CLAIMS

What is claimed is:

1. A process for producing acetic acid comprising:

contacting methanol and carbon monoxide in the presence of a liquid reaction medium under carbonylation conditions sufficient to form acetic acid, wherein the liquid reaction medium comprises:

a carbonylation catalyst selected from rhodium catalysts, iridium catalysts and palladium catalysts;

from 1 wt.% to 14 wt.% water; and

one or more additives, in-situ generated derivatives of the one or more additives and combinations thereof;

wherein the one or more additives are independently selected from non-benzoyl containing pentavalent phosphine oxides, compound mixtures of at least four phosphine oxides and pentavalent aryl or alkaryl phosphine oxides comprising one or more benzoyl groups;

wherein the non-benzoyl containing pentavalent phosphine oxides have the formula $R_3P=O$, wherein each R is independently selected from substituted or unsubstituted alkyls, aryls, aralkyls and combinations thereof; and

wherein each phosphine oxide of the compound mixtures has the formula OPX_3, wherein O is oxygen, P is phosphorous and X is independently selected from C_4-C_{18} alkyls, C_4-C_{18} aryls, C_4-C_{18} cyclic alkyls, C_4-C_{18} cyclic aryls and combinations thereof and wherein each phosphine oxide has at least 15 carbon atoms; and

recovering acetic acid from the process.

2. The process of claim 1, wherein the one or more additives comprise an additive package comprising at least two additives, in-situ generated derivatives of the at least two additives and combinations thereof and wherein the at least two additives are independently selected from the non-benzoyl containing pentavalent phosphine oxides, the compound mixtures of at least four phosphine oxides and the pentavalent aryl or alkaryl phosphine oxides comprising one or more benzoyl groups.

3. The process of claim 1, wherein the reaction medium comprises from 1 wt.% to 10 wt.% water.

4. The process of claim 1, wherein the reaction medium comprises a concentration of additive of from 0.005 mol/L to 2.0 mol/L.
5. The process of claim 1, wherein the reaction medium comprises a molar ratio of additive to iodide of from 0.005:1 to 5:1.
6. The process of claim 1 exhibiting a corrosion rate that is at least 80% less than that of an identical process absent the additive package.
7. The process of claim 1, wherein the compound mixture comprises from 1 wt.% to 60 wt.% of each phosphine oxide based on the total weight of compound mixture.
8. The process of claim 1, wherein the compound mixture comprises tri-n-octylphosphine oxide (TOPO), tri-n-hexylphosphine oxide (THPO), dihexylmonooctylphosphine oxide and dioctylmonohexylphosphine oxide.
9. The process of claim 1, wherein the compound mixture comprises from 12 wt.% to 16 wt.% tri-n-octylphosphine oxide (TOPO), from 8 wt.% to 16 wt.% tri-n-hexylphosphine oxide (THPO), from 28 wt.% to 32 wt.% dihexylmonooctylphosphine oxide and from 40 wt.% to 44 wt.% dioctylmonohexylphosphine oxide.
10. The process of claim 1, wherein the pentavalent aryl or alkaryl phosphine oxides comprising one or more benzoyl groups are selected from bis(2,4,6-trimethylbenzoyl) phenyl phosphine oxide (BAPO), (2,4,6-trimethylbenzoyl) diphenyl phosphine oxide (TMDPO) and combinations thereof.
11. The process of claim 1, wherein the non-benzoyl containing pentavalent phosphine oxides are selected from triethyl phosphine oxide, tributyl phosphine oxide, tripentyl phosphine oxide, diphenylmethyl phosphine oxide, triphenyl phosphine oxide and combinations thereof.
12. The process of claim 1, wherein the non-benzoyl containing pentavalent phosphine oxides comprise a phenyl group directly bonded to the phosphorous atom.
13. The process of claim 2, wherein the additive package comprises essentially equal concentrations of each of the at least two additives.
14. The process of claim 1 further comprising introducing a second concentration of the additive into the process downstream of the reaction zone.
15. The process of claim 14 further comprising adjusting the second concentration in response to a downstream iodide content.
16. The process of claim 14, wherein the second concentration comprises a molar ratio of additive to iodide of from 2.5:1 to 3.5:1.

17. The process of claim 1, wherein the additive comprises the non-benzoyl containing pentavalent phosphine oxide and the reaction mixture comprises from 0.001M to less than 0.20M additive, in-situ generated additive derivatives and combinations thereof.

18. The process of claim 1, wherein the additive comprises the non-benzoyl containing pentavalent phosphine oxide and the carbonylation catalyst comprises iridium catalysts.

19. A process for determining corrosion comprising:

providing a batch reactor;

disposing a solution comprising components of a liquid reaction medium of a target reaction within the batch reactor, wherein the solution is absent catalyst and feedstock for the target reaction;

operating the batch reactor at reaction conditions simulating the target reaction for a reaction time sufficient to determine the corrosion of the batch reactor;

retrieving the solution from the batch reactor; and

analyzing the solution for a metal concentration therein.

20. The process of claim 19, wherein the one or more phosphine oxide additives are selected from non-benzoyl containing pentavalent phosphine oxides, compound mixtures of at least four phosphine oxides and pentavalent aryl or alkaryl phosphine oxides comprising one or more benzoyl groups.

CLAIMS

What is claimed is:

1. A process for producing acetic acid comprising:

contacting methanol and carbon monoxide in the presence of a liquid reaction medium under carbonylation conditions sufficient to form acetic acid, wherein the liquid reaction medium comprises:

a carbonylation catalyst selected from rhodium catalysts, iridium catalysts and palladium catalysts;

from 1 wt.% to 14 wt.% water; and

one or more additives, in-situ generated derivatives of the one or more additives and combinations thereof;

wherein the one or more additives are independently selected from non-benzoyl containing pentavalent phosphine oxides, compound mixtures of at least four phosphine oxides and pentavalent aryl or alkaryl phosphine oxides comprising one or more benzoyl groups;

wherein the non-benzoyl containing pentavalent phosphine oxides have the formula $R_3P{=}O$, wherein each R is independently selected from substituted or unsubstituted alkyls, aryls, aralkyls and combinations thereof; and

wherein each phosphine oxide of the compound mixtures has the formula OPX_3, wherein O is oxygen, P is phosphorous and X is independently selected from C_4-C_{18} alkyls, C_4-C_{18} aryls, C_4-C_{18} cyclic alkyls, C_4-C_{18} cyclic aryls and combinations thereof and wherein each phosphine oxide has at least 15 carbon atoms; and

recovering acetic acid from the process.

2. The process of claim 1, wherein the one or more additives comprise an additive package comprising at least two additives, in-situ generated derivatives of the at least two additives and combinations thereof and wherein the at least two additives are independently selected from the non-benzoyl containing pentavalent phosphine oxides,

the compound mixtures of at least four phosphine oxides and the pentavalent aryl or alkaryl phosphine oxides comprising one or more benzoyl groups.

3. The process of claim 1, wherein the reaction medium comprises a concentration of additive of from 0.005 mol/L to 2.0 mol/L.

4. The process of claim 1, wherein the reaction medium comprises a molar ratio of additive to iodide of from 0.005:1 to 5:1.

5. The process of claim 1 exhibiting a corrosion rate that is at least 80% less than that of an identical process absent the additive package.

6. The process of claim 1, wherein the compound mixture comprises tri-n-octylphosphine oxide (TOPO), tri-n-hexylphosphine oxide (THPO), dihexylmonooctylphosphine oxide and dioctylmonohexylphosphine oxide.

7. The process of claim 1, wherein the compound mixture comprises from 12 wt.% to 16 wt.% tri-n-octylphosphine oxide (TOPO), from 8 wt.% to 16 wt.% tri-n-hexylphosphine oxide (THPO), from 28 wt.% to 32 wt.% dihexylmonooctylphosphine oxide and from 40 wt.% to 44 wt.% dioctylmonohexylphosphine oxide.

8. The process of claim 1, wherein the pentavalent aryl or alkaryl phosphine oxides comprising one or more benzoyl groups are selected from bis(2,4,6-trimethylbenzoyl) phenyl phosphine oxide (BAPO), (2,4,6-trimethylbenzoyl) diphenyl phosphine oxide (TMDPO) and combinations thereof.

9. The process of claim 1, wherein the non-benzoyl containing pentavalent phosphine oxides are selected from triethyl phosphine oxide, tributyl phosphine oxide, tripentyl phosphine oxide, diphenylmethyl phosphine oxide, triphenyl phosphine oxide and combinations thereof.

10. The process of claim 1, wherein the non-benzoyl containing pentavalent phosphine oxides comprise a phenyl group directly bonded to the phosphorous atom.

11. The process of claim 1 further comprising introducing a second concentration of the additive into the process downstream of the reaction zone.

12. The process of claim 11, wherein the second concentration comprises a molar ratio of additive to iodide of from 2.5:1 to 3.5:1.

13. The process of claim 1, wherein the additive comprises the non-benzoyl containing pentavalent phosphine oxide and the reaction mixture comprises from 0.001M to less than 0.20M additive, in-situ generated additive derivatives and combinations thereof.

14. A process for determining corrosion comprising:
providing a batch reactor;
disposing a solution comprising components of a liquid reaction medium of a target reaction within the batch reactor, wherein the solution is absent catalyst and feedstock for the target reaction;
operating the batch reactor at reaction conditions simulating the target reaction for a reaction time sufficient to determine the corrosion of the batch reactor;
retrieving the solution from the batch reactor; and
analyzing the solution for a metal concentration therein.

15. The process of claim 14, wherein the one or more phosphine oxide additives are selected from non-benzoyl containing pentavalent phosphine oxides, compound mixtures of at least four phosphine oxides and pentavalent aryl or alkaryl phosphine oxides comprising one or more benzoyl groups.