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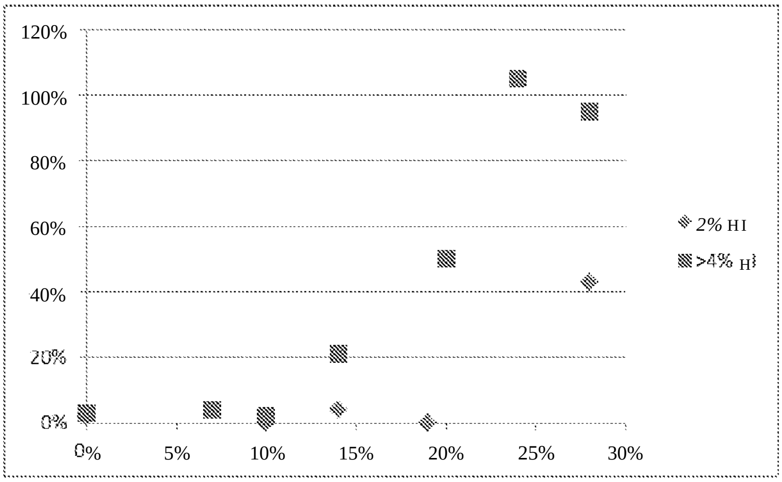

FIGURE 1

(57) Abstract: Methods are provided for recovering catalyst values from liquids containing catalyst and tar by combining the liquids with one or more aqueous solutions containing acetic acid and/or hydrogen iodide.

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CATALYST RECOVERY USING AQUEOUS HYDROGEN IODIDE AND ACETIC ACID

BACKGROUND OF THE INVENTION

This invention pertains to a process for recovering catalyst values from tars formed during the preparation of acetic anhydride by the carbonylation of methyl acetate, dimethyl ether or a combination of the two. More specifically, this invention pertains to a process for the recovery of values which normally are not extractable from the tars.

Carbonylation processes that produce acetic anhydride generate tars as byproduct. The formation of tar and the resulting problems that it creates in recovering catalyst values are described, for example, in U.S. Patents 4,388,21 7 and 4,944,927, European Patent Applications EP0087870 and EP0008396, and PCT Application having Publication No. 91/07372. One of the problems associated with tar formation, as discussed in some of the foregoing applications, is the interference of tars with the recovery and reuse of catalyst. Extraction processes have been developed in which catalyst is separated into an aqueous phase from tar which is contained in an organic phase, such as a methyl iodide solution. However, given the high cost of many catalyst components, there is continuing need to improve upon the efficiency of methods to separate catalyst from tar and thereby recover the catalyst.

BRIEF SUMMARY OF THE INVENTION

The invention provides processes for recovering a catalyst from a liquid containing catalyst and tar. In some embodiments, the process includes combining the with at least one aqueous solution that contains acetic acid and hydrogen iodide and methyl iodide under conditions effective to cause formation of an aqueous phase that contains acetic acid and hydrogen iodide and can organic phase that contains methyl iodide, wherein at least some of the catalyst is concentrated into the aqueous phase. The process further includes: feeding the liquid containing catalyst and tar to a main feed location on the vessel; feeding the at least one aqueous solution containing acetic acid to at least one aqueous feed location on the vessel, in which the aqueous feed location is vertically below the main feed location; recovering at least some of the organic phase from the vessel at an organic phase recovery location, in which the organic phase recovery location being is vertically below the main feed location; and recovering at least some of the aqueous phase from the vessel at an aqueous phase recovery location, the aqueous phase recovery location being vertically above the main feed location. Optionally, this embodiment may further include feeding at least one liquid stream that includes methyl iodide to at least one organic feed location on the vessel, which is vertically above the main feed location.

In some embodiments, the process includes combining the liquid containing catalyst and tar with at least one aqueous solution containing acetic acid in the presence of hydrogen iodide and methyl iodide under conditions effective to cause formation of an aqueous phase containing acetic acid and hydrogen iodide and an organic phase containing methyl iodide, wherein at least some of the catalyst is concentrated into the aqueous phase, wherein the process further includes: feeding the liquid containing catalyst and tar to a main feed location on the vessel; feeding at least one liquid stream containing methyl iodide to at least one organic feed location on the vessel, which is vertically above the main feed location; feeding the at least one aqueous solution containing acetic acid to at least one aqueous feed location on the vessel the aqueous feed location, which is vertically below the main feed location; recovering at least some of the organic phase from the vessel at an organic phase recovery location, which is vertically below the main feed location; and recovering at least some of the aqueous phase from the vessel at an aqueos phase recovery location, which is vertically above the main feed location. Optionally, the aqueous stream fed to the vessel also contains hydrogen iodide.

In some embodiments, the liquid including catalyst and tar prior further includes methyl iodide, acetic acid, hydrogen iodide or any combination of two or three of the foregoing. In some embodiments, the combining occurs in the presence of elemental iodine. For example, the liquid including catalyst and tar may contain at least some of the elemental iodine fed to the reactor.

In some embodiments, the at least one aqueous solution including acetic acid may include a first solution that includes hydrogen iodide but does not contain acetic acid and a second solution that includes acetic acid but does not contain hydrogen iodide. In some embodiments, the at least one aqueous solution including acetic acid includes at least one single solution that includes both hydrogen iodide and acetic acid.

In some embodiments, the catalyst includes at least one Group VIII metal. In some embodiments, at least one Group VIII metal is rhodium.

In some embodiments, at least one aqueous phase recovery location is located vertically above the at least one organic feed location. In some embodiments, at least one organic phase recovery location is located vertically below the at least one aqueous feed location. In some embodiments, the vessel includes an upper vertical third, a middle vertical third, and a lower vertical third, and at least one aqueous feed location is located in the lower vertical third of the vessel. In some embodiments, at least one organic feed location is located in the upper vertical third of the vessel. In some embodiments, the vessel includes a column, the column including at least one reciprocating plate agitator.

In some embodiments, 22.5% to 55% by weight of all materials fed to the vessel is acetic acid. In some embodiments, 0.5 to 10% by weight of all materials fed to the vessel is hydrogen iodide.

BRIEF DESCRIPTION OF THE DRAWINGS

FIGURE 1 is a graph showing Rhodium extraction efficiency using aqueous solutions at a variety of acetic acid and hydrogen iodide concentrations. Data is presented in Table 2B. Acetic acid concentrations of the composition are shown on the x-axis. Rhodium extraction efficiency is shown on the y-axis. The diamond-shaped datapoints represent solutions in which the hydrogen iodide concentration was 2%. The square data points represent solution in which hydrogen iodide concentration was greater than 4%.

FIGURE 2 is a graph showing the catalyst extraction percentages obtained in laboratory separations of liquids containing catalyst and tar. Data is presented in Table 3B. The x-axis represents percent acetic acid in the total composition. Rhodium extraction efficiency is shown on the y-axis. The square data points show the extraction efficiency percentages for extractions in which the composition contains 8% hydrogen iodide as well as the amount of acetic acid indicated by the x-axis. The diamond-shaped data points show the extraction percentages in which the hydrogen iodide level is 0%.

DETAILED DESCRIPTION

The invention provides a method for separating catalyst components from tars by concentrating them in an aqueous phase. A liquid containing catalyst and tar is combined with at least one aqueous solution containing acetic acid in the presence of hydrogen iodide and methyl iodide under conditions effective to cause formation of an aqueous phase containing acetic acid and hydrogen iodide and an organic phase containing methyl iodide. As used throughout this application, "hydrogen iodide," "iohydroic acid," "hydroiodic acid" and "HI" shall be used synonymously. This method achieves more efficient catalyst recovery than either aqueous HI alone or aqueous acetic acid alone. It has been found that combining both aqueous HI and aqueous acetic acid with the liquid containing catalyst and tar results in concentration of more catalyst into the aqueous phase than use of either acetic acid or HI alone. The combination of aqueous HI and acetic acid can be used as a primary extraction technique or as a secondary extraction technique after previous extractions, recovering rhodium that cannot be extracted by only aqueous HI. As used throughout this application, percentages, parts or other designation of partial components of a composition shall refer to weight percentages or components, unless specifically stated otherwise.

Liquid Containing or Comprising Catalyst and Tar

The liquid subjected to the process of the present invention, referred to herein as the "liquid containing catalyst and tar" or "liquid comprising catalyst and tar," contains at least catalyst and tar, and may contain many additional components. Tars refer to compounds of the type formed as a byproduct during the carbonylation of methyl acetate and downstream processes. Tars are described, for example, in U.S. Patent Nos. 4,388,21 7 and 4,944,927. The catalyst may be any effective catalyst that can be separated from tar using the methods set forth herein. In some embodiments, the catalyst includes one or more Group VIII Noble metals *{i.e.* selected from iron, cobalt, nickel, ruthenium, rhodium, palladium, osmium, iridium and platinum or combinations thereof). In some embodiments, the catalyst includes one or more Group VIII Noble metals *(i.e.* selected from ruthenium, rhodium, palladium, osmium, iridium, or platinum or combinations thereof). In some embodiments the Group VIII metal is selected from nickel, rhodium and iridium or combinations thereof. In some embodiments the metal is a nickel compound. In some embodiments the metal is a rhodium compound. In some embodiments the metal is an iridium compound. The metal may be present in any state of ionization or coordination, including, for example, as a metal, as a salt, or as a complex such as a carbonyl complex.

The catalyst and tar will be contained in a liquid material. The liquid may have any suitable composition, and the composition of the liquid will depend on the source from which it was derived. In some embodiments, the liquid containing catalyst and tar is prepared by combining the tar with one or more liquids. In some embodiments, the tar is diluted with methyl iodide. In some embodiments, the liquid is derived from a methyl acetate carbonylation process. By "derived," it is meant that the liquid comes directly from such process or from some downstream equipment associated with such a process, such as described subsequently. Some example liquid components can include methyl iodide, acetic acid, water, ethylidene diacetate, acetone, acetic anhydride, methanol, or suitable combinations of two or more of the foregoing. Other components can include, for example, one or more of: iodine-containing compounds (for example, lithium iodide) and residual compounds from promoters used in carbonylation reactions (such as lithium compounds, chromium compounds, nitrogen containing compounds such as those that result from the use of amine promoters, and phosphorous compounds such as those that result from the use of phosphine promoters). The invention is useful in the particularly difficult process of recovering one or more catalyst metals that are present in very small concentrations, such as is the case when some of the catalyst metal has already been removed. Thus, in some embodiments, the amount of one or more catalyst metals in the liquid containing catalyst and tar is less than 10% prior to processing. In some embodiments, this amount is less than 7.5%, less than 5%, less than 3%, less than 2%, less than 1% or less than 0.5%. In some embodiments the amount of one or more catalyst metals present prior to processing is at least 0.001 %, at least 0.01 %, or at least 0.05%.

Tar is also present in the liquid composition. In some embodiments, the liquid containing catalyst and tar contains tar in an amount less than 30%. In various embodiments, the tar amount is less than 20%, less than 15%, less than 10%, less than 7.5%, less than 5%, less than 3%, less than 2%, less than 1% or less than 0.5%. In some embodiments the amount of tar present can be from 0.5 to 20%, from 0.5 to 10% or from 0.5 to 7.5%.

In some embodiments, at least 50% of the total liquid composition is methyl iodide and/or acetic acid. In some embodiments, this amount is at least 60%, at least 70% or at least 80%. In some embodiments, this amount is from 60 to 95%. In some embodiments, this amount is from 70 to 90%. In some embodiments, at least 30% of the composition is methyl iodide. In some embodiments, this amount is at least 40%, at least 50%, or at least

60%. Some other example methyl iodide levels in the composition are from 30 to 90%, from 35 to 80%, from 40 to 70%, from 45 to 65%, and from 70 to 90%. In some embodiments, at least 20% of the composition is acetic acid. In some embodiments, this amount is at least 25%, at least 30%, or at least 40%. Some example acetic acid levels in the composition are from 20 to 50%, from 20 to 40%, from 25 to 50%, from 30 to 50%, from 25 to 40%, from 35 to 45% and from 30 to 40%.

In addition to methyl iodide, other iodine containing compounds may also be present. As used throughout this application, "iodine-containing compounds" means any compounds that include at least one iodine atom. Examples include methyl iodide, elemental iodine, acetyl iodide, hydrogen iodide, and lithium iodide. In some embodiments, where lithium is present, the liquid containing catalyst and tar contains lithium iodide in an amount less than 20%. In some embodiments, the lithium iodide amount is less than 15%, less than 10%, less than 7.5%, less than 5%, less than 3%, less than 2%, less than 1% or less than 0.5%. In some embodiments the amount of lithium iodide present is from 0.5 to 20%, from 0.5 to 10% or from 0.5 to 7.5%.

Elemental iodine is another iodine-containing compound that may be present in some embodiments, in view of the advantages of the presence of elemental iodine as taught by PCT Application having Publication No. WO 91/07372. In some embodiments, the liquid containing catalyst and tar contains elemental iodine in an amount less than 15%. In some embodiments, the elemental iodine amount less than 10%, less than 7.5%, less than 5%, less than 3%, less than 2%, less than 1% or less than 0.5%. In various embodiments the amount of elemental iodine present may be from 0.5 to 10%, from 0.5 to 7.5% or from 0.5 to 5%.

Water may be present as well. In some embodiments, the liquid containing catalyst and tar contains water in an amount less than 20%. In some embodiments, the water amount is less than 15%, less than 10%, less than 7.5%, less than 5%, less than 3%, less than 2%, less than 1% or less than 0.5%. In some embodiments the amount of water present is from 0.5 to

20%, from 0.5 to 10% or from 0.5 to 7.5%. In some embodiments, sufficient water is present to assure that the acetic anhydride amount is, for example, below 0.01 %, below 0.001 %, or not detectable in the composition.

Methyl acetate may also be present. However, in some embodiments, methyl acetate can serve as a cosolvent for the aqueous phase and the methyl iodide in the organic phase, limiting the abilities of the phases to separate, and thus should be limited. In some embodiments, the methyl acetate amount is less than 20%, less than 15%, less than 10%, less than 7.5%, less than 5%, less than 3%, less than 2%, less than 1% or less than 0.5%. In some embodiments the amount of methyl acetate present is from 0.001 to 15%, from 0.001 to 10%, from 0.001 to 7.5%, from 0.001 to 5% or from 0.001 to 2.5%.

Ethylidene diacetate (EDA), a byproduct of methyl acetate carbonylation, may also be present. In some embodiments, the EDA amount is less than 15%, less than 10%, less than 7.5%, less than 5%, less than 3%, less than 2%, less than 1% or less than 0.5%. In some embodiments the amount of EDA present is from 0.001 to 20%, from 0.001 to 10%, from 0.001 to 7.5%, from 0.001 to 5%, from 0.001 to 2.5%, or from 0.001 to 1%. Acetone, also a byproduct, may be present. In some embodiments, the acetone amount is less than 15%, less than 10%, less than 7.5%, less than 5%, less than 3%, less than 2%, less than 1% or less than 0.5%. In some embodiments the amount of acetone present is from 0.001 to 20%, from 0.001 to 10%, from 0.001 to 7.5%, from 0.001 to 5%, from 0.001 to 2.5%, or from 0.001 to 1%.

Any combinations of the above compositions are also within the invention. Thus, for example, in some embodiments, the liquid composition contains from 30 to 90% methyl iodide, from 15 to 50% acetic acid, from 0.001 to 10% catalyst metal, from 0.5 to 20% tar, from 0.5 to 5% lithium iodide, from 0.5 to 10% elemental iodine, from 0.5 to 20% water. Such embodiments may further contain from 0.001 to 20% methyl acetate, from 0.001 to 20% acetone and from 0.001 to 20% EDA. As another example, in some embodiments, the liquid composition contains from 40 to 60% methyl iodide, from 20 to 40% acetic acid, from 0.001 to 1% catalyst metal, from 0.5 to 7.5% tar, from 0.5 to 5% lithium iodide, from 0.5 to 10% elemental iodine, from 0.5 to 5% water. Such embodiments may further contain from 0.001 to 2.5% methyl acetate, from 0.001 to 1% acetone and from 0.001 to 1% EDA.

In some embodiments, the process from which the liquid containing catalyst and tar is obtained includes preparation of acetic anhydride by the liquid phase carbonylation of methyl acetate, dimethyl ether or both by reaction with carbon monoxide in the presence of a catalyst and an iodine compound at elevated pressure and temperature, wherein a feed mixture containing methyl acetate, dimethyl ether or both is continuously fed to a carbonylation reactor and a reaction mixture containing acetic anhydride is continuously removed. Optionally, the reaction may be carried out in the presence of one or more inorganic or organic promoter such as one or more lithium compound, chromium compounds, amine promoters, or phosphine promoters, or combinations thereof. In some embodiments of the process, the feed to the reactor is such as to maintain within the reaction mixture of reactant, catalyst, promoter and methyl iodide. The remainder of the reactor contents includes mostly acetic anhydride product with minor amounts of by-products such as ethylidene diacetate and acetone. The reactor feed optionally may contain a solvent such as acetic acid, e.g. in an amount that will maintain about 5 to 40 weight percent in the reaction mixture. In some embodiments, carbon monoxide is fed gas may contain hydrogen.

In some embodiments, the carbonylation process is a process designed for the coproduction of acetic acid and acetic anhydride by the inclusion of water and/or methanol in the reactor feed, for example as described in European Patent No 0087870. In some embodiments, the carbonylation process is a process for the production of ethylidene diacetate or the coproduction of ethylidene diacetate and acetic anhydride, such as by contacting methyl acetate and/or dimethyl ether and methyl iodide with a mixture of hydrogen and carbon monoxide, *e.g.* as described in Belgian Patent 839,321 .

The carbonylation process may be carried out, for example, in a liquid or vapor take-off mode of operation. In some embodiments of a liquid take-off system, the catalyst components, e.g. the catalyst, promoters, methyl iodide, and unreacted methyl acetate, dimethyl ether, or both are recovered from the reactor effluent and are recycled. In some embodiments, fresh metal catalyst and fresh promoters are added to the catalyst recycle. The fresh components can optionally be added as a solution in acetic acid. In some embodiments, iodine-containing compounds may be supplemented by adding elemental iodine (I_2), as methyl iodide or, at least in part, as lithium iodide. In a vapor take-off system, many catalyst components remain in the reactor and thus, the risk of their depletion from the process is reduced considerably.

Processing Prior to Combining Step

In some embodiments, the liquid containing catalyst and tar can be derived continuously or intermittently from a carbonylation process, for example, via a mixture of the compounds present in the system. Such a mixture may be removed either from the reactor or from downstream equipment. For example, in the case of a system employing a liquid product take-off from the reactor, the liquid can be removed from some point in the catalyst recycle stream. This mixture can then serve as liquid containing catalyst and tar, or can subjected to further processing to form the liquid containing catalyst and tar. In some embodiments, a stream from the carbonylation process is reduced, for example by evaporation, then optionally combined with one or more other liquids, for example, one or more liquids that contain methyl iodide. In some embodiments, the further processing includes filtration. In some embodiments, the further processing includes stripping in a flash evaporator, combining it with other liquids in an agitated stripped tar receiver similar to that disclosed in Example 12 of U.S. Patent No. 4,388,217, then filtering material from the stripped tar receiver and feeding it to the combining step. In some embodiments, the liquid is combined with methyl iodide prior to introduction into the combining step, either within the stripped tar receiver or otherwise. In some embodiments, hydrogen iodide is also fed into the stripped tar receiver, where it may react with lithium acetate (if present in the stripped tar receiver feed) to form lithium iodide and acetic acid, and water is fed to the stripped tar receiver where it may react with residual acetic anhydride (if present in the stripped tar receiver feed) to form acetic acid. In some embodiments, the presence of the HI in the receiver may also stabilize catalyst and reduce the potential for catalyst to precipitate and to plate out on the walls of the receiver and equipment downstream. In some embodiments, a stripped tar receiver and the equipment in which the combining step is performed are configured such that a portion of the HI and water used in the combining step is transferred from the combining step to the stripped tar receiver to serve as a source of HI and water for the stripped tar receiver.

In some embodiments, elemental iodine is added during upstream processing, for example by combining it with the liquid containing catalyst and tar before extraction, or adding during an extraction step. Methods for combining elemental iodine may be found, for example, in PCT Application having Publication No. 91/07372. Any effective amount of elemental iodine can be added to the system. In some embodiments, the amount of elemental iodine present in the liquid containing catalyst and tar is from 0.5 to 100 parts of I_2 per mole of metal catalyst *{e.g.* per moles of [Rh] when the metal catalyst is rhodium). In some embodiments, the elemental iodine is used in an amount which gives from 3 to 20 parts of I_2 per mole of metal catalyst.

Combining Step of the Process

The process includes combining the liquid containing catalyst and tar with amounts of aqueous acetic acid that, in the presence of hydrogen iodide and methyl iodide, can be used to concentrate catalyst values from the liquid containing catalyst and tar into the aqueous phase. By "concentrate," it is meant that a greater amount by weight of the catalyst values are contained in the aqueous phase than in the organic phase. Ionic catalyst species, such as an anionic rhodium species that is present in some liquid containing catalyst and tar, is soluble in the quantity of methyl iodide that is normally used in the process of this invention. In the presence of water, however, the ionic species are preferentially dissolved in the aqueous phase. It has been found that the presence of both HI and acetic acid in the aqueous phase results in higher levels of catalyst in the aqueous phase that when using either HI or acetic acid alone. While not wanting to be bound to any particular theory, it is possible that HI affects different catalyst complexes present in organic phase than those affected by acetic acid, in each case causing them to convert to one or more complex ionic species that preferentially dissolve in the aqueous phase.

The liquid containing catalyst and tar is combined with at least one aqueous solution containing acetic acid. In some embodiments, the at least one aqueous solution also contains HI. In some embodiments, a single aqueous solution containing both acetic acid and HI is combined with the liquid containing catalyst and tar. In some embodiments, at least two aqueous solutions are combined with the liquid containing catalyst and tar. Where two or more solutions that contain both HI and acetic acid are used, at least some of the acetic acid and HI may be optionally contained in separate solutions, or both in multiple solutions, but in differing amounts. Likewise, the two or more solutions can optionally be combined with liquid containing catalyst and tar simultaneously, or at separate times or locations. As noted above, the liquid containing catalyst and tar may contain acetic acid, HI, water or a combination of two or more of the foregoing prior to the combination step.

The amount of acetic acid and, where applicable, HI combined with the liquid containing catalyst and tar will vary based on a variety of process factors, including composition of the liquid containing catalyst and tar, the amount of additional methyl iodide combined with the liquid, if any, the order in which the components are combined, and the configuration of the equipment in which the combination is to take place. HI levels may depend, for example, on the desired pH, the levels of HI already present in the solution containing catalyst and tar (if any) and whether there is a desire to convert acetate ions are present in the liquid (if any) to acetic acid. Acetic acid levels should be sufficient to assist in the separation, but not present in such high levels as to hinder the separation from the aqueous and organic phases. In addition, higher acetic acid levels in the aqueous phase can increase the solubility of tar in the aqueous phase. The enhancements to catalyst solubility conferred by additional acetic acid in the aqueous phase should be balanced against these considerations.

As mentioned above, the one or more aqueous solutions contain acetic acid. In some embodiments, the one or more aqueous solutions contain 0.5 to 80% acetic acid. In some embodiments, the one or more aqueous solutions contain 10 to 70% acetic acid. In some embodiments, the one or more aqueous solutions contain 10 to 50% acetic acid. In some embodiments, the one or more aqueous solutions contain 15 to 40% acetic acid.

In some embodiments, the one or more aqueous solutions also contain HI. In some embodiments, the one or more aqueous solutions contain 20 to 70% HI. In some embodiments, the one or more aqueous solutions contain 40 to 70% HI. In some embodiments, the one or more aqueous solutions contain 30 to 60% HI. In some embodiments, the one or more aqueous solutions contain 0.5 to 20% HI. In some embodiments, the one or more aqueous solutions contain 10 to 20% HI. The one or more aqueous solutions may optionally contain other components that do not unduly interfere with the function of the process. For example, the aqueous solutions may contain elemental iodine. Other components present in the composition can depend on the source of the water, HI and acetic acid, and some examples of other possible components include corrosion metals, methyl acetate, acetone or combinations thereof. Thus, in some embodiments, the one or more aqueous solutions fed to the extractor contains (collectively, if multiple streams are used) 0.5 to 30% HI by weight, from 0.5 to 60% acetic acid, from 20 to 98% water, and optionally less than 1% elemental iodine. In some embodiments, the one or more aqueous solutions contain 10 to 20% HI, 15 to 40% acetic acid, from 40 to 75% water and optionally less than 1% elemental iodine. Where two or more aqueous solutions are used, they may have the same or differing compositions, and the foregoing percentage may optionally viewed as describing the aggregate composition of such two or more streams.

The combining step occurs in the presence of HI and methyl iodide under conditions effective to cause formation of an aqueous phase containing acetic acid and hydrogen iodide and an organic phase containing methyl iodide. As noted above, in some embodiments, at least some of the HI may be present as a result of having been in one or more of the aqueous solutions. Alternatively, the HI may be present as a result of HI being present in the liquid containing catalyst and tar, or may have come from both locations. Similarly, in some embodiments, at least some of the methyl iodide is present in the liquid containing catalyst and tar. In some embodiments, an additional stream containing methyl iodide is combined with the liquid containing catalyst and tar. In some embodiments, methyl iodide is both present in the liquid containing catalyst and tar and in an additional stream with which it is combined. Where an additional stream containing methyl iodide is used, it may optionally contain other components that do not unduly interfere with the function of the process. Some examples of additional components that may be present include elemental iodine, methyl acetate, water, acetic acid, and acetone.

Since acetic acid, HI, water and methyl iodide may also be components of the liquid containing catalyst and tar, the amounts of these components present or added may also be considered as a fraction or percentage of the total feed to the combining step; that is, a fraction or percentage of the combined composition of the liquid containing catalyst and tar, the one or more aqueous streams that contain HI, acetic acid, or both, as well as any streams containing methyl iodide. In some embodiments, the total amount of

HI fed to the combining step is from 0.5 to 15% of the total feed to the combining step. In some embodiments, the total amount of HI fed is from 0.5 to 10% or from 0.5 to 5% of the total feed to the combining step. In some embodiments, sufficient hydrogen iodide is used so that the pH of the aqueous phase is 2 or less, in some embodiments less than 1.

In some embodiments, the total amount of methyl iodide fed to the combining step is from 20 to 80% of the total feed to the combining step. In some embodiments, the total amount of methyl iodide fed is from 30 to 70% of the total feed to the combining step. In some embodiments, this number is from 35 to 65%.

In some embodiments, the total amount of acetic acid fed to the combining step is from 0.5 to 55% of the total feed to the combining step. In some embodiments, the total amount of acetic acid fed is from 10 to 50% or from 20 to 40% of the total feed to the combining step. However, several considerations are factors with respect to acetic acid content. In some embodiments, it has been found that acetic acid's beneficial effect on recovery of catalyst into the aqueous phase increases rather dramatically at feed rates above 20% based on the total feed to the combining step. At the same time, as noted above, increases in the total amount of acetic acid fed to the combining step should be balanced against considerations that it may interfere with the maintenance of separate phases in the solution. This is a function of the amounts of water and methyl iodide present, and can be readily ascertained from literature references that describe the phase separations of solutions that contain acetic acid, methyl iodide, and water. One such example is E. T. Shepelev, et al., Zhurnal Prikladnoi Khimii Vol. 64, No 11, P. 2441 -2443, November 1991 . Furthermore, higher levels of acetic acid can result in undesirable levels of tar remaining in the resulting aqueous phase. Thus, in some embodiments, the amount of acetic acid fed to the combining step is from 22.5 to 55%, in some embodiments from 25 to 40%, based on the total feed.

In some embodiments, the combination takes place in a batch process, for example in a tank, a column or other vessel. In some embodiments, the combination takes place continuously, such as in a continuous extraction vessel, such as an extraction column. The vessel or column may be optionally equipped with internals to allow mixing, such as baffles, trays, or combination thereof. Agitation mechanisms may also be used, such as one or more impellers, one or more reciprocating agitators, or both. In some embodiments, the vessel is a column equipped with at least one reciprocating agitator, the agitator contain plates. In some embodiments, the column is a Karr Reciprocating Plate Extraction Column.

The combination occurs under conditions effective to cause formation of an aqueous phase containing acetic acid and hydrogen iodide and an organic phase containing methyl iodide, wherein at least some of the catalyst is concentrated into the aqueous phase. Any effective conditions may be used. In some embodiments, the combination occurs in a vessel, for example, a decanter allowing the vertical separation of different phases or a column, such as a column allowing two or more streams to flow in a generally countercurrent manner. By "generally countercurrent," it is meant that the overall flow of the two or more streams is in opposite directions but that localized areas of flow in other directions may be observed due to feed and offtake points. In some embodiments, the liquid containing catalyst and tar moves in a generally countercurrent manner to an aqueous stream, a stream containing methyl iodide, or both. In some embodiments, the liquid containing catalyst and tar is fed to a column in which an aqueous stream and a stream containing methyl iodide are both fed in a manner in which they flow in a generally concurrent manner. The locations depend in part on the relative densities of the various feeds and resulting streams. For example, in some embodiments in which the resulting aqueous phase is less dense than the resulting organic phase *{e.g.* an organic phase in which methyl iodide is the main component) the combination can occur in a vessel in which at least a portion of the one or more aqueous solutions is fed at a location vertically below the feed location for the liquid containing catalyst and tar, with the resulting aqueous phase being removed from a location vertically above the feed location for the liquid containing catalyst and tar and the resulting organic phase being removed from a location vertically below the feed location for the liquid containing catalyst and tar. The locations also depend in part on the desired degree of countercurrent flow, design of the vessel and any vessel internals, and overall flow rates of each stream.

In various embodiments, the feed location for at least a portion of one or more aqueous solutions can be in the lower vertical 80%, lower vertical 60%, the lower vertical half, lower vertical 40%, lower vertical third, lower vertical 30%, lower vertical 20% or lower vertical 10% of the vessel. In some embodiments, a separate organic stream is added. In some embodiments in which an organic stream containing methyl iodide is added, and the resulting aqueous phase is less dense than the resulting organic phase, at least a portion of the organic stream is added in the upper vertical half, upper vertical 40%, upper vertical third, upper vertical 30%, upper vertical 20% or upper vertical 10% of the vessel.

Likewise, in various embodiments, the location at which at least a portion of the organic phase is removed from the vessel can be in the lower vertical 60% lower vertical half, lower vertical 40%, lower vertical third, lower vertical 30%, lower vertical 20% or lower vertical 10% of the vessel. Similarly, in various embodiments, the location at which at least a portion of the aqueous phase is removed from the vessel can be in the upper vertical 60%, upper vertical half, upper vertical 40%, upper vertical third, upper vertical 30%, upper vertical 20% or upper vertical 10% of the vessel.

Vessel configuration can also be described as percentage of the total height of the vessel between the different addition points. In some embodiments, the distance between the addition locations for one or more aqueous streams is at least 10% of the vessel height below the point at which the liquid containing catalyst and tar are added. In other embodiments, this distance is at least 20%, at least 30%, at least 40%, at least 50%, or at least

60% below the feed point for the liquid containing catalyst and tar. Similarly, in some embodiments, the distance between the addition locations for an organic stream is at least 10% of the vessel height above the point at which the liquid containing catalyst and tar are added. In other embodiments, this number is at least 20%, at least 30%, at least 40% at least 50%, or at least 60% above the feed point for the liquid containing catalyst and tar.

The liquid containing catalyst and tar may be fed at any point (the main feed point) above the aqueous feed point, and, if an organic phase containing methyl iodide is fed, below that organic feed point.

In embodiments in which the result organic phase is less dense than the aqueous phase, the locations set forth in the previous three paragraphs can be reversed. That is, the main feed location for the liquid containing catalyst and tar is below one or more aqueous feed locations as well as one or more organic phase recovery location, and above one or more organic feed location as well as one or more aqueous recovery locations. Likewise, in such embodiments, a location described as being in the "upper vertical third" above can be in the "lower vertical third," a location describe as being "20% of the vessel height above" another location can be "20% of the vessel height below the other location," *etc.).* As used throughout this application, references to a location as being in an "upper" or "lower" vertical fraction of the vessel, means that that the location is at a vertical height that is within the referenced fraction of the overall height of the vessel from the vertical top or bottom of the vessel, respectively. Thus, a location in the "upper 40%" of a vessel that is 100 meters tall is no more than 40 meters from the top of the vessel, and a location that is in the "lower half" of such a vessel would be no more than 50 meters from the bottom of the vessel. Similarly, a reference in this application to a location on a vessel as being "vertically above" or "vertically below" another location simply means that it is at a greater or lesser height on the vessel than the other location, irrespective of whether or not they are "directly" above or below one another or that they be circumferentially or horizontally aligned.

As mentioned above, in some embodiments the vessel may also be equipped with offtake locations to transfer components of the vessel to upstream equipment, such as a stripped tar received as described in U.S. Patent No. 4,388,217. Such an offtake may appear at a point in the upper vertical 20%, upper vertical third, upper vertical 40%, upper vertical 50%, upper vertical 60%, upper vertical 70%, lower vertical 70%, lower vertical 60%, lower vertical 50%, lower vertical 40%, lower vertical third, or lower vertical 20% of the vessel. The height of the vessel will depend on the location of other feeds and offtakes and the desired composition of the feed to the other equipment.

In some embodiments, several combinations occur in a series of columns, other vessels or other separation processes. For example, in some embodiments, the liquid containing catalyst and tar has already undergone an extraction process with aqueous HI and, in a second step, is combined with aqueous solutions of both HI and acetic acid. Such, secondary extraction processes can be similar to the primary extraction process in terms of, for example, the concentrations of HI and acetic acid the aqueous mixture.

Optionally, the combination takes place in the presence of elemental iodine. As noted above, elemental iodine may be present in the liquid containing catalyst and tar as a result of upstream processing. It may be combined with the liquid containing catalyst and tar during the combining step, or may be originate through a combination of the foregoing ways.

Subsequent Processing

As noted, the combining step results in the formation of an aqueous phase into which the catalyst has been concentrated. The catalyst may then be reused in a carbonylation process. Prior to such carbonylation step, this aqueous phase may be further processed prior to reuse, for example to concentrate the catalyst and thereby reduce the amount of water before it is returned to the process. Doing so can reduce the amount of anhydride decomposition that is caused by water which could significantly affect the overall anhydride yield of the process. A secondary benefit from the use of acetic acid in the combining step is the replacement of some of the water with acetic acid in the resulting aqueous stream. This further reduces the need to separate liquid from the catalyst by reducing the amount of water that would react with the acetic anhydride.

This organic phase containing methyl iodide and tar may be separated, for example, by distillation, and the methyl iodide recovered in the process can optionally be reused in the combining step or otherwise used in any number of aspects of the methyl acetate carbonylation process and related equipment. The viscous tar-methyl iodide residue can be treated further to remove any iodine or catalyst values present. Some examples of methods for such treatments include pyrolysis, either with or without deposition on solid support, precipitation from solution, and adsorption. Examples of the foregoing are disclosed in U.S. Patent No. 4,476,237.

EXAMPLES

This invention can be further illustrated by the following examples of preferred embodiments thereof, although it will be understood that these examples are included merely for purposes of illustration and are not intended to limit the scope of the invention unless otherwise specifically indicated. For Comparative Example A and Example B, all rhodium concentrations and amounts provide the amount of the rhodium complex $(Rh(CO)_2I2)^-$ in the examples reported below. For laboratory experiments 1-38, rhodium concentrations are based upon rhodium only, not the complex.

Comparative Example A

A catalyst-tar solution containing mean concentrations of 72 parts methyl iodide, 5 parts acetone, 244 parts methyl acetate, 377 parts acetic acid, 643 parts acetic anhydride, 10 parts ethylidene diacetate (EDA), 11 parts lithium iodide, 21 parts lithium acetate (LiOAc), 5.3 parts Rhodium, and

75 parts tar is processed in a flash evaporator, filter and continuous counter-current fractional extraction column arrayed in a manner similar to that described in Example 12 of U.S. Patent No. 4,388,217. The filtered stream fed from the stripped tar receiver to a location above the midpoint of the extractor is modeled to contain mean concentrations of 1113 parts methyl iodine, 1 part acetone, 28 parts methyl acetate, 40 parts water, 6.6 parts rhodium, 503 parts acetic acid, 8 parts EDA, 76 parts lithium iodide, 49 parts iodine, and 95 parts tar. The stream taken from the midpoint of the continuous extractor and recycled to the stripped tar receiver is modeled to contain mean concentrations of 182 parts methyl iodide, 1 part acetone, 1.2 parts rhodium, 4 parts methyl acetate, 88 parts water, 91 parts acetic acid, 1 part EDA, 20 parts lithium iodide, 13 parts HI, 15 parts iodine, and 20 parts tar. The methyl iodide stream fed to the upper portion (above the feed point from the stripped tar receiver) contains mean concentrations of 240 parts methyl iodide, 0.2 parts methyl acetate, and 0.3 parts water. The aqueous HI solution containing 375 parts water, 58 parts HI, and 1 part iodine is fed to the lower portion of the extractor (below the feed point from the stripped tar receiver).

An overflow stream mostly containing the aqueous phase containing acetic acid and most of the catalyst values and an underflow stream mostly containing the organic methyl iodide phase containing the tar are each continuously removed from the extractor. The overflow stream contains mean concentrations of 215 parts methyl iodide, 14 parts methyl acetate, 379 parts water, 438 parts acetic acid, 55 parts lithium iodide, 58 parts HI, 5.3 parts Rh, and 31 parts iodine. The extractor underflow stream contains mean concentrations of 802 parts methyl iodide, 3 parts methyl acetate, 7 parts EDA, 6 parts iodine, 0.2 parts Rh, and 74 parts tar.

The rhodium extraction efficiency of this system may be described as the amount of rhodium in the underflow divided by the sum of the amount of rhodium in the underflow and overflow (i.e. the total output of the system). This amount is 5.3 ÷ (5.3 + 0.2) = 0.96 or 96%.

Example B

A process similar to Comparative Example 1 was operated. The catalyst-tar solution contained 52 parts methyl iodide, 2 parts acetone, 219 parts methyl acetate, 335 parts acetic acid, 647 parts Ac20, 3 parts EDA, 11 parts lithium iodide, 22 parts lithium acetate, 4.3 parts Rh, and 73 parts tar. The filtered stream from the stripped tar receiver that is fed to the extraction column contains mean concentrations of 990 parts methyl iodide, 1 part acetone, 25 parts methyl acetate, 148 parts water, 435 parts acetic acid, 4 parts EDA, 68 parts lithium iodide, 45 parts elemental iodine, 91 parts tar, and 6.3 parts Rh. A stream containing mean concentrations of 239 parts methyl iodide, 1 part methyl acetate, and 0.2 parts water is fed to the upper portion of the extractor. The stream, taken from the midpoint of the continuous extractor, is modeled to contain mean concentrations of 84 parts methyl iodide, 3 parts methyl acetate, 197 parts water, 20 parts acetic acid, 1 part EDA, 20 parts lithium iodide, 11 parts HI (100% hydrogen iodide), 13 parts iodine, and 18 parts tar. An aqueous solution containing mean concentrations of 252 parts water, 123 parts acetic acid, 57 parts HI, and 1 part iodine is fed to the lower portion of the extractor.

The extractor overflow stream contains 361 parts methyl iodide, 220 parts water, 686 parts acetic acid, 68 parts lithium iodide, 71 parts HI, 30 parts iodine, 13 parts tar, and 5.1 parts Rh. The extractor underflow stream contained 694 parts methyl iodide, 1 part methyl acetate, 10 parts acetic acid, 4 parts EDA, 0.1 parts Rh, 1 part iodine, and 47 parts tar.

The rhodium extraction efficiency of this system is 5.1 ÷ (5.1 + 0.1) = 0.98 or 98%.

Laboratory Extractions: Examples 1-38

Examples 1-17

The nonaqueous (methyl iodide) underflow from an extraction process similar to that described in Comparative Example A was obtained. A tar stream obtained from the organic phase underflow contained 91.9% methyl iodide, 6.8% tar, 52 ppm Rh, 0.5% I_2, 0.4% methyl acetate, 0.1 % EDA, and 0.04% acetic acid.

This tar stream (40 ml_) was submitted to four batch extractions with a mixture of HI, acetic acid, and water (40 ml_ each). The mixture was shaken in a separatory funnel for two minutes and the layers were allowed to separate for at least two minutes. The bottom layer was contacted with fresh aqueous mixtures for subsequent extractions. This was repeated so that a total of four extractions were conducted on the bottom (organic) layer. Each top layer was collected and sampled. A portion (5 ml_) of the bottom layer was collected and sampled after the first extraction only. Samples were analyzed for rhodium concentration and tar concentration.

Mass balance ranged from 97.6 to 98.5% over 17 experiments. Rhodium balance ranged from 65 to 108%. Mass balance for tar ranged from 66 to 86%. Rhodium extraction was calculated as the cumulative amount of rhodium measured in the aqueous layers compared to the amount of rhodium originally measured in the tar stream. Tar extraction in the aqueous stream was calculated in the same manner. The 17 experiments were designed to measure the impact of HI, acetic acid, and water concentrations on rhodium extraction and tar extraction. HI concentration was varied from 5 to 20%. Acetic acid concentration was varied from 0 to 60%. Water concentration was varied from 20 to 95%. Rhodium extraction ranged from 6 to 72%. Tar extraction ranged from 1 to 27%.

Table 1A presents the compositions of aqueous streams alone used in these examples. Table 1B presents the composition of the total combined aqueous organic phases for each extraction and the rhodium and tar extraction efficiencies. The Table 1B weight percentages are adjusted to show tar solution concentration of 3% and methyl iodide concentration of 63%.

Table 1A. Composition of aqueous stream used in Examples 1-17.

Example	HI concentration	acetic acid concentration	H_2O concentration
1	5%	0%	95%
2	5%	0%	95%
3	5%	30%	65%
4	5%	60%	35%
5	5%	60%	35%
6	9%	15%	76%
7	9%	45%	46%
8	13%	0%	87%
9	13%	60%	27%
10	15%	20%	65%
11	16%	45%	39%
12	20%	0%	80%
13	20%	0%	80%
14	20%	30%	50%
15	20%	30%	50%
16	20%	60%	20%
17	20%	60%	20%

Table 1B - Extraction Results

Example	HI concentration	acetic acid concentration	H_2O concentration	Rhodium extraction	Tar extraction
1	2%	0%	32%	6%	4%
2	2%	0%	32%	8%	1%
3	2%	10%	22%	9%	8%
4	2%	20%	12%	27%	10%
5	2%	20%	12%	28%	13%
6	3%	5%	25%	15%	5%
7	3%	15%	15%	15%	9%
8	4%	0%	29%	14%	5%
9	4%	20%	9%	66%	12%
10	5%	7%	22%	12%	3%
11	5%	15%	13%	41%	12%
12	7%	0%	27%	23%	4%
13	7%	0%	27%	24%	3%
14	7%	10%	17%	39%	6%
15	7%	10%	17%	50%	6%
16	7%	20%	7%	66%	27%
17	7%	20%	7%	72%	21%

The data shows that acetic acid increases rhodium extraction regardless of HI concentration. The same is true for tar extraction, but to a lesser degree. Comparison of Examples 1 and 2 with Examples 3 and 5, Example 8 with Example 9, Example 10 with Example 11, and Examples 12 and 13 with Examples 14 and 17 demonstrate the benefit of acetic acid.

Examples 18-29

A separate but similar experiment used a tar stream obtained from the processing of tar twice through two rhodium extraction column processes effectively operated in series. Each extraction process was operated in a manner similar to that set forth in Comparative Example A above, except that the organic phase underflow from the first extraction process was fed to an agitated tank prior where it was held prior to being fed to the second extraction. Nothing else was fed to the agitated tank, so that the primary feed to the second extraction had the same composition as the underflow from the first column extraction. Feeds of aqueous HI and methyl iodide solutions to the second extraction were the same as the first. The underflow of the second column had a composition of 94.0% methyl iodide, 5.0% tar, 27 ppm Rh, 0.5% I_2, 0.1 % methyl acetate, and 0.1 % EDA.

This underflow stream (30 mI_) was submitted to four batch extractions with a mixture of HI, acetic acid, and water (40 mI_ each). The mixture was shaken in a separatory funnel for two minutes and the layers were allowed to separate for at least two minutes. The bottom layer was contacted with fresh aqueous mixtures for subsequent extractions. This was repeated so that a total of four extractions were conducted on the bottom (organic) layer. Each top layer was collected and sampled. Samples were analyzed for rhodium concentration and tar concentration.

Mass balance ranged from 96.3 to 98.6% over 12 experiments. Rhodium mass balance ranged from 64 to 137%. Tar mass balance ranged from 61 to 90%. Rhodium extraction was calculated as the cumulative amount of rhodium recovered in the aqueous layers compared to the amount of rhodium present in the tar stream. Tar extraction into the aqueous stream was calculated in the same manner. The 12 experiments were designed to measure the impact of HI, acetic acid, and water concentrations on rhodium extraction and tar extraction. HI concentration was varied from 5 to 20%. Acetic acid concentration was varied from 0 to 70%. Water concentration was varied from 10 to 95%. Rhodium extraction ranged from 0 to 105%. Tar extraction ranged from 2 to 49%.

Table 2A presents the compositions of aqueous streams alone used in these Examples. Table 2B presents the composition of the total combined aqueous organic phases for each extraction and the rhodium and tar extraction efficiencies. The Table 2B weight percentages are adjusted to show tar solution concentration of 3% and methyl iodide concentration of 57%.

Table 2A.

Example	HI concentration	acetic acid concentration	Water Concentration
18	5%	0%	95%
19	5%	25%	70%
20	5%	35%	60%
21	5%	47%	48%
22	5%	70%	25%
23	12%	70%	18%
24	16%	17%	67%
25	15%	50%	35%
26	20%	0%	80%
27	20%	24%	56%
28	20%	35%	45%
29	20%	60%	20%

Table 2B. Rhodium extraction with a mixture of HI, acetic acid, and water from a tar stream obtained from processing tar through two extractor columns operated in series. (Tar concentration = 3%, methyl iodide = 57%).

Example	HI concentration	acetic acid concentration	H_2O concentration	Rhodium extraction	Tar extraction
18	2%	0%	38%	2%	3%
19	2%	10%	28%	0 (< 9%)*	3%
20	2%	14%	24%	4%	9%
21	2%	19%	19%	0 (< 7%)*	5%
22	2%	28%	10%	43%	25%
23	5%	28%	7%	95%	49%
24	6%	7%	27%	4% (< 8%)*	5%
25	6%	20%	14%	50%	13%
26	8%	0%	32%	3%	2%
27	8%	10%	22%	2% (< 9%)*	6%
28	8%	14%	18%	21%	8%
29	8%	24%	8%	105%	22%

* Parenthetical numbers reflect summation of detection limits where one or more non-detect readings were made over four extractions.

The data demonstrates that adding acetic acid increases rhodium extraction regardless of HI concentration, even after the tar has been subjected to two runs through a continuous extractor process having an HI feed. The same is true for tar extraction, but to a lesser degree. Comparison of Examples 18 through 22 with each other demonstrates that the acetic acid is beneficial at high concentration (70% in Table 2A; 28% in Table 2B) when the HI concentrations are low (5% in Table 2A; 2% in Table 2B). Comparison of Examples 26 through 30 with each other demonstrates that acetic acid is beneficial again only at high concentration but that the threshold lower, (specifically 35% and higher in Table 2A, 14% and higher in Table 2B) acetic acid when HI concentration is high (20% in Table 2A; 8% in Table 2B).

Comparison of Example 18 with Example 26 demonstrates that for these streams that have previously been subjected to two HI extractions, rhodium is essentially unextractable regardless of the HI concentration when acetic acid is not present. Comparison of Example 20 with Example 28 and Example 22 with Example 23 demonstrate the benefit of HI when acetic acid is present. HI concentration has an effect on tar extraction at very high acetic acid concentrations only.

High concentrations of acetic acid result in mass reduction of the organic layer. No effect was apparent with acetic acid concentrations up to 35% (Table 2A), but the mass of the organic layer decreased significantly after four extractions when acetic acid concentration was above 35% (Table 2A).

Figure 1 presents this data graphically, and shows the importance of having both HI and acetic acid concentration. As can be seen, increasing the acetic acid concentration (x-axis) increases the rhodium extraction efficiency (y-axis). However, the increase with acetic acid concentration occurs more sharply and at lower acetic acid concentrations with higher HI concentrations (square data points) than at lower HI concentrations (diamond-shaped data points). This sharp increase can be readily seen by comparing Table 2B data for all samples having 8% HI (Examples 26 through 29) or comparing data for all samples having 6% HI (Examples 24 through 25).

Examples 30-38

A stream collected from a methyl acetate carbonylation reactor was distilled at 95 °C and 7 torr absolute pressure. The concentrated sample was diluted with acetic acid and methyl iodide such that it contained 78.7% methyl iodide, 15.6% acetic acid, 5.6% tar, and 713 ppm Rh.

This tar stream (100 g) was submitted to up to four batch extractions with a mixture of HI, acetic acid, and water (100 g each). The mixture was shaken in a separatory funnel for two minutes and the layers were allowed to separate for at least two minutes. The bottom layer was collected. The top layer was collected and sampled. The bottom layer was returned to the separatory funnel for the next extraction with fresh portion of the same extractant. A portion (5 mL) of the bottom layer was collected and sampled after each extraction and the amount of extractant was adjusted accordingly. Samples were analyzed for rhodium concentration and tar concentration.

Mass balance ranged from 95.9 to 98.1 % over 9 experiments. Rhodium balance ranged from 45 to 96%. Tar balance ranged from 30 to

44%. Rhodium extraction was calculated as the cumulative amount of rhodium recovered in the aqueous layers compared to the amount of rhodium present in the tar stream. Tar extraction was calculated in the same manner. The 9 experiments were designed to measure the impact of HI, acetic acid, and water concentrations on rhodium extraction and tar extraction. HI concentration was varied from 0 to 15%. Acetic acid concentration was varied from 0 to 75%. Water concentration was varied from 25 to 100%. Rhodium extraction ranged from 13 to 96%. Tar extraction after the first extraction ranged from 2 to 11%. Tar extraction after the first extraction was not measured.

Table 3A presents the compositions of aqueous streams alone used in these Examples. Table 3B presents the composition of the total combined aqueous and organic phases for each extraction and the rhodium and tar extraction efficiencies. The Table 3B weight percentages are adjusted to show tar solution concentration of 3% and methyl iodide concentration of 39%. All samples are based on a series of four extractions except where Table 3B indicates otherwise.

Table 3A.

Example	HI concentration	acetic acid concentration	Water concentration
30	15%	0%	85%
31	15%	30%	55%
32	15%	60%	25%
33	0%	0%	100%
34	0%	15%	85%
35	0%	30%	70%
36	0%	45%	55%
37	0%	60%	40%
38	0%	75%	25%

Table 3B. Rhodium extraction with a mixture of HI, acetic acid. (Tar concentration = 3%, methyl iodide = 39%).

Example	HI concentration	acetic acid concentration	H_2O concentration	Rhodium extraction	Tar extraction***
30	8%	8%	43%	84%	3%
31	8%	23%	28%	91%	7%
32	8%	38%	13%	96%	10%
33	0%	8%	50%	13%*	2%
34	0%	15%	43%	25%	3%
35	0%	23%	35%	63%	7%
36	0%	30%	28%	63%	5%
37	0%	38%	20%	84%	7%
38	0%	45%	13%	93%**	11%

[*] Only 1 extraction was conducted due to shortage of laboratory materials. This is not expected to have significantly reduced efficiency given the observation in Examples 1 through 17 that at least 92% of the total amount of rhodium extracted was extracted in the first extraction and in view of the other data points for 0% HI solutions.

[**] Only 3 extractions were conducted; insufficient amount of organic phase remained after third extraction to permit a fourth extraction.

[***] For all samples, tar was measured after the first extraction only.

The data shows that the addition of acetic acid to HI increases rhodium extraction regardless of HI concentration. The same is true for tar extraction, but to a lesser degree. Comparison of Examples 30 through 32 to each other and Examples 33 through 38 to each other demonstrate the benefit of acetic acid. Comparison of Example 30 with Example 33, Example 31 with Example 35, and Example 32 with Example 37 demonstrate the benefit of HI. The combination of HI and acetic acid in an aqueous stream is extremely powerful for rhodium extraction.

FIGURE 2 presents the data from Table 3B graphically and again shows the separate effects of HI and acetic acid concentration. As can be seen, increasing the acetic acid concentration (x-axis) increases the rhodium extraction efficiency (y-axis), for both the samples that contain no HI (diamond-shaped data points). And those that contain 8% HI (square data points). As the figure shows, the extraction efficiency at 38% acetic acid concentration without HI is 84%, the same as that at 8% acetic acid in 8% HI (compare Examples 30 and 37 in Table 3B). It is noteworthy that the extractions of Example 38, in which acetic acid concentration is 45%, led to miscibility of the aqueous and organic phases to such a degree that insufficient organic phase remained after three extractions, and had the highest concentration of undesirable tar in the aqueous phase. These demonstrate the advantage of using the HI and acetic acid together at lower concentrations (rather than higher concentrations of acetic acid) to allow efficient rhodium extraction with drawing excess tar into the recovered aqueous phase.

The invention has been described in detail with particular reference to preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention.

CLAIMS

What is claimed is:

1. A process for recovering a catalyst from a liquid comprising catalyst and tar, said process comprising combining said liquid comprising catalyst and tar with at least one aqueous solution comprising acetic acid and hydrogen iodide and methyl iodide under conditions effective to cause formation of an aqueous phase comprising acetic acid and hydrogen iodide and an organic phase comprising methyl iodide, wherein at least some of said catalyst is concentrated into said aqueous phase, wherein said process further comprises:

feeding said liquid comprising catalyst and tar to a main feed location on said vessel,

feeding said at least one aqueous solution comprising hydrogen iodide and acetic acid to at least one aqueous feed location on said vessel, said aqueous feed location being vertically below said main feed location,

recovering at least some of said organic phase from said vessel at an organic phase recovery location, said organic phase recovery location being vertically below said main feed location and

recovering at least some of said aqueous phase from said vessel at an aqueous phase recovery location, said aqueous phase recovery location being vertically above said main feed location.

2. The process of claim 1, wherein the process further comprises feeding at least one liquid stream comprising methyl iodide to at least one organic feed location on said vessel, said at least one organic feed location being vertically above said main feed location.

3. A process for recovering a catalyst from a liquid comprising catalyst and tar, said process comprising combining said liquid comprising catalyst and tar with at least one aqueous solution comprising acetic acid in the presence of hydrogen iodide and methyl iodide under conditions effective to cause formation of an aqueous phase comprising acetic acid and hydrogen iodide and an organic phase comprising methyl iodide, wherein at least some of said catalyst is concentrated into said aqueous phase, wherein said process further comprises:

feeding said liquid comprising catalyst and tar to a main feed location on said vessel,

feeding at least one liquid stream comprising methyl iodide to at least one organic feed location on said vessel, said at least one organic feed location being vertically above said main feed location,

feeding said at least one aqueous solution comprising acetic acid to at least one aqueous feed location on said vessel, said aqueous feed location being vertically below said main feed location,

recovering at least some of said organic phase from said vessel at an organic phase recovery location, said organic phase recovery location being vertically below said main feed location and

recovering at least some of said aqueous phase from said vessel at an aqueous phase recovery location, aqueous phase recovery location being vertically above said main feed location.

4. The process of claim 3, wherein the aqueous stream further comprises hydrogen iodide.

5. The process of any of claims 1-4, wherein said liquid comprising catalyst and tar prior further comprises methyl iodide.

6. The process of any of Claims 1-5, wherein said liquid comprising catalyst and tar prior further comprises acetic acid.

7. The process of any of Claims 1-6, wherein said liquid comprising catalyst and tar prior further comprises hydrogen iodide.

8. The process of any of Claims 1-7, wherein said combining occurs in the presence of elemental iodine.

9. The process of claim 8, wherein said liquid comprising catalyst and tar comprises at least some of said elemental iodine.

10. The process of any of claims 1-9, wherein said at least one aqueous solution comprising acetic acid comprises at least a first solution that comprises hydrogen iodide but does not contain acetic acid and a second solution that comprises acetic acid but does not contain hydrogen iodide.

11. The process of any of claims 1-10, wherein said at least one aqueous solution comprising acetic acid comprises at least one single solution that comprises both hydrogen iodide and acetic acid.

12. The process of any of claims 1-11, wherein said catalyst comprises at least one Group VIII metal.

13. The process of claim 12, wherein at least one Group VIII metal is rhodium.

14. The process of any of claims 1-13, wherein said at least one aqueous phase recovery location is located vertically above said at least one organic feed location.

15. The process of any of claims 1-14, wherein said at least one organic phase recovery location is located vertically below said at least one aqueous feed location.

16. The process of any of claims 1-15, wherein said vessel comprises an upper vertical third, a middle vertical third, and a lower vertical third, and said at least one aqueous feed location is located in the lower vertical third of said vessel.

17. The process of any of claims 3-16, wherein said vessel comprises an upper vertical third, a middle vertical third, and a lower vertical third, and said at least one organic feed location is located in said upper vertical third of said vessel.

18. The process of any of claims 1-17, wherein said vessel comprises a column, said column comprising at least one reciprocating plate agitator.

19. The process of any of claims 1-18, wherein 22.5% to 55% by weight of all materials fed to said vessel is acetic acid.

20. The process of any of claims 1-19, wherein 0.5 to 10% by weight of all materials fed to said vessel is hydrogen iodide.

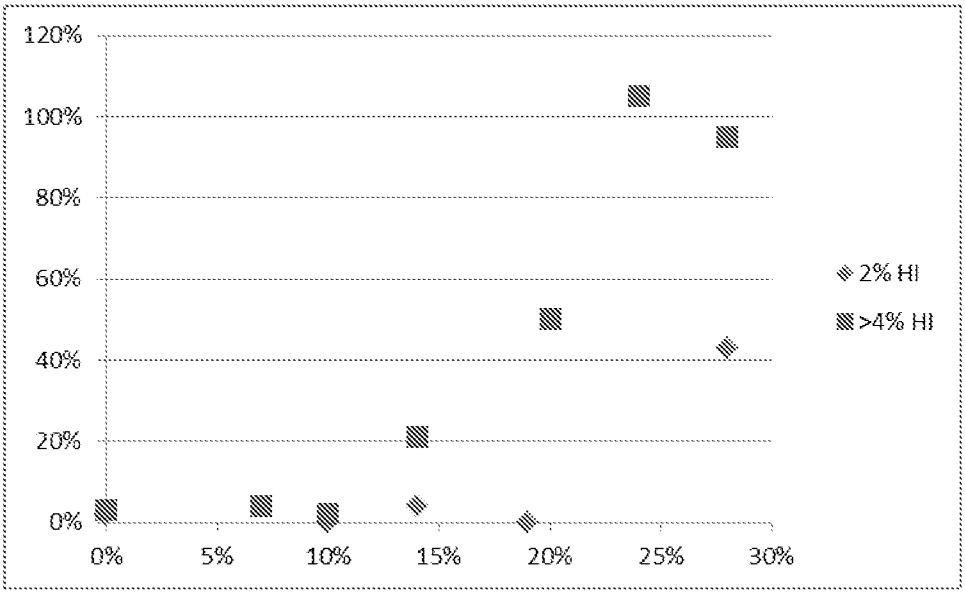

FIGURE 1

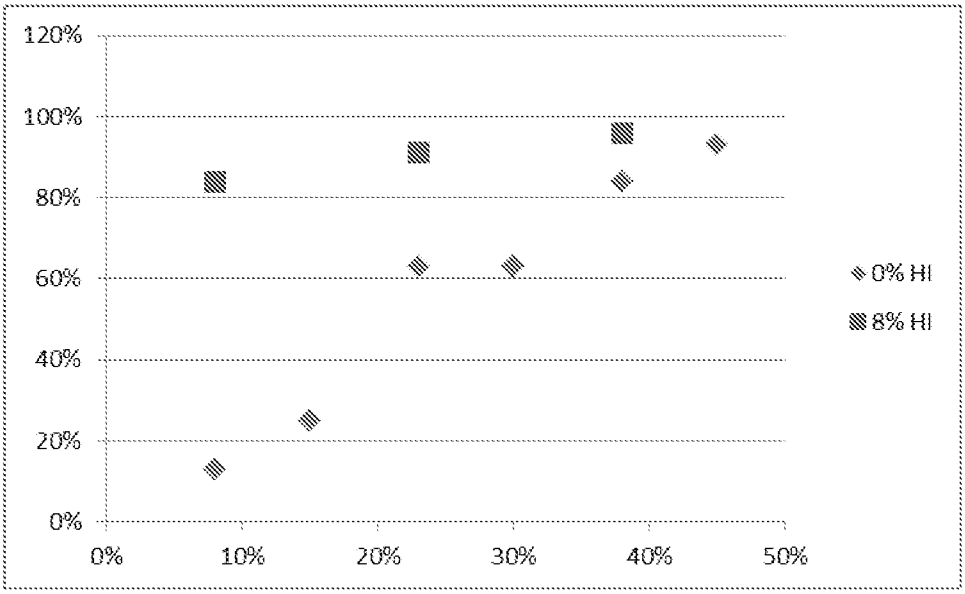

FIGURE 2

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 11/67702

A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - B01J 38/48 (2012.01)
USPC - 502/22; 502/28; 423/22

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)
USPC - 502/22; 502/28; 423/22

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
PubWEST (USPT, PGPB, JPAB, EPAB); Google
Search Terms; catalyst, recover, recycle, tar, acetic acid, hydrogen iodide, methyl iodide, organic, vapor, liquid, phase, column, reactor, botom, top, feed, stream,

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 4,388,217 A (Hembre et al.) 14 Jun 1983 (14.06.1983), entire document especialy Abstract, col 2, ln 30-40, col 5, ln 5-15, col 2, ln 49-62, col 4, ln 40-50 and Example 1	1-5
Y	US 4,944,927 A (Gulliver) 31 Jul 1990 (31.07.1990), entire document especially Abstract, Fig. 1	1-5

☐ Further documents are listed in the continuation of Box C.

* 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 16 Apr 2012 (16.04.2012)	Date of mailing of the international search report 27 APR 2012
Name and mailing address of the ISA/US Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-3201	Authorized officer: Lee W. Young PCT Helpdesk: 571-272-4300 PCT OSP: 571-272-7774

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 11/67702

Box No. II Observations where certain claims were round unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article I7(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.: 6-20
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. Ill 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.