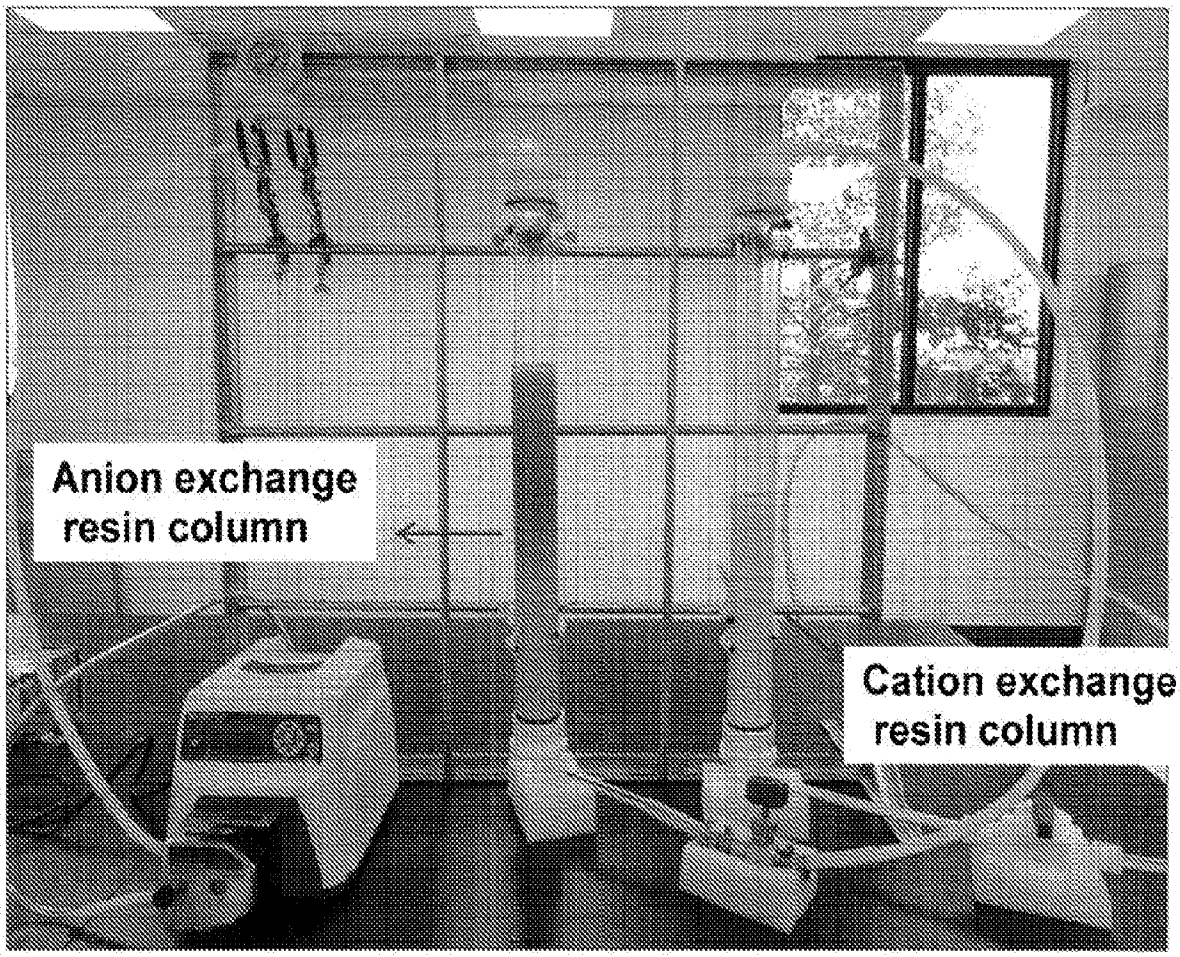


Fig. 18: Additional View of Resin Bed Set-Up

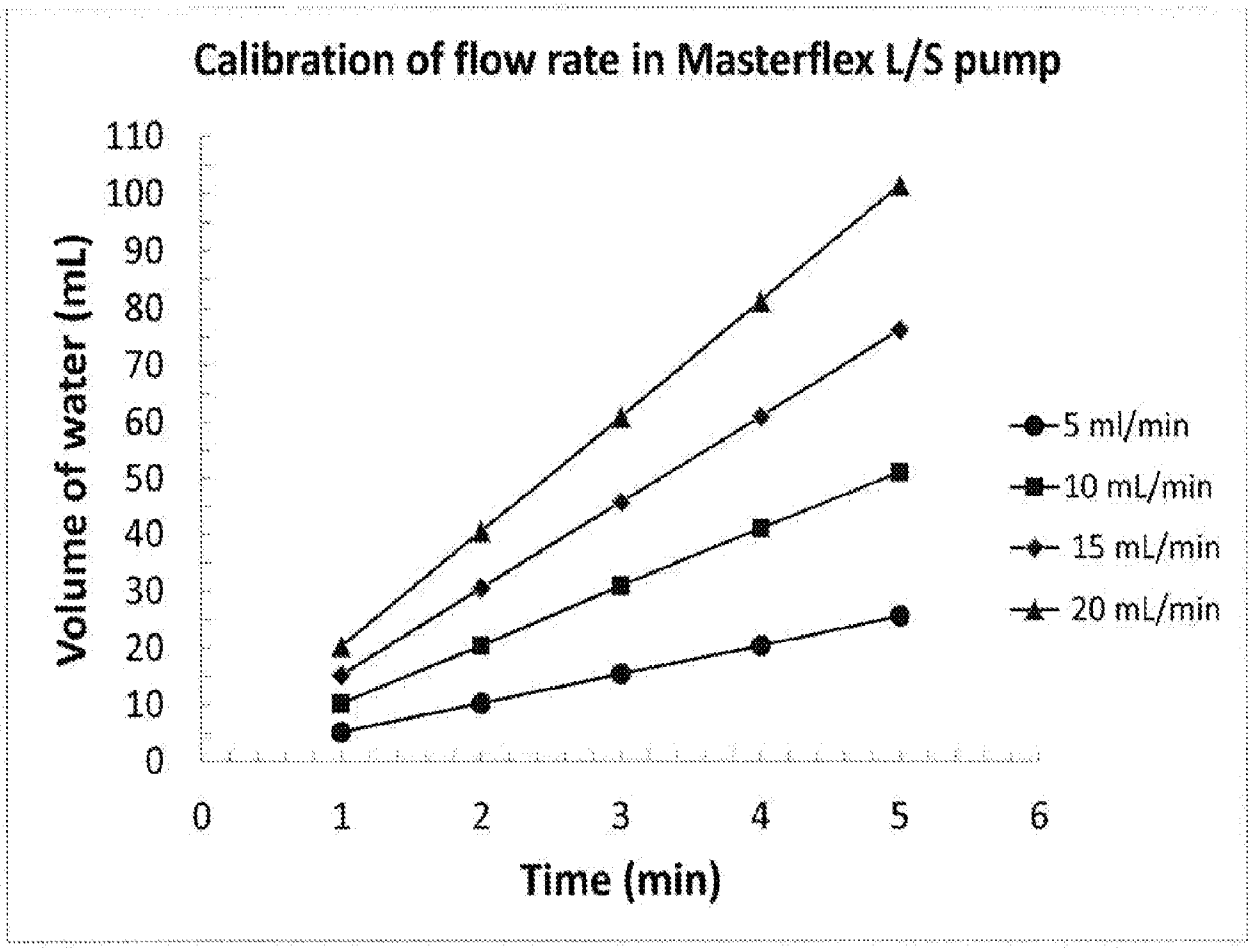


Fig. 19: Calibration of Flow Rate of Masterflex L/S Pump

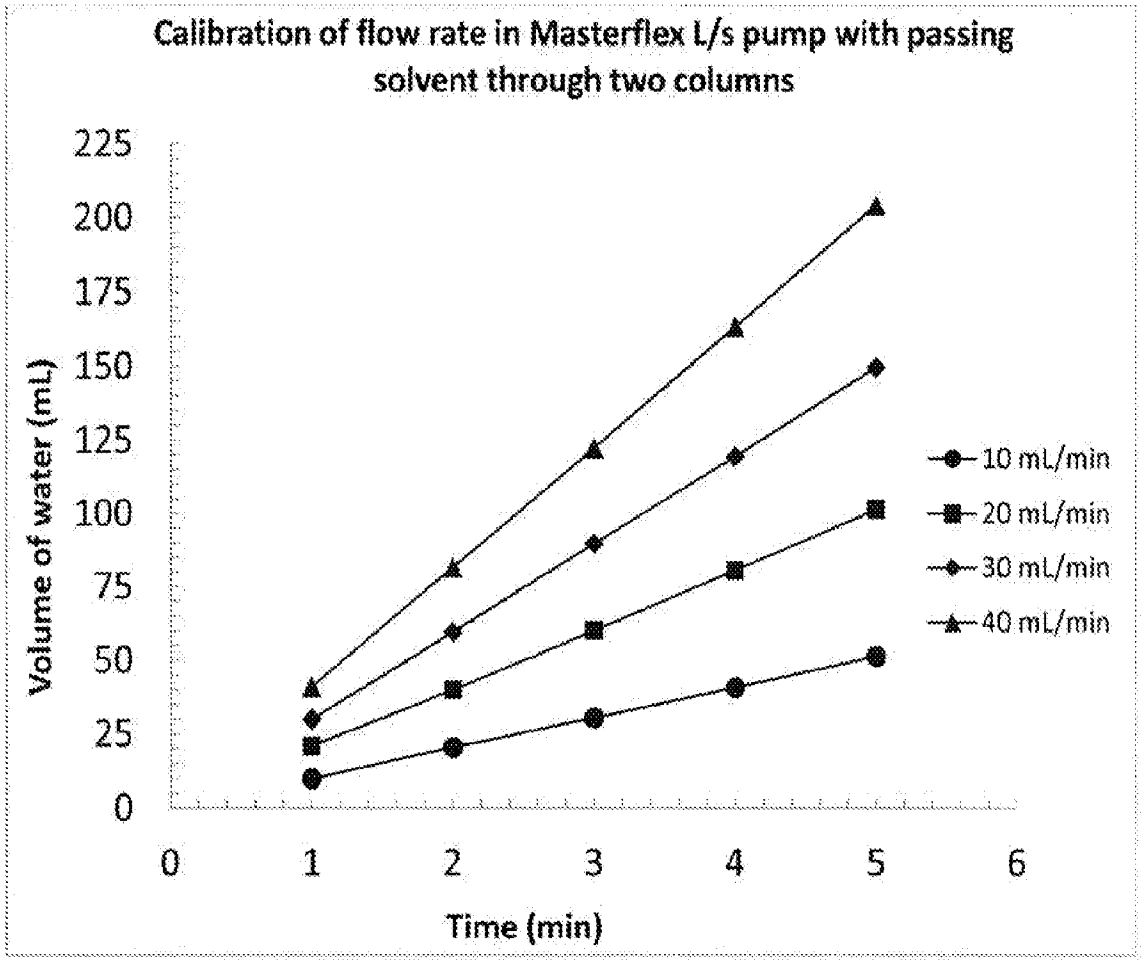


Fig. 20: Calibration of Flow Rate of Masterflex L/S Pump through 2 Columns

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US17/14290

A. CLASSIFICATION OF SUBJECT MATTER
IPC - B01J 38/74, 39/04, 39/08, 41/08, 43/00; C07B 61/00; C07C 51/47 (2017.01)
CPC - B01J 31/4015, 31/4053, 38/74, 39/08, 41/08, 43/00; C07C 51/47

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)
See Search History document

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

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X --- Y	WO 01/12318 A1 (MOBILE PROCESS TECHNOLOGY, CO.) 22 February 2001; abstract; figure 1; page 5, lines 20-35; page 6, lines 5-30; page 11, lines 5-20; page 14, lines 5-20; page 15, lines 1-2, 26-31; page 16, lines 10-25; page 19, lines 5-20; page 20, lines 1-25; claims 1, 48, 51-52	1, 8/1, 10/8/1, 11/10/8/1, 12/8/1, 13-14, 19-20, 21/19-20, 22-23, 24/22-23, 25/13-14, 27/13-14, 28/27/13-14, 29/28/27/13-14 ---- 2, 3/1-2, 4/1-2, 5/1-2, 6/1-2, 7/1-2, 8/2, 9/8/1-2, 10/8/2, 11/10/8/2, 12/8/2, 15/13-14, 16/13-14, 17/13-14, 18/13-14, 26/13-14, 31/28/27/13-14, 32/13-14, 33/13-14, 34-35, 36/34-25, 37/34-35, 38/34-35, 39/34-35, 40/34-35, 41/34-35, 42/34-35, 43/34-35, 44/34-35
X -- Y	US 5,773,665 A (SILVERMAN, GS et al.) 30 June 1998; abstract; figure 1; column 9, lines 55-60; column 11, lines 25-60; column 13, lines 40-55; column 14, lines 1-15; column 15, lines 57-60	1, 6/1, 7/1 ---- 6/1-2, 7/1-2, 16/13-14, 17/13-14, 18/13-14, 33/13-14, 42/34-35

☒ 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	Date of mailing of the international search report
27 February 2017 (27.02.2017)	07 APR 2017
Name and mailing address of the ISA/ Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-8300	Authorized officer Shane Thomas PCT Helpdesk: 571-272-4300 PCT OSP: 571-272-7774

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US17/14290

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	(WU, J et al.) Peroxopolyoxotungsten-based ionic hybrid as a highly efficient recyclable catalyst for epoxidation of vegetable oil with H2O2. Bulletin of the Korean Chemical Society. Vol. 35. No. 6. 2014; abstract; 1675, column 1, paragraph 1; page 1676, column 1, paragraph 6; page 1676, column 2, paragraph 2; page 1677, column 2, paragraph 3	2, 3/1-2, 4/1-2, 5/2, 6/2, 7/2, 8/2, 9/8/2, 10/8/2, 11/10/8/2, 12/8/2, 15/13-14, 35, 36/34-35, 37/35, 38/35, 39/35, 40/35, 41/35, 43/35, 44/35
Y	US 7,090,812 B2 (JOYCE, PJ et al.) 15 August 2006; column 3, lines 5-15; claim 13	4/1-2, 5/1-2, 42/34-35
Y	WO 2012/143394 A1 (SOLVAY SA) 26 October 2012; page 7, lines 5-15	9/8/1-2, 38/34-35
Y	US 5,518,628 A (CAREY, RJ) 21 May 1996; abstract; column 3, lines 1-15; column 5, lines 10-45; column 6, lines 5-10, 20-30	26/13-14, 32/13-14, 34, 36/34-35, 37/34-35, 38/34-35, 39/34-35, 40/34-35, 41/34-35, 42/34-35, 43/34-35, 44/34-35
Y	US 5,437,848 A (HARD, RA) 1 August 1995; column 6, lines 20-35	31/28/27/13-14, 40/34-35
Y	(MILCHERT, E). Technological aspects of chemoenzymatic epoxidation of fatty acids, fatty acid esters and vegetable oils: a review. Molecules. Vol. 20. No. 12. 2015. 21481-21493; abstract; page 21487, paragraph 1; page 21484, paragraphs 2-3	34-35, 36/34-35, 37/34-35, 38/34-35, 39/34-35, 40/34-35, 41/34-35, 42/34-35, 43/34-35, 44/34-35
Y	US 3,527,718 A (COBURN, AE) 8 September 1970; column 2, lines 15-40	42/34-35
A	US 2009/0163640 A1 (ONG, C et al.) 25 June 2009; entire document	1-44
A	US 3,711,401 A (HAMILTON, RS et al.) 16 January 1973; entire document	1-44
A	US 6,589,492 B2 (MATSUMOTO, M et al.) 8 July 2003; entire document	1-44

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US17/14290

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.:
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:

3. ☒ Claims Nos.: 30
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 additional fees, this Authority did not invite payment of 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.