PROCESS FOR BETA-LACTONE PRODUCTION

Cross-Reference to Related Applications

The present application claims priority to U.S. Provisional Patent Application serial numbers 61/167,711, filed April 8, 2009, 61/286,382, filed December 15, 2009, and 61/310,257 filed March 3, 2010, the contents of each of which are herein incorporated by reference.

Background of the Invention

Beta-lactones are useful intermediates in the synthesis of other chemical compounds including acrylic acid and acrylates. Acrylic acid is used as a precursor in a wide variety of chemical industries. Acrylic acid is typically produced from a feedstock of propene, which is itself a byproduct of ethylene and gasoline production. Economic and environmental circumstances have lead to interest in other methods of production of acrylic acid and other acrylates from a variety of feedstocks. Additional feedstocks can include epoxides.

Summary ~~of the Invention~~

In a first aspect, there is provided a method comprising the steps of reacting the contents of a feed stream including an epoxide, a solvent with a carbonylation catalyst and carbon monoxide to produce a reaction product stream including a beta-lactone, separating a portion of the beta-lactone in the reaction product stream from the solvent and carbonylation catalyst to produce: i) a beta-lactone stream with the beta-lactone, and ii) a catalyst recycling stream including the carbonylation catalyst; and adding the catalyst recycling stream to the feed stream.

In ~~various aspects~~one embodiment, the present ~~invention~~ disclosure provides a method including the steps of reacting the contents of a feed stream including an epoxide, a solvent with a carbonylation catalyst and carbon monoxide to produce a reaction product stream including a beta-lactone, separating a portion of the beta-lactone in the reaction product stream from the solvent and carbonylation catalyst to produce: i) a beta-lactone stream with the beta-lactone, and ii) a catalyst recycling stream including the carbonylation catalyst; and adding the catalyst recycling stream to the feed stream.

In some embodiments, the method further includes treating the beta-lactone stream under conditions to convert the beta lactone into a compound selected from the group consisting of: acrylic acid, methyl acrylate, ethyl acrylate, n-butyl acrylate, isobutyl acrylate, 2-ethylhexyl acrylate.

In some embodiments, the reacting step is performed at a pressure from about 50 psi to about 5000 psi. In some embodiments, the reacting step is performed at a pressure from about 50 psi to about 1500 psi. In some embodiments, the reacting step is performed at a pressure from about 200 psi to about 800 psi. In some embodiments, the reacting step is performed at a pressure of about 400 psi.

In some embodiments, the reacting step is performed at a temperature from about 0 °C to about 125 °C.

In some embodiments, the reacting step is performed at a temperature from about 30 °C to about 100 °C. In some embodiments, the reacting step is performed at a temperature from about 40 °C to about 80 °C.

In some embodiments, the carbon monoxide in the reacting step is supplied as an industrial gas stream comprising carbon monoxide and one or more additional gases. In some embodiments, the industrial gas stream comprises syngas. In some embodiments, the carbon monoxide in the reacting step is supplied in substantially pure form.

In some embodiments, the beta-lactone stream comprises residual unreacted epoxide, carbon monoxide, or solvent. In some embodiments, the epoxide, carbon monoxide or solvent are returned to the feed stream. In some embodiments, a portion of the beta-lactone stream is returned to the feed.

~~In various aspects t~~The present ~~invention~~ disclosure further provides a method including steps of reacting the contents of a feed stream comprising an epoxide, a solvent, a carbonylation catalyst and carbon monoxide to produce a reaction product stream comprising a beta-lactone; separating at least a portion of the beta-lactone in the reaction product stream from the solvent and carbonylation catalyst to produce: i) a beta-lactone stream comprising the beta-lactone, and ii) a catalyst recycling stream comprising the carbonylation catalyst; and adding the catalyst recycling stream to the feed stream.

In some embodiments, the separating step includes steps of a first separating step to separate the reaction product stream into i) a gaseous stream comprising carbon monoxide, and the epoxide; and ii) a liquid stream comprising the beta-lactone, and the carbonylation catalyst; and a second separating step to separate at least a portion of the beta-lactone in the liquid stream

from the solvent and carbonylation catalyst to produce: i) a beta-lactone stream comprising the beta-lactone; and ii) the catalyst recycling stream comprising the carbonylation catalyst.

In some embodiments, the first separating step includes steps of separating the reaction product stream into i) a gaseous stream comprising carbon monoxide and a portion of the epoxide, and ii) a liquid stream comprising a remainder of the epoxide, the beta-lactone, and the carbonylation catalyst; and separating the liquid stream into i) an epoxide stream comprising the remainder of the epoxide; and ii) the nonvolatile stream comprising the beta-lactone, and the carbonylation catalyst.

In some embodiments, the catalyst recycling stream further includes at least a portion of the solvent, where the solvent has a boiling point higher than the boiling point of the beta-lactone. In some embodiments, the method includes the step of returning the gaseous stream to the feed stream. In some embodiments, the method includes the step of returning the beta-lactone stream to the feed stream. In some embodiments, the method includes the step of returning the catalyst recycling stream to the feed stream.

In some embodiments, the gaseous stream further includes a portion of the solvent, where the solvent has a boiling point lower than the boiling point of the beta-lactone. In some embodiments, the gaseous stream is returned to the feed stream. In some embodiments, the method includes the step of returning at least one of the gaseous stream and the epoxide stream to the feed stream. In some embodiments, the method includes the step of returning the liquid stream to the feed stream. In some embodiments, the method includes the step of returning the nonvolatile stream to the feed stream. In some embodiments, the epoxide stream further comprises a portion of the solvent, where the solvent has the boiling point lower than the boiling point of the beta-lactone. In some embodiments, the gaseous stream is returned to the feed stream.

In some embodiments, the feed stream further comprises a Lewis base additive. In some embodiments, the Lewis base additive is selected from modified THF; 2,6-lutidine; imidazole; 1-methylimidazole 4- dimethylaminopyridine; trihexylamine, and triphenylphosphine.

In yet another aspect, there is provided a method comprising steps of: reacting the contents of a feed stream comprising an epoxide, a solvent with a carbonylation catalyst and carbon monoxide to produce a reaction product stream comprising a beta-lactone; returning the

entirety of the reaction product stream to the feed stream until the weight percent of beta-lactone in the reaction product stream is in a predetermined range; then separating at least a portion of the beta-lactone in the reaction product stream from the solvent and carbonylation catalyst to produce: i) a beta-lactone stream comprising the beta-lactone, and ii) a catalyst recycling stream comprising the carbonylation catalyst and the solvent; and adding the catalyst recycling stream to the feed stream.

In ~~various~~ one ~~aspects~~embodiment, the ~~invention~~ present disclosure includes a method including steps of: reacting the contents of a feed stream comprising an epoxide, a solvent with a carbonylation catalyst and carbon monoxide to produce a reaction product stream comprising a beta-lactone; returning the

22. The method of claim 1, further comprising treating the catalyst recycling stream, prior to the adding step by performing at least one step selected from the group consisting of: adding fresh carbonylation catalyst, removing spent carbonylation catalyst; adding solvent; adding epoxide, adding a portion of the beta-lactone stream; and any combination of two or more of these.

23. The method of claim 1, wherein the separating step comprises volatilizing at least a portion of the beta-lactone from the reaction product stream.

24. The method of claim 1, wherein the separating step comprises exposing the reaction product stream to reduced pressure.

25. The method of claim 24, wherein the reduced pressure is between about 5 Torr and about 500 Torr.

26. The method of claim 24, wherein the reduced pressure is between about 10 Torr and about 100 Torr.

~~27. The method of claim 24, wherein the reduced pressure is sufficient to reduce the boiling point of the beta-lactone by about 20 to about 100 °C below its boiling point at atmospheric pressure.~~

~~28.~~27. The method of claim 1, wherein the separating step comprises exposing the reaction product stream to elevated temperature.

~~29.~~28. The method of claim ~~28~~27, wherein the elevated temperature is greater than the boiling point of the beta-lactone but less than the boiling point of the solvent.

~~30.~~29. The method of claim 23, wherein the separating step comprises exposing the reaction product stream to reduced pressure and elevated temperature.

~~31. The method of claim 23, further comprising a step of condensing the volatilized beta-lactone from the separating step.~~

~~32.~~30. The method of claim 1, further comprising adding beta-lactone to the feed stream.

~~33.~~31. The method of claim ~~32~~30, wherein the beta-lactone added to the feed stream comprises a portion of the beta-lactone stream.

34.32. The method of claim 33-31 wherein the beta-lactone stream is added to the feed until the weight percent of beta-lactone in the reaction product stream is in the range of about 10% to about 90%, then withdrawing a portion of the beta-lactone stream as a product to maintain the weight percent of beta-lactone in the reaction product stream in the range of about 10% to about 90%.

35.33. The method of claim 31 33-wherein the beta-lactone stream is added to the feed until the weight percent of beta-lactone in the reaction product stream is in the range of about 30% to about 65%, then withdrawing a portion of the beta-lactone stream as a product to maintain the weight percent of beta-lactone in the reaction product stream in the range of about 30% to about 65%.

36.34. The method of claim 31 33-wherein the beta-lactone stream is added to the feed until the weight percent of beta-lactone in the reaction product stream is in the range of about 43% to about 53%, then withdrawing a portion of the beta-lactone stream as a product to maintain the weight percent of beta-lactone in the reaction product stream in the range of about 43% to about 53%.

37.35. The method of claim 2, further comprising adding a second solvent to the beta lactone prior to the treating step.

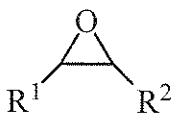
38.36. The method of claim 2, wherein the treating step is performed in the gas phase.

39.37. The method of claim 1, wherein the boiling point of the solvent is at least 20 °C higher than the boiling point of the beta lactone.

40.38. The method of claim 1, wherein the boiling point of the solvent is between about 20 and about 80 °C higher than the boiling point of the beta-lactone.

41.39. The method of claim 1, wherein the boiling point of the solvent is about 30 to about 60 °C higher than the boiling point of the beta lactone.

42.40. The method of claim 1, wherein the epoxide has the formula



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where, R^1 and R^2, are each independently selected from the group consisting of: –H; optionally substituted C_{1-6} aliphatic; optionally substituted phenyl; optionally substituted C_{1-6} heteroaliphatic; optionally substituted 3- to 6-membered carbocycle; and optionally substituted 3- to 6-membered heterocycle,

where R^1 and R^2 can optionally be taken together with intervening atoms to form a 3- to 6-membered, substituted or unsubstituted ring optionally containing one or more heteroatoms.

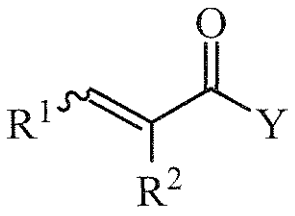
~~43.~~41. The method of claim 1, wherein the epoxide is chosen from the group consisting of: ethylene oxide; propylene oxide; 1,2-butylene oxide; 2,3-butylene oxide; epichlorohydrin; cyclohexene oxide; cyclopentene oxide; 3,3,3-Trifluoro-1,2-epoxypropane, styrene oxide; a glycidyl ether; and a glycidyl ester.

~~44.~~42. The method of claim 1, wherein the epoxide comprises ethylene oxide.

~~45.~~43. The method of claim 1, wherein the epoxide comprises propylene oxide.

~~46.~~44. The method of claim 2, wherein the treating step is performed in the presence of a compound selected from the group consisting of: an alcohol, an amine and a thiol, under conditions that produce the corresponding acrylic ester, acrylamide, or a thioacrylate respectively.

~~47.~~45. The method of claim 2, wherein the treating step is performed in the presence of a compound of formula H-Y to afford an acrylate having the formula



wherein, R^1 and R^2, are each independently selected from the group consisting of: –H, optionally substituted C_{1-6} aliphatic, optionally substituted C_{1-6} heteroaliphatic, optionally substituted 3- to 12-membered carbocycle, and optionally substituted 3- to 12-membered heterocycle, or R^1 and R^2 can optionally be taken together with intervening

atoms to form an optionally substituted ring optionally containing one or more heteroatoms;

wherein, Y is selected from the group consisting of OR^{13}, $NR^{11}R^{12}$, and SR^{13};

wherein, R^{11}, R^{12}, and R^{13} are independently selected from the group consisting of: –H; optionally substituted C_{1-32} aliphatic, optionally substituted C_{1-32} heteroaliphatic, optionally substituted 3- to 14-membered carbocycle, and optionally substituted 3- to 14-membered heterocycle, or R^{11} and R^{12} can optionally be taken together with intervening atoms to form an optionally substituted ring optionally containing one or more heteroatoms.

~~48.~~46. The method of claim 1, wherein the feed stream comprises ethylene oxide and a high boiling solvent that has a boiling point of at least 172 °C at atmospheric pressure; and the reaction product stream contains beta-propiolactone.

~~49.~~47. The method of claim 1, wherein the feed stream comprises propylene oxide and a high boiling solvent that has a boiling point of at least 180 °C at atmospheric pressure; and the reaction product stream contains beta-butyrolactone.

~~50.~~48. The method of claim 1, wherein the solvent is selected from the group consisting of: esters; ethers; sulfolane; cyclic carbonates; imidazolidinones; and pyrolidones.

~~51.~~49. The method of claim 1, wherein the solvent is selected from the group consisting of: sulfolane; N-methyl pyrrolidone; 1,3-Dimethyl-2-imidazolidinone; diglyme; triglyme; tetraglyme; ethylene carbonate; propylene carbonate; dibasic esters; THF; THF modified with a C_{1-32} aliphatic; and mixtures of any two or more of these.

~~52.~~50. The method of claim ~~51~~49, wherein the solvent comprises THF.

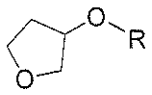
~~53.~~51. The method of claim 49~~51~~, wherein the solvent comprises sulfolane.

~~54.~~52. The method of claim 49~~51~~, wherein the solvent comprises a dibasic ester.

~~55.~~53. The method of claim 49~~51~~, wherein the solvent comprises a mixture of sulfolane and THF.

~~56.~~54. The method of claim 49~~51~~, wherein the solvent comprises a mixture of sulfolane and THF modified with a C_{1-32} aliphatic.

~~57.~~55. The method of claim 49~~51~~, wherein the modified THF has the form:



wherein, R is selected from the group consisting of: optionally substituted aliphatic; optionally substituted acyl, optionally substituted aromatic, and polyether.

~~58.~~56. The method of claim ~~49~~51, wherein the solvent further comprises isosorbide dimethyl ether.

~~59.~~57. The method of either claim ~~48~~46 or ~~49~~47, wherein the feed stream comprises sulfolane.

~~60.~~58. The method of either claim ~~48~~46 or ~~49~~47, wherein the feed stream comprises one of THF, and THF modified with a $C_{1\text{-}32}$ aliphatic.

~~61.~~59. The method of either claim ~~48~~46 or ~~49~~47, wherein the feed stream comprises a dibasic-ester.

~~62.~~60. The method of claim 1, wherein the carbonylation catalyst comprises a metal carbonyl compound.

~~63.~~61. The method of claim ~~62~~60, wherein the metal carbonyl compound has the general formula

$[QM_y(CO)_w]^x$,

where: Q is any ligand and need not be present;

M is a metal atom;

y is an integer from 1 to 6 inclusive;

w is a number such as to provide the stable metal carbonyl; and

x is an integer from -3 to +3 inclusive.

~~64. The method of claim 63, wherein M is selected from the group consisting of Ti, Cr, Mn, Fe, Ru, Co, Rh, Ni, Pd, Cu, Zn, Al, Ga and In.~~

~~65. The method of claim 63, wherein M is Co.~~

~~66. The method of claim 63, wherein M is Co, y is 1, and w is 4.~~

~~67. The method of claim 63, wherein the carbonylation catalyst further comprises a Lewis acidic co-catalyst.~~

~~68. The method of claim 67, wherein the metal carbonyl compound is anionic, and the Lewis acidic co-catalyst is cationic.~~

~~69. The method of claim 68, wherein the metal carbonyl complex comprises a carbonyl cobaltate and the Lewis acidic co-catalyst comprises a metal-centered cationic Lewis acid.~~

~~70. The method of claim 69, wherein the metal-centered cationic Lewis acid is a metal complex of formula $[M'(L)_b]^{c+}$;~~

~~where, M' is a metal;~~

~~each L is a ligand;~~

~~b is an integer from 1 to 6 inclusive;~~

~~c is 1, 2, or 3; and~~

~~where, if more than one L is present, each L may be the same or different.~~

~~71. The method of claim 70, where M' is selected from the group consisting of: a transition metal, a group 13 or 14 metal, and a lanthanide.~~

~~72. The method of claim 70, where M' is a transition metal or a group 13 metal.~~

~~73. The method of claim 70, where M' is selected from the group consisting of aluminum, chromium, indium and gallium.~~

~~74. The method of claim 70, where M' is aluminum.~~

~~75. The method of claim 70, where M' is chromium.~~

~~76. The method of claim 70, where the Lewis acid includes a dianionic tetradentate ligand.~~

~~77. The method of claim 76, where the dianionic tetradentate ligand is selected from the group consisting of: porphyrin derivatives; salen derivatives; dibenzotetramethyltetraaza[14]annulene (tmtaa) derivatives; phthalocyaninate derivatives; and derivatives of the Trost ligand.~~

~~78.~~62. The method of claim 2, wherein the treating step is mediated by a catalyst.

~~79.~~63. The method of claim ~~78~~62, wherein the catalyst in the treating step is an acid catalyst.

~~80.~~64. The method of claim ~~78~~62, wherein the catalyst in the treating step is a basic catalyst.

~~81.~~65. The method of claim 1, wherein the reacting step is performed in adiabatic reactor.

~~82.~~66. The method of claim ~~81~~65, wherein the adiabatic reactor is a tubular reactor.

~~83. The method of claim 81, wherein the adiabatic reactor is a shell and tube reactor.~~

~~84.~~67. The method of claim 1, wherein the reacting step is performed at a pressure from about 50 psi to about 5000 psi.

~~85.~~68. The method of claim 1, wherein the reacting step is performed at a pressure from about 50 psi to about 2000 psi.

~~86.~~69. The method of claim 1, wherein the reacting step is performed at a pressure from about 200 psi to about 1000 psi.

~~87.~~70. The method of claim 1, wherein the reacting step is performed at a pressure from about 200 psi to about 600 psi.

~~88.~~71. The method of claim 1, wherein the reacting step is performed at a temperature from about 0 °C to about 125 °C.

~~89.~~72. The method of claim 1, wherein the reacting step is performed at a temperature from about 30 °C to about 100 °C.

~~90.~~73. The method of claim 1, wherein the reacting step is performed at a temperature from about 40 °C to about 80 °C.

~~91.~~74. The method of claim 1, wherein the carbon monoxide in the reacting step is supplied as an industrial gas stream comprising carbon monoxide and one or more additional gases.

~~92.~~75. The method of claim ~~91~~74, wherein the industrial gas stream comprises syngas.

~~93.~~76. The method of claim 1, wherein the carbon monoxide in the reacting step is supplied in substantially pure form.

~~94.~~77. The method of claim 1, wherein the beta-lactone stream comprises unreacted epoxide.

~~95.~~78. The method of claim 1, wherein the beta-lactone stream comprises carbon monoxide.

~~96.~~79. The method of claim 1, wherein the beta-lactone stream comprises solvent.

~~97.~~80. The method of any of claims ~~94~~77 to ~~96~~79, wherein the epoxide, carbon monoxide or solvent are returned to the feed stream.

~~98.~~ 81. The method of claim ~~97~~80, wherein a portion of the beta-lactone stream is returned to the feed.

~~99. A method comprising steps of:~~

~~reacting the contents of a feed stream comprising an epoxide, a solvent a carbonylation catalyst and carbon monoxide to produce a reaction product stream comprising a beta-lactone;~~

~~separating at least a portion of the beta-lactone in the reaction product stream from the carbonylation catalyst to produce:~~

~~i) a beta-lactone stream comprising beta-lactone, and~~

~~ii) a catalyst recycling stream comprising the carbonylation catalyst; and~~

~~adding the catalyst recycling stream to the feed stream.~~

~~100. The method of claim 99, wherein the separating step comprises steps of;~~

~~a first separating step to separate the reaction product stream into~~

~~i) a volatile stream comprising carbon monoxide, and the epoxide; and~~

~~ii) a nonvolatile stream comprising the beta-lactone, and the carbonylation catalyst; and~~

~~a second separating step to separate at least a portion of the beta-lactone in the nonvolatile stream from the solvent and carbonylation catalyst to produce:~~

~~i) a beta-lactone stream comprising beta-lactone; and~~

~~ii) the catalyst recycling stream comprising the carbonylation catalyst.~~

~~101. The method of claim 100, wherein the first separating step comprises steps of;~~

~~separating the reaction product stream into~~

~~i) a gaseous stream comprising carbon monoxide and a portion of the epoxide, and~~

~~ii) a liquid stream comprising a remainder of the epoxide, the beta-lactone, and the carbonylation catalyst; and~~

~~separating the liquid stream into~~

~~i) an epoxide stream comprising additional epoxide; and~~

~~ii) the nonvolatile stream comprising the beta-lactone, and the carbonylation catalyst.~~

~~102. The method of claim 99, wherein the catalyst recycling stream further comprises solvent, where at least a portion of the solvent has a boiling point higher than the boiling point of the beta-lactone.~~

~~103. The method of claim 100, further comprising the step of returning the volatile stream to the feed stream.~~

~~104. The method of claim 101, wherein the volatile stream further comprises solvent, where at least a portion of the solvent has a boiling point lower than the boiling point of the beta-lactone.~~

~~105. The method of claim 101, wherein the epoxide stream further comprises solvent, where at least a portion of the solvent has a boiling point lower than the boiling point of the beta-lactone.~~

~~106. The method of claim 101, further comprising the step of returning at least one of the gaseous stream and the epoxide stream to the feed stream.~~

~~107. The method of claim 1, wherein the feed stream further comprises a Lewis base additive.~~

~~108. The method of claim 107, wherein the Lewis base additive is selected from the group consisting of compounds having a Lewis basic nitrogen atom, phosphorous atom, or oxygen atom.~~

~~109. The method of claim 108, wherein the Lewis base additive is selected from the group consisting of phosphines, amines and ethers.~~

~~110. The method of claim 107, where the Lewis base additive is selected from modified THF; 2,6-lutidine; imidazole; 1-methylimidazole; 4-dimethylaminopyridine; trihexylamine and triphenylphosphine.~~

~~111.~~82. A method comprising steps of:

reacting the contents of a feed stream comprising an epoxide, a solvent, a carbonylation catalyst and carbon monoxide to produce a reaction product stream comprising a beta-lactone;

returning the entirety of the reaction product stream to the feed stream until the weight percent of beta-lactone in the reaction product stream is in a predetermined range; then separating at least a portion of the beta-lactone in the reaction product stream from the solvent and carbonylation catalyst to produce:

i) a beta-lactone stream comprising beta-lactone, and

ii) a catalyst recycling stream comprising the carbonylation catalyst and the solvent; and

adding the catalyst recycling stream to the feed stream.

~~112.~~83. The method of claim ~~111~~ 82 wherein the reaction product stream is returned to the feed until the weight percent of beta-lactone in the reaction product stream is in the range of about 10% to about 90%, then withdrawing a portion of the beta-lactone stream as a product to maintain the weight percent of beta-lactone in the reaction product stream in the range of about 10% to about 90%.

~~113.~~84. The method of claim ~~111~~ 82 wherein the reaction product stream is returned to the feed until the weight percent of beta-lactone in the reaction product stream is in the range of about 30% to about 65%, then withdrawing a portion of the beta-lactone stream as a product to maintain the weight percent of beta-lactone in the reaction product stream in the range of about 30% to about 65%.

~~114.~~85. The method of claim ~~111~~ 82 wherein the reaction product stream is returned to the feed until the weight percent of beta-lactone in the reaction product stream is in the range of about 43% to about 53%, then withdrawing a portion of the beta-lactone stream as a product to maintain the weight percent of beta-lactone in the reaction product stream in the range of about 43% to about 53%.