$$\text{Hourly Catalytic Productivity} = \frac{\text{TON}}{\text{Total reaction time, hr}}$$

Where total reaction time as used herein refers to a multiple of the reactor residence time, typically five times the residence time for purposes of the Examples. This reaction time allows for unattended operation of a steady state reaction with no catalyst deactivation.

As used herein, the term "reaction mixture" refers to the liquid mass in the reactive distillation area that contains reagents, catalyst, and optionally solvent.

As used herein, the term "reactor residence time" refers to the average amount of time a discrete quantity of reagent spends in the reactor. The mean residence time is determined by dividing the reactor volume by the volumetric flow rate of the carboxylic acid mixture fed to the reactor.

As used herein, the reaction temperature refers to an average of multiple temperature readings taken at various points between the location of the carboxylic acid feed and the vinyl acetate feed. Preferably, at least two temperature readings are averaged, and more preferably, at least three temperature readings are averaged.

Various carboxylic acids known in the art can be employed in the process of this invention to form corresponding vinyl esters. The acids that are suitable in this invention may include, but not necessarily be limited to vinyl esters of the following acids:

2-ethylhexanoic acid, benzoic acid, neodecanoic acid, propionic acid, butyric acid, valeric acid, heptanoic acid, acrylic acid, methacrylic acid, stearic acid, and palmitic acid.

about 120°C. Preferably the temperature of the reaction is maintained from about 90°C to about 110°C. However, low catalyst concentrations require higher reaction temperatures. The molar ratio of vinyl acetate to the reactant carboxylic acid charged to the reactor is about 2.2:1 to about 9:1. Ratios may be less than about 4:1, and ratios of less than 2:1 have been achieved in some cases. The reaction time ranges from less than about 3 hours to about 36 hours depending upon the catalyst concentration and acetic acid removal rate.

*Continuous inhibitor addition.* An inhibitor is added to the reaction and to the crude and purified products to prevent vinyl ester polymerization. Without inhibitor addition, side reactions may occur resulting in homopolymers or copolymers of the vinyl ester reactant and/or product. Such reactions impact quality and yield and have adverse safety implications. Any suitable inhibitor may used, such as hydroquinone (HQ), methoxy hydroquinone (MeHQ), buylated hydroxytoluene (BHT), tert-butyl catechol (TBC), or phenothiazine.

*Coproduction of acetic acid-VAM mix.* This process produces a mixture rich in acetic acid. This mixture is drawn off from the process and may be utilized directly or with minimal processing in VAM plants. Alternatively, acetic acid may be separated from the mix. Byproduct acetic acid may be used as a reactant in subsequent processes. Experiments using the Pd catalyst complex of the invention resulted in VAM:acetic acid molar ratios ranging from 0.5:1 to 14.4:1 in the recovered mixture. Preferably, the vinyl acetate:acetic acid molar ratio removed from the reaction mixture is from about 1.5:1 to about 10:1 or about 1:1 to about 9:1. More preferably, the process results in a molar ratio of VAM:acetic acid of from about 2:1 to about 7:1; and even more preferably, the process results in a molar ratio of VAM:acetic acid 2.5:1 to 6:1.

*Purification of carboxylic acid reagent.* Surprisingly, in some cases, carboxylic acid reagents demonstrating otherwise high levels of purity have been found to contain impurities that cause deactivation of the catalyst during

as VAM started distilling out from rectification column **116,** the addition of pre-mixed feed of CA, catalyst, VAM & inhibitor was started at predetermined feed rate through column **114**. The crude product that overflowed out of bubble reactor **112** through product cooler **128** was collected. Similarly the acetic acid overflowed continuously out of reboiler **120** and was separately collected. The excess VAM was continuously recovered and recycled through the condenser **122** to the VAM metering system.

In production of crude vinyl benzoate, a crystallization step might not be necessary in conjunction with reactive distillation, due to the high conversion rate achievable. Crude vinyl ester product produced through the continuous reactive distillation might need less intensive purification than is necessary for a comparable vinyl ester product from a semi-continuous process because all or almost all of the lights (i.e., vinyl acetate and acetic acid) are removed during the reaction.

Optionally, residual carboxylic acid and catalyst recovered from the crude vinyl ester product may be recycled to the reactor.

stripping column **118;** a reboiler **120;** a condenser **122;** a VAM feed vessel **124;** a VAM pre-heater / vaporizer **126;** and a product cooler **128.**

A pre-mixed feed of CA, VAM and catalyst from the carboxylic acid feed vessel **110** was charged to column **114** via line **136.** VAM from VAM feed vessel **124** was passed through preheater **126** via line **130.** The CA along with catalyst flowed downward though column **114** to bubble column reactor **112** via **134,** countercurrent to superheated VAM vapor, introduced to the reactor **112** via line **132** from preheater **126,** which rose upward through bubble column reactor **112** and subsequently column **114** via **134.** The reaction took place in the bubble column reactor **112** as well as in column **114,** producing vinyl ester and acetic acid. The VAM vapor became saturated with acetic acid. The combined vapors of VAM & acetic acid emitted out of column **114** via line **138** and entered between columns **116** and **118,** a separation system where VAM & acetic acid are continuously separated. Line **140** indicates lighter components rising through the rectification portion of the separation system represented by column **116** and line **142** indicates heavier components falling through the stripping portion of the separation system represented by column **118.** The product vinyl benzoate or vinyl-2-ethyl hexanoate along with catalyst, unconverted CA, residual VAM, and a small amount of acetic acid was continuously removed from the reactor **112** via line **144,** cooled in condenser **128,** and collected via line **146.** Heavier components from column **118** collected in reboiler **120** via line **148.** The overflow of reboiler **120** produced acetic acid and was collected in via line **150.** Lighter components from column **116** were collected via line **152,** condensed in condenser **122,** and recycled to VAM feed vessel **124** via line **154.**

**Procedure:** The bubble column reactor **112** was first charged with a composition comprising vinyl acetate, carboxylic acid, and catalyst, and heated by conventional means to 98 to 102°C. Then the VAM at a predetermined rate was pumped though the VAM pre-heater **126** which was maintained at 70°C to 100°C, the VAM vapor entered at the bottom of the bubble column reactor **112.** As soon

and is herein identified as crude V-2-EH. When distillation ceased, the contents were cooled and the vacuum released. The residue was preserved for recycle. This residue contained mainly 2-EHA, a small amount of V-2-EH and the catalyst.

*Crystallization of un-reacted BA and Recovery of VB*

The reaction mass transferred from the rotary evaporator was cooled in the crystallizer and held for several hours. The slurry was removed and filtered over a vacuum filter. The solid, semi-dried cake of BA was weighed, and the solid cake of BA was preserved for recycle in the next cycle. The mother liquor was weighed and transferred to a conventional evaporator (not shown) for recovery of VB.

Vacuum was applied and the temperature was raised. VB was allowed to distill out and was separately collected. The distillate mainly contained VB and a small amount of acetic acid and BA. This is identified herein as crude VB. Recovery continued until solid BA started appearing in the distillation still at which stage recovery ceased.

When distillation stopped, the contents were cooled and the vacuum released. The residue of unreacted BA & catalyst was preserved for recycle. This residue contained mainly BA, a small amount of VB and the catalyst.

*Purification of crude vinyl ester*

The crude V-2-EH, VB or NAVE-10 was charged to a conventional fractional distillation column (not shown) under vacuum. Around 25 ppm of HQ was added as a stabilizer. The crude mass was heated. Distillate was collected with reflux set to 1. This distillate contained VAM and acetic acid and was recycled to the reactor.

The pressure was increased as the temperature reached the point at which V-2-EH or VB starts distilling. After removing a small initial cut (fore cut), the main pure vinyl ester cut was collected. The fore cut was recycled in the next

Table 16. C-10 Acid Conversion as a Function of Catalyst Concentration.

| Example No. | 52 | 53 | 54 | 55 |
|---|---|---|---|---|
| Reaction volume, Liters | 1.10 | 1.10 | 1.10 | 1.10 |
| Pd concentration, ppm | 250 | 500 | 750 | 1000 |
| Maximum formation of NAVE-10, wt % | 55 | 97 | 90 | 86 |
| Time required to attain max. formation, hr | 11 | 11 | 11 | 11 |
| Moles of product formed, gm mol | 1.29 | 2.25 | 0.28 | 2.02 |
| Product formation rate, gm mol / gm Pd per hr | 1.18 | 1.03 | 0.63 | 0.63 |
| Hourly Catalytic Productivity, kg NAVE-10 / gm Pd per hr | 0.233 | 0.203 | 0.125 | 0.125 |
| Product (NAVE-10) formation rate, kg/liter reactor volume-hr | 0.15 | 0.26 | 0.23 | 0.23 |

Temperature: 100°C; Molar ratio of acid:VAM 1:6.

As Table 16 shows, palladium concentrations of greater than 250 ppm are preferable to achieve satisfactory formation of vinyl neodecanoate. Further analysis has shown that at concentrations from 250 to 750 ppm, equilibrium conversion was not achieved. Therefore, concentrations of greater than 750 ppm are preferable.

Table 17: C-10 Acid Conversion as a Function of Temperature.

| Example No. | 56 | 55 | 57 |
|---|---|---|---|
| Reaction volume, Liters | 1.10 | 1.10 | 1.10 |
| Temperature, °C | 90 | 100 | 110 |
| Maximum formation of NAVE-10, wt % | 80 | 87 | 92 |
| Time required to attain max. formation, hr | 10 | 6 | 5 |
| Moles of product formed, gm mol | 1.84 | 2.02 | 2.14 |
| Product formation rate, gm mol / gm Pd per hr | 0.42 | 0.63 | 1.08 |
| Hourly Catalytic Productivity, kg NAVE-10 / gm Pd per hr | 0.084 | 0.125 | 0.125 |
| Product (NAVE-10) formation rate, kg/liter reactor volume-hr | 0.21 | 0.23 | 0.24 |

Catalyst loading: 1000 ppm; molar ratio of acid:VAM 1:6.

As Table 17 shows, as the temperature increases, the rate of formation of vinyl neodecanoate increases.

to 4:1. In still another embodiment, the concentration of acetic acid in the crude product mixture is less than 15 weight % acetic acid with a vinyl acetate:carboxylic acid reactant molar ratio of from about 1.5:1 up to about 3:1. In yet another embodiment, the concentration of acetic acid in the crude product mixture is less than 15 weight % acetic with a vinyl acetate:carboxylic acid reactant molar ratio of more than 2:1.

The process generally comprises separating residual carboxylic acid from the crude vinyl ester product mixture and recycling the residual carboxylic acid to the reaction mixture. Typically, the process further comprises separating the homogeneous transvinylation catalyst from the crude vinyl ester product mixture and recycling the catalyst to the reaction mixture.

Generally, the separated vinyl acetate is recycled at a rate of less than about 8 kg of vinyl acetate for every kg of vinyl ester produced. Preferably, vinyl acetate is recycled at a rate of less than about 7 kg of vinyl acetate per kg of vinyl product. More preferably, the vinyl acetate is recycled at a rate of less than about 6 kg of vinyl acetate per kg of vinyl product. Typically, from about 4 kg to about 8 kg of vinyl acetate is recycled per kg of vinyl product. Still more preferably, from about 6 to about 7 kg of vinyl acetate is recycled per kg of vinyl product.

The inhibitor is generally selected from the group consisting of hydroquinone (HQ), methoxy hydroquinone (MEHQ), butylated hydroxytoluene (BHT), tert-butyl catechol (TBC), diphenylamine, phenothiazine and a hindered phenol. The carboxylic acid is generally selected from the group consisting of 2-ethylhexanoic acid, benzoic acid, methacrylic acid, neodecanoic acid, propionic acid, butyric acid, valeric acid, heptanoic acid, acrylic acid, stearic acid, and palmitic acid.

In one embodiment, more than 60 weight % of the carboxylic acid provided is converted to vinyl ester. In another embodiment, more than 65 weight

% of the carboxylic acid provided is converted to vinyl ester. Preferably, more than 70 weight % of the carboxylic acid provided is converted to vinyl product. More preferably, more than 75 weight % of the carboxylic acid provided is converted to vinyl ester. The carboxylic acid conversion recited may likewise refer to ester conversion as defined herein.

In one aspect of the invention, the process generally provides a vinyl ester product at a selectivity of greater than 90 mole %, typically greater than 95 mole %, based on the carboxylic acid provided. In another aspect of the invention, the process provides a vinyl ester product at a selectivity of greater than 99 mole % based on the carboxylic acid provided.

In accordance with the invention, the reaction is carried out under reactive distillation conditions wherein vinyl acetate and by-product acetic acid are removed as distillate from the reaction mixture. The temperature of the reaction is generally maintained at from about 80°C up to about 120°C. Preferably, the temperature is from about 90°C to about 110°C. More preferably, the temperature is from about 90°C to about 105°C.

Typically, unreacted vinyl acetate and acetic acid are continuously removed from the reaction mixture in a vinyl acetate:acetic acid molar ratio of from about 5:1 to about 25:1, and in some cases, in a vinyl acetate:acetic acid molar ratio of from about 6:1 to about 10:1.

Preferably, the process is characterized by an Hourly Catalytic Productivity of at least 0.1 kg vinyl product per gm catalyst metal per hour. More preferably, the process is characterized by an Hourly Catalytic Productivity of at least 0.3 or 0.5 kg vinyl product per gm catalyst metal per hour. Still more preferably, the Hourly Catalytic Productivity is at least 0.7 kg vinyl product per gm catalyst metal per hour.

In an aspect of the invention, the reaction may carried out in a bubble column. The process is generally operated at a residence time for reactant carboxylic acid of from about 15 minutes or about 4 or 5 hours to about 20 hours. The residence time is preferably from about 10 to about 20 hours and more preferably from about 5 to about 15 hours.

Preferably, the homogeneous transvinylation catalyst comprises a platinum group metal.

A particularly useful commercial embodiment is a continuous process for selective formation of vinyl ester by reactive distillation from its corresponding carboxylic acid. Carboxylic acid and vinyl acetate are fed to a reactor and reacted in the presence of a palladium acetate – bidentate ligand catalyst complex in a reaction mixture to form a vinyl ester product and acetic acid while the acetic acid and vinyl acetate are continuously removed from the reaction mixture. At least a portion of the removed vinyl acetate is separated from the removed acetic acid and recycled to the reaction mixture. The reaction mixture is withdrawn as a crude vinyl ester product mixture which includes residual carboxylic acid, residual vinyl acetate, residual acetic acid, and palladium acetate – bidentate ligand catalyst complex. Residual reactants including carboxylic acid and vinyl acetate; residual acetic acid byproduct, and palladium acetate – bidentate ligand catalyst complex are separated from the crude vinyl ester product mixture to form a purified vinyl ester product.

The process is characterized by a vinyl product selectivity of at least 80 mole % and an acetic acid concentration in the crude product mixture of less than 15 weight % as well as a vinyl acetate:carboxylic acid molar ratio of from 1:1 to 6:1 maintained in the reaction mixture. These characteristics are achieved by catalyst selection and control of the reaction conditions, feed to the reaction mixture, removal of acetic acid from the reaction mixture, and the separation and recycling of vinyl acetate to the reaction mixture.

The catalyst concentration provided is typically from about 50 or 150 parts palladium per million to about 2325 or about 3000 parts palladium per million parts of carboxylic acid provided. Preferably, the catalyst concentration provided is from about 500 to about 1500 parts palladium per million parts of carboxylic acid.

Generally, the process is characterized by an initial turnover number of more than about 10 kg of vinyl ester per gram of palladium contained in the palladium acetate – bidentate ligand catalyst complex utilized. In one embodiment, the initial turnover number is more than about 20 kg of vinyl ester per gram of palladium. In another embodiment, the turnover number is more than 30 kg of vinyl ester per gram of palladium. In a further embodiment, the initial turnover number is more than 40 kg of vinyl ester per gram of palladium

Typically, the process is operated in a continuous mode, wherein vinyl product is continuously withdrawn from the reaction mixture.

The palladium acetate – bidentate ligand catalyst complex is characterized by a mole ratio of palladium acetate to bidentate ligand of from about 1:1 to about 1:1.5 or about 1:2. The bidentate ligand is selected from the group consisting of 2,2'-bipyridyl, 1,10-phenanthroline, N,N,N',N'-tetramethylethylenediamine and P,P,P',P'-tetraphenyl-1,2-diphosphinoethane.

In an aspect of the invention, the carboxylic acid may be purified prior to reaction. A purified carboxylic acid is generally evidenced by a bromine value of less than 20 mmoles of $Br_2$/g, a peroxide value of less than 200 ppm, or a permanganate time of at least 30 minutes.

One embodiment provides for a continuous process for selective formation of vinyl ester from neodecanoic acid. Raw neodecanoic acid is purified and then

reacted with vinyl acetate in the presence of a homogeneous transvinylation catalyst to form a vinyl neodecanoate product and acetic acid. Acetic acid and vinyl acetate are preferably continuously removed from the reaction mixture and at least a portion of the vinyl acetate is separated from the acetic acid and recycled to the reaction mixture. The reaction mixture may be continuously withdrawn and vinyl neodecanoate product may be separated from residual neodecanoic acid, residual vinyl acetate, residual acetic acid, and homogeneous transvinylation catalyst. The process is generally characterized by a conversion of neodecanoic acid to vinyl ester product with a selectivity of at least 80 mole %, and a crude product mixture containing less than 15 weight % acetic acid. A molar ratio of vinyl acetate:carboxylic acid of from 1:1 to 9:1 is generally maintained in the reaction mixture.

More specifically, one embodiment provides for a process for purifying a carboxylic acid. In this embodiment, a raw carboxylic acid is purified using a method selected from the group consisting of flash distillation; fractionation; extraction; hydrogenation; and combinations thereof. The purification process is characterized by a purified carboxylic acid containing less than 1 weight % impurities selected from the group consisting of compounds having alcohol functional groups; compounds having ester functional groups; compounds having alkene functional groups; compounds having peroxide functional groups; sulfur; and other electropositive metals.

The purification method may include at least hydrogenation. The hydrogenation may be performed with a palladium catalyst supported on carbon or another suitable catalyst that remains active for several cycles of hydrogenation; such as for at least about 25 cycles and up to about 50 cycles of hydrogenation or for at least 50 cycles of hydrogenation; in any case, the catalyst preferably remains active for more than about 30 cycles of hydrogenation. The conditions may include a temperature in the range of about 50-150°C temperature and a temperature in the range of about 5-25 $kg/cm^2$ pressure.

Alternatively, the purification method may include at least multistage extraction with water. In the extraction step, the carboxylic acid is agitated with water for from about ½ hour to about 6 hours, such as for about 2 hours. The carboxylic acid is subsequently recovered by phase separation, for which the carboxylic acid-water mixture is allowed to settle for from about 10 minutes to about 2 hours.

In another embodiment, a process is provided for selective formation of a vinyl ester from a corresponding carboxylic acid of suitable purity to ameliorate catalyst poisoning. In this process, a carboxylic acid, vinyl acetate, and a homogeneous transvinylation platinum-group metal catalyst are provided to a reaction mixture. The carboxylic acid is generally characterized by at least one of the following parameters: a bromine value of less than 20 mmoles of $Br_2$/g; a peroxide value of less than 200 ppm; or permanganate time of at least 30 minutes. The carboxylic acid and vinyl acetate are reacted in the presence of the homogeneous transvinylation catalyst in the reaction mixture to form a vinyl ester product and acetic acid. Acetic acid and vinyl acetate are removed from the reaction mixture and at least a portion of the vinyl acetate is separated and recycled to the reaction mixture. Residual carboxylic acid and vinyl acetate reactants, acetic acid, and catalyst are separated from the crude vinyl ester product mixture to form a purified vinyl ester product. The process is characterized by a selectivity of at least 80 mole %, less than 15 weight % acetic acid in the crude product mixture, and a molar ratio of vinyl acetate:carboxylic acid of from 1:1 to 9:1 maintained in the reaction mixture. In one aspect of the invention, the carboxylic acid is neodecanoic acid.

Preferably, the carboxylic acid is characterized by at least one of: a bromine value of 18 mmoles of $Br_2$/g or less, a peroxide value of less than 100 ppm, or a permanganate time of more than 60 minutes. More preferably, the carboxylic acid is characterized by at least one of: a bromine value of less than 10

mmoles of $Br_2$/g, a peroxide value of less than 20 ppm, or a permanganate time of more than 120 minutes.

While the invention has been described in detail, modifications within the spirit and scope of the invention will be readily apparent to those of skill in the art. In view of the foregoing discussion, relevant knowledge in the art and references including co-pending applications discussed above in connection with the Background and Detailed Description, the disclosures of which are all incorporated herein by reference, further description is deemed unnecessary. In addition, it should be understood that aspects of the invention and portions of various embodiments may be combined or interchanged either in whole or in part. Furthermore, those of ordinary skill in the art will appreciate that the foregoing description is by way of example only, and is not intended to limit the invention.

WHAT IS CLAIMED IS:

1. A continuous process for selective formation of a vinyl ester from its corresponding carboxylic acid, the process comprising:

(a) providing a carboxylic acid, vinyl acetate, and a homogeneous transvinylation catalyst to a reaction mixture;

(b) reacting the carboxylic acid and vinyl acetate in the presence of the homogeneous transvinylation catalyst in the reaction mixture to form a vinyl ester product and acetic acid;

(c) continuously removing acetic acid and vinyl acetate from the reaction mixture;

(d) separating at least a portion of the removed vinyl acetate from the removed acetic acid and recycling the separated vinyl acetate to the reaction mixture;

(e) continuously withdrawing reaction mixture as a crude vinyl ester product mixture which includes residual carboxylic acid, residual vinyl acetate, residual acetic acid, and homogeneous transvinylation catalyst; and

(f) separatin g residual carboxylic acid, residual vinyl acetate, residual acetic acid, and homogeneous transvinylation catalyst from the crude vinyl ester product mixture to form a purified vinyl ester product;

wherein the reaction conditions, feed to the reaction mixture, removal of acetic acid from the reaction mixture, and the separation and recycling of vinyl acetate to the reaction mixture are controlled and the catalyst is selected such that carboxylic acid is converted to vinyl ester product with a selectivity of at

least 80 mole %, and there is less than 15 weight % acetic acid in the crude product mixture as well as a molar ratio of vinyl acetate:carboxylic acid of from 1:1 to 10:1 maintained in the reaction mixture.

2. The process according to Claim 1, wherein the reaction conditions, feed to the reaction mixture, removal of acetic acid from the reaction mixture, and the separation and recycling of vinyl acetate to the reaction mixture are controlled and the catalyst is selected such that carboxylic acid is converted to vinyl ester product with a selectivity of at least 80 mole %, and there is less than 10 weight % acetic acid in the crude product mixture as well as a molar ratio of vinyl acetate:carboxylic acid of from 1:1 to 6:1 maintained in the reaction mixture.

3. The process according to Claim 1, wherein the reaction conditions, feed to the reaction mixture, removal of acetic acid from the reaction mixture, and the separation and recycling of vinyl acetate to the reaction mixture are controlled and the catalyst is selected such that carboxylic acid is converted to vinyl ester product with a selectivity of at least 80 mole %, and there is less than 5 weight % acetic acid in the crude product mixture as well as a molar ratio of vinyl acetate:carboxylic acid of from 1:1 to 4:1 maintained in the reaction mixture.

4. The process according to Claim 1, wherein the reaction conditions, feed to the reaction mixture, removal of acetic acid from the reaction mixture, and the separation and recycling of vinyl acetate to the reaction mixture are controlled and the catalyst is selected such that carboxylic acid is converted to vinyl ester product with a selectivity of at least 80 mole %, and there is less than 15 weight % acetic acid in the crude product mixture as well as a molar ratio of vinyl acetate:carboxylic acid of from about 1.5:1 up to about 3:1 maintained in the reaction mixture.

5. The process according to Claim 4, wherein the reaction conditions, feed to the reaction mixture, removal of acetic acid from the reaction mixture, and the separation and recycling of vinyl acetate to the reaction mixture are controlled and the catalyst is selected such that carboxylic acid is converted to vinyl ester product with a selectivity of at least 80 mole %, and there is less than 15 weight % acetic acid in the crude product mixture as well as a molar ratio of vinyl acetate:carboxylic acid of more than 2:1 is maintained in the reaction mixture.

6. The process according to Claim 1, wherein the process further comprises separating residual carboxylic acid from the crude vinyl ester product mixture and recycling the residual carboxylic acid to the reaction mixture.

7. The process according to Claim 1, wherein the process further comprises separating the homogeneous transvinylation catalyst from the crude vinyl ester product mixture and recycling the catalyst to the reaction mixture.

8. The process according to Claim 1, wherein the separated vinyl acetate is recycled at a rate of less than about 8 kg of vinyl acetate for every kg of vinyl ester produced.

9. The process according to Claim 1, wherein more than 60 weight % of the carboxylic acid provided is converted to vinyl ester.

10. The process according to Claim 1, wherein the carboxylic acid is selected from the group consisting of 2-ethylhexanoic acid, benzoic acid, neodecanoic acid, propionic acid, butyric acid, valeric acid, heptanoic acid, acrylic acid, methacrylic acid, stearic acid, and palmitic acid.

11. The process according to Claim 1, wherein the temperature of the reaction (b) is maintained at from about 80°C up to about 120°C.

12. The process according to Claim 1, wherein unreacted vinyl acetate and acetic acid are continuously removed from the reaction mixture in a vinyl acetate:acetic acid molar ratio of from about 5:1 to about 25:1.

13. A continuous process for selective formation of vinyl ester by reactive distillation from its corresponding carboxylic acid, the process comprising:

(a) providing carboxylic acid, vinyl acetate, and a palladium acetate – bidentate ligand catalyst complex to a reaction mixture;

(b) reacting the carboxylic acid and vinyl acetate in the presence of the palladium acetate – bidentate ligand catalyst complex in the reaction mixture to form a vinyl ester product and acetic acid;

(c) continuously removing acetic acid and vinyl acetate from the reaction mixture;

(d) separating at least a portion of the removed vinyl acetate from the removed acetic acid and recycling the separated vinyl acetate to the reaction mixture;

(e) withdrawing reaction mixture as a crude vinyl ester product mixture which includes residual carboxylic acid, residual vinyl acetate, residual acetic acid, and palladium acetate – bidentate ligand catalyst complex; and

(f) separatin g residual carboxylic acid, residual vinyl acetate, residual acetic acid, and palladium acetate – bidentate ligand catalyst complex from the crude vinyl ester product mixture to form a purified vinyl ester product;

wherein the reaction conditions, feed to the reaction mixture, removal of acetic acid from the reaction mixture, and the separation and recycling of vinyl acetate to the reaction mixture are controlled and the catalyst is selected such that carboxylic acid is converted to vinyl ester product with a selectivity of at least 80 mole %, and there is less than 15 weight % acetic acid in the crude product mixture as well as a molar ratio of vinyl acetate:carboxylic acid of from 1:1 to 6:1 maintained in the reaction mixture.

14. The process according to Claim 13, wherein the catalyst concentration provided is from about 50 parts palladium per million parts of carboxylic acid provided to about 3,000 parts palladium per million parts of carboxylic acid provided.

15. A continuous process for selective formation of vinyl ester from neodecanoic acid, the process comprising:

(a) purifying raw neodecanoic acid;

(b) providing the neodecanoic acid, vinyl acetate, and a homogeneous transvinylation catalyst to a reaction mixture;

(c) reacting the neodecanoic acid and vinyl acetate in the presence of the homogeneous transvinylation catalyst in the reaction mixture to form a vinyl ester product and acetic acid;

(d) continuously removing acetic acid and vinyl acetate from the reaction mixture;

(e) separating at least a portion of the removed vinyl acetate from the removed acetic acid and recycling the separated vinyl acetate to the reaction mixture;

(f) continuousl y withdrawing reaction mixture as a crude vinyl ester product mixture which includes residual carboxylic acid, residual vinyl acetate, residual acetic acid, and homogeneous transvinylation catalyst; and

(g) separating residual carboxylic acid, residual vinyl acetate, residual acetic acid, and homogeneous transvinylation catalyst from the crude vinyl ester product mixture to form a purified vinyl ester product;

wherein the reaction conditions, feed to the reaction mixture, removal of acetic acid from the reaction mixture, and the separation and recycling of vinyl acetate to the reaction mixture are controlled and the catalyst is selected such that carboxylic acid is converted to vinyl ester product with a selectivity of at least 80 mole %, and there is less than 15 weight % acetic acid in the crude product mixture as well as a molar ratio of vinyl acetate:carboxylic acid of from 1:1 to 9:1 maintained in the reaction mixture.

16. A process for purifying a carboxylic acid, wherein the raw carboxylic acid is purified using a method selected from the group consisting of flash distillation; fractionation; extraction; hydrogenation; and combinations thereof;

wherein the purification process is operated under conditions selected such that the purified carboxylic acid contains less than 1 weight % impurities selected from the group consisting of compounds having alcohol functional groups; compounds having ester functional groups; compounds having alkene functional groups; compounds having peroxide functional groups; sulfur; and other electropositive metals.

17. A process for selective formation of a vinyl ester from its corresponding carboxylic acid, the process comprising:

(a) providing a carboxylic acid, vinyl acetate, and a homogeneous transvinylation platinum-group metal catalyst to a reaction mixture;

wherein the carboxylic acid is of suitable purity to ameliorate catalyst poisoning, the carboxylic acid being characterized by at least one of:

(i) a bromine value of less than 20 mmoles of $Br_2$/g;
(ii) a peroxide value of less than 200 ppm; or
(iii) permanganate time of at least 30 minutes;

(b) reacting the carboxylic acid and vinyl acetate in the presence of the homogeneous transvinylation catalyst in the reaction mixture to form a vinyl ester product and acetic acid;

(c) removing acetic acid and vinyl acetate from the reaction mixture;

(d) separating at least a portion of the removed vinyl acetate from the removed acetic acid and recycling the separated vinyl acetate to the reaction mixture; and

(e) separating residual carboxylic acid, residual vinyl acetate, residual acetic acid, and homogeneous transvinylation catalyst from the crude vinyl ester product mixture to form a purified vinyl ester product;

wherein the reaction conditions, feed to the reaction mixture, removal of acetic acid from the reaction mixture, and the separation and recycling of vinyl acetate to the reaction mixture are controlled and the catalyst is selected such

that carboxylic acid is converted to vinyl ester product with a selectivity of at least 80 mole %, and there is less than 15 weight % acetic acid in the crude product mixture as well as a molar ratio of vinyl acetate:carboxylic acid of from 1:1 to 9:1 maintained in the reaction mixture.

18. The process according to Claim 17, wherein the carboxylic acid is neodecanoic acid.

WHAT IS CLAIMED IS:

1. A continuous process for selective formation of a vinyl ester from its corresponding carboxylic acid, the process comprising:

(a) providing a carboxylic acid, vinyl acetate, and a homogeneous transvinylation catalyst comprising a platinum group metal selected from the group consisting of iridium, osmium, palladium, platinum and rhodium to a reaction mixture;

(b) reacting the carboxylic acid and vinyl acetate in the presence of the homogeneous transvinylation catalyst in the reaction mixture to form a vinyl ester product and acetic acid;

(c) continuously removing acetic acid and vinyl acetate from the reaction mixture;

(d) separating at least a portion of the removed vinyl acetate from the removed acetic acid and recycling the separated vinyl acetate to the reaction mixture;

(e) continuously withdrawing reaction mixture as a crude vinyl ester product mixture which includes residual carboxylic acid, residual vinyl acetate, residual acetic acid, and homogeneous transvinylation catalyst; and

(f) separating residual carboxylic acid, residual vinyl acetate, residual acetic acid, and homogeneous transvinylation catalyst from the crude vinyl ester product mixture to form a purified vinyl ester product;

wherein the reaction conditions, feed to the reaction mixture, removal of acetic acid from the reaction mixture, and the separation and recycling of vinyl acetate to the reaction mixture are controlled and the catalyst is selected such that carboxylic acid is converted to vinyl ester product with a selectivity of at least 80 mole %, and there is less than 15 weight % acetic acid in the crude product mixture as well as a molar ratio of vinyl acetate:carboxylic acid of from 1:1 to 10:1 maintained in the reaction mixture.

2. The process according to Claim 1, wherein the reaction conditions, feed to the reaction mixture, removal of acetic acid from the reaction mixture, and the separation and recycling of vinyl acetate to the reaction mixture are controlled and the catalyst is selected such that carboxylic acid is converted to vinyl ester product with a selectivity of at least 80 mole %, and there is less than 10 weight % acetic acid in the crude product mixture as well as a molar ratio of vinyl acetate:carboxylic acid of from 1:1 to 6:1 maintained in the reaction mixture.

3. The process according to Claim 1, wherein the reaction conditions, feed to the reaction mixture, removal of acetic acid from the reaction mixture, and the separation and recycling of vinyl acetate to the reaction mixture are controlled and the catalyst is selected such that carboxylic acid is converted to vinyl ester product with a selectivity of at least 80 mole %, and there is less than 5 weight % acetic acid in the crude product mixture as well as a molar ratio of vinyl acetate:carboxylic acid of from 1:1 to 4:1 maintained in the reaction mixture.

4. The process according to Claim 1, wherein the reaction conditions, feed to the reaction mixture, removal of acetic acid from the reaction mixture, and the separation and recycling of vinyl acetate to the reaction mixture are controlled and the catalyst is selected such that carboxylic acid is converted to vinyl ester product with a selectivity of at least 80 mole %, and there is less than 15 weight % acetic acid in the crude product mixture as well as a molar ratio of

vinyl acetate:carboxylic acid of from 1.5:1 up to 3:1 maintained in the reaction mixture.

5. The process according to Claim 4, wherein the reaction conditions, feed to the reaction mixture, removal of acetic acid from the reaction mixture, and the separation and recycling of vinyl acetate to the reaction mixture are controlled and the catalyst is selected such that carboxylic acid is converted to vinyl ester product with a selectivity of at least 80 mole %, and there is less than 15 weight % acetic acid in the crude product mixture as well as a molar ratio of vinyl acetate:carboxylic acid of more than 2:1 is maintained in the reaction mixture.

6. The process according to Claim 1, wherein the process further comprises separating residual carboxylic acid from the crude vinyl ester product mixture and recycling the residual carboxylic acid to the reaction mixture.

7. The process according to Claim 1, wherein the process further comprises separating the homogeneous transvinylation catalyst from the crude vinyl ester product mixture and recycling the catalyst to the reaction mixture.

8. The process according to Claim 1, wherein the separated vinyl acetate is recycled at a rate of less than 8 kg of vinyl acetate for every kg of vinyl ester produced.

9. The process according to Claim 1, wherein more than 60 weight % of the carboxylic acid provided is converted to vinyl ester.

10. The process according to Claim 1, wherein the carboxylic acid is selected from the group consisting of 2-ethylhexanoic acid, benzoic acid, neodecanoic acid, propionic acid, butyric acid, valeric acid, heptanoic acid, acrylic acid, methacrylic acid, stearic acid, and palmitic acid.

11. The process according to Claim 1, wherein the temperature of the reaction (b) is maintained at from 80°C up to 120°C.

12. The process according to Claim 1, wherein unreacted vinyl acetate and acetic acid are continuously removed from the reaction mixture in a vinyl acetate:acetic acid molar ratio of from 5:1 to 25:1.

13. The process according to Claim 1, wherein the formation of vinyl ester is performed by reactive distillation and the homogeneous transvinylation catalyst is a palladium catalyst complex, and wherein a molar ratio of vinyl acetate:carboxylic acid of from 1:1 to 6:1 is maintained in the reaction mixture.

14. The process according to Claim 13, wherein the catalyst concentration provided is from 50 parts palladium per million parts of carboxylic acid provided to 3,000 parts palladium per million parts of carboxylic acid provided.

15. The process according to Claim 1, wherein the carboxylic acid is a purified neodecanoic acid, and the process further comprises a step of purifying raw neodecanoic acid to form a purified neodecanoic acid, and wherein a molar ratio of vinyl acetate:carboxylic acid of from 1:1 to 9:1 is maintained in the reaction mixture.

16. A process for purifying a carboxylic acid, wherein the raw carboxylic acid is purified using a method selected from the group consisting of multistage extraction with water; hydrogenation; and combinations thereof; optionally followed by flash distillation or fractionation;
wherein the purification process is operated under conditions selected such that the purified carboxylic acid contains less than 1 weight % impurities

selected from the group consisting of compounds having alcohol functional groups; compounds having ester functional groups; compounds having alkene functional groups; compounds having peroxide functional groups; sulfur; and electropositive metals.

17. The process according to Claim 1, wherein the carboxylic acid is of suitable purity to ameliorate catalyst poisoning, the carboxylic acid being characterized by at least one of:

(i) a bromine value of less than 20 mmoles of $Br_2$/g;
(ii) a peroxide value of less than 200 ppm; or
(iii) permanganate time of at least 30 minutes;

and wherein a molar ratio of vinyl acetate:carboxylic acid of from 1:1 to 9:1 is maintained in the reaction mixture.

18. The process according to Claim 17, wherein the carboxylic acid is neodecanoic acid.

19. The process according to Claim 16, wherein the raw carboxylic acid is purified by hydrogenation, operated at a temperature of from 50°C to 150°C.

$$\text{Hourly Catalytic Productivity} = \frac{\text{TON}}{\text{Total reaction time, hr}}$$

Where total reaction time as used herein refers to a multiple of the reactor residence time, typically five times the residence time for purposes of the Examples. This reaction time allows for unattended operation of a steady state reaction with no catalyst deactivation.

As used herein, the term "reaction mixture" refers to the liquid mass in the reactive distillation area that contains reagents, catalyst, and optionally solvent.

As used herein, the term "reactor residence time" refers to the average amount of time a discrete quantity of reagent spends in the reactor. The mean residence time is determined by dividing the reactor volume by the volumetric flow rate of the carboxylic acid mixture fed to the reactor.

As used herein, the reaction temperature refers to an average of multiple temperature readings taken at various points between the location of the carboxylic acid feed and the vinyl acetate feed. Preferably, at least two temperature readings are averaged, and more preferably, at least three temperature readings are averaged.

Various carboxylic acids known in the art can be employed in the process of this invention to form corresponding vinyl esters. The acids that are suitable in this invention may include, but not necessarily be limited to, the following acids:

2-ethylhexanoic acid, benzoic acid, neodecanoic acid, propionic acid, butyric acid, valeric acid, heptanoic acid, acrylic acid, methacrylic acid, stearic acid, and palmitic acid.

about 120°C. Preferably the temperature of the reaction is maintained from about 90°C to about 110°C. However, low catalyst concentrations require higher reaction temperatures. The molar ratio of vinyl acetate to the reactant carboxylic acid charged to the reactor is about 2.2:1 to about 9:1. Ratios may be less than about 4:1, and ratios of less than 2:1 have been achieved in some cases. The reaction time ranges from less than about 3 hours to about 36 hours depending upon the catalyst concentration and acetic acid removal rate.

*Continuous inhibitor addition.* An inhibitor is added to the reaction and to the crude and purified products to prevent vinyl ester polymerization. Without inhibitor addition, side reactions may occur resulting in homopolymers or copolymers of the vinyl ester reactant and/or product. Such reactions impact quality and yield and have adverse safety implications. Any suitable inhibitor may used, such as hydroquinone (HQ), methoxy hydroquinone (MeHQ), butylated hydroxytoluene (BHT), tert-butyl catechol (TBC), or phenothiazine.

*Coproduction of acetic acid-VAM mix.* This process produces a mixture rich in acetic acid. This mixture is drawn off from the process and may be utilized directly or with minimal processing in VAM plants. Alternatively, acetic acid may be separated from the mix. Byproduct acetic acid may be used as a reactant in subsequent processes. Experiments using the Pd catalyst complex of the invention resulted in VAM:acetic acid molar ratios ranging from 0.5:1 to 14.4:1 in the recovered mixture. Preferably, the vinyl acetate:acetic acid molar ratio removed from the reaction mixture is from about 1.5:1 to about 10:1 or about 1:1 to about 9:1. More preferably, the process results in a molar ratio of VAM:acetic acid of from about 2:1 to about 7:1; and even more preferably, the process results in a molar ratio of VAM:acetic acid 2.5:1 to 6:1.

*Purification of carboxylic acid reagent.* Surprisingly, in some cases, carboxylic acid reagents demonstrating otherwise high levels of purity have been found to contain impurities that cause deactivation of the catalyst during

stripping column **118**; a reboiler **120**; a condenser **122**; a VAM feed vessel **124**; a VAM pre-heater / vaporizer **126**; and a product cooler **128**.

A pre-mixed feed of CA, VAM and catalyst from the carboxylic acid feed vessel **110** was charged to column **114** via line **136**. VAM from VAM feed vessel **124** was passed through preheater **126** via line **130**. The CA along with catalyst flowed downward through column **114** to bubble column reactor **112** via **134**, countercurrent to superheated VAM vapor, introduced to the reactor **112** via line **132** from preheater **126**, which rose upward through bubble column reactor **112** and subsequently column **114** via **134**. The reaction took place in the bubble column reactor **112** as well as in column **114**, producing vinyl ester and acetic acid. The VAM vapor became saturated with acetic acid. The combined vapors of VAM & acetic acid emitted out of column **114** via line **138** and entered between columns **116** and **118**, a separation system where VAM & acetic acid are continuously separated. Line **140** indicates lighter components rising through the rectification portion of the separation system represented by column **116** and line **142** indicates heavier components falling through the stripping portion of the separation system represented by column **118**. The product vinyl benzoate or vinyl-2-ethyl hexanoate along with catalyst, unconverted CA, residual VAM, and a small amount of acetic acid was continuously removed from the reactor **112** via line **144**, cooled in condenser **128**, and collected via line **146**. Heavier components from column **118** collected in reboiler **120** via line **148**. The overflow of reboiler **120** produced acetic acid and was collected in via line **150**. Lighter components from column **116** were collected via line **152**, condensed in condenser **122**, and recycled to VAM feed vessel **124** via line **154**.

**Procedure:** The bubble column reactor **112** was first charged with a composition comprising vinyl acetate, carboxylic acid, and catalyst, and heated by conventional means to 98 to 102°C. Then the VAM at a predetermined rate was pumped through the VAM pre-heater **126** which was maintained at 70°C to 100°C, the VAM vapor entered at the bottom of the bubble column reactor **112**.

As soon as VAM started distilling out from rectification column **116**, the addition of pre-mixed feed of CA, catalyst, VAM & inhibitor was started at predetermined feed rate through column **114**. The crude product that overflowed out of bubble reactor **112** through product cooler **128** was collected. Similarly the acetic acid overflowed continuously out of reboiler **120** and was separately collected. The excess VAM was continuously recovered and recycled through the condenser **122** to the VAM metering system.

In production of crude vinyl benzoate, a crystallization step might not be necessary in conjunction with reactive distillation, due to the high conversion rate achievable. Crude vinyl ester product produced through the continuous reactive distillation might need less intensive purification than is necessary for a comparable vinyl ester product from a semi-continuous process because all or almost all of the lights (i.e., vinyl acetate and acetic acid) are removed during the reaction.

Optionally, residual carboxylic acid and catalyst recovered from the crude vinyl ester product may be recycled to the reactor.

and is herein identified as crude V-2-EH. When distillation ceased, the contents were cooled and the vacuum released. The residue was preserved for recycle. This residue contained mainly 2-EHA, a small amount of V-2-EH and the catalyst.

*Crystallization of un-reacted BA and Recovery of VB*

The reaction mass transferred from the rotary evaporator was cooled in the crystallizer and held for several hours. The slurry was removed and filtered over a vacuum filter. The solid, semi-dried cake of BA was weighed, and the solid cake of BA was preserved for recycle in the next cycle. The mother liquor was weighed and transferred to a conventional evaporator (not shown) for recovery of VB.

Vacuum was applied and the temperature was raised. VB was allowed to distill out and was separately collected. The distillate mainly contained VB and a small amount of acetic acid and BA. This is identified herein as crude VB. Recovery continued until solid BA started appearing in the distillation still at which stage recovery ceased.

When distillation stopped, the contents were cooled and the vacuum released. The residue of unreacted BA & catalyst was preserved for recycle. This residue contained mainly BA, a small amount of VB and the catalyst.

*Purification of crude vinyl ester*

The crude V-2-EH, VB or NAVE-10 was charged to a conventional fractional distillation column (not shown) under vacuum. Around 25 ppm of HQ was added as an inhibitor. The crude mass was heated. Distillate was collected with reflux set to 1. This distillate contained VAM and acetic acid and was recycled to the reactor.

The pressure was increased as the temperature reached the point at which V-2-EH or VB starts distilling. After removing a small initial cut (fore cut), the main pure vinyl ester cut was collected. The fore cut was recycled in the next

Table 16. C-10 Acid Conversion as a Function of Catalyst Concentration.

| Example No. | 52 | 53 | 54 | 55 |
|---|---|---|---|---|
| Reaction volume, Liters | 1.10 | 1.10 | 1.10 | 1.10 |
| Pd concentration, ppm | 250 | 500 | 750 | 1000 |
| Maximum formation of NAVE-10, wt % | 55 | 97 | 90 | 86 |
| Time required to attain max. formation, hr | 11 | 11 | 11 | 11 |
| Moles of product formed, gm mol | 1.29 | 2.25 | 0.28 | 2.02 |
| Product formation rate, gm mol / gm Pd per hr | 1.18 | 1.03 | 0.63 | 0.63 |
| Hourly Catalytic Productivity, kg NAVE-10 / gm Pd per hr | 0.233 | 0.203 | 0.125 | 0.125 |
| Product (NAVE-10) formation rate, kg/liter reactor volume-hr | 0.15 | 0.26 | 0.23 | 0.23 |

Temperature: 100°C; Molar ratio of C-10 acid:VAM 1:6.

As Table 16 shows, palladium concentrations of greater than 250 ppm are preferable to achieve satisfactory formation of vinyl neodecanoate. Further analysis has shown that at concentrations from 250 to 750 ppm, equilibrium conversion was not achieved. Therefore, concentrations of greater than 750 ppm are preferable.

Table 17: C-10 Acid Conversion as a Function of Temperature.

| Example No. | 56 | 55 | 57 |
|---|---|---|---|
| Reaction volume, Liters | 1.10 | 1.10 | 1.10 |
| Temperature, °C | 90 | 100 | 110 |
| Maximum formation of NAVE-10, wt % | 80 | 87 | 92 |
| Time required to attain max. formation, hr | 10 | 6 | 5 |
| Moles of product formed, gm mol | 1.84 | 2.02 | 2.14 |
| Product formation rate, gm mol / gm Pd per hr | 0.42 | 0.63 | 1.08 |
| Hourly Catalytic Productivity, kg NAVE-10 / gm Pd per hr | 0.084 | 0.125 | 0.125 |
| Product (NAVE-10) formation rate, kg/liter reactor volume-hr | 0.21 | 0.23 | 0.24 |

Catalyst loading: 1000 ppm; molar ratio of C-10 acid:VAM 1:6.

As Table 17 shows, as the temperature increases, the rate of formation of vinyl neodecanoate increases.

to 4:1. In still another embodiment, the concentration of acetic acid in the crude product mixture is less than 15 weight % acetic acid with a vinyl acetate:carboxylic acid reactant molar ratio of from about 1.5:1 up to about 3:1. In yet another embodiment, the concentration of acetic acid in the crude product mixture is less than 15 weight % acetic with a vinyl acetate:carboxylic acid reactant molar ratio of more than 2:1.

The process generally comprises separating residual carboxylic acid from the crude vinyl ester product mixture and recycling the residual carboxylic acid to the reaction mixture. Typically, the process further comprises separating the homogeneous transvinylation catalyst from the crude vinyl ester product mixture and recycling the catalyst to the reaction mixture.

Generally, the separated vinyl acetate is recycled at a rate of less than about 8 kg of vinyl acetate for every kg of vinyl ester produced. Preferably, vinyl acetate is recycled at a rate of less than about 7 kg of vinyl acetate per kg of vinyl ester product. More preferably, the vinyl acetate is recycled at a rate of less than about 6 kg of vinyl acetate per kg of vinyl ester product. Typically, from about 4 kg to about 8 kg of vinyl acetate is recycled per kg of vinyl ester product. Still more preferably, from about 6 to about 7 kg of vinyl acetate is recycled per kg of vinyl ester product.

The inhibitor is generally selected from the group consisting of hydroquinone (HQ), methoxy hydroquinone (MEHQ), butylated hydroxytoluene (BHT), tert-butyl catechol (TBC), diphenylamine, phenothiazine and a hindered phenol. The carboxylic acid is generally selected from the group consisting of 2-ethylhexanoic acid, benzoic acid, methacrylic acid, neodecanoic acid, propionic acid, butyric acid, valeric acid, heptanoic acid, acrylic acid, stearic acid, and palmitic acid.

In one embodiment, more than 60 weight % of the carboxylic acid provided is converted to vinyl ester. In another embodiment, more than 65 weight% of the carboxylic acid provided is converted to vinyl ester. Preferably, more than 70 weight % of the carboxylic acid provided is converted to vinyl ester product. More preferably, more than 75 weight % of the carboxylic acid provided is converted to vinyl ester. The carboxylic acid conversion recited may likewise refer to ester conversion as defined herein.

In one aspect of the invention, the process generally provides a vinyl ester product at a selectivity of greater than 90 mole %, typically greater than 95 mole %, based on the carboxylic acid provided. In another aspect of the invention, the process provides a vinyl ester product at a selectivity of greater than 99 mole % based on the carboxylic acid provided.

In accordance with the invention, the reaction is carried out under reactive distillation conditions wherein vinyl acetate and by-product acetic acid are removed as distillate from the reaction mixture. The temperature of the reaction is generally maintained at from about 80°C up to about 120°C. Preferably, the temperature is from about 90°C to about 110°C. More preferably, the temperature is from about 90°C to about 105°C.

Typically, unreacted vinyl acetate and acetic acid are continuously removed from the reaction mixture in a vinyl acetate:acetic acid molar ratio of from about 5:1 to about 25:1, and in some cases, in a vinyl acetate:acetic acid molar ratio of from about 6:1 to about 10:1.

Preferably, the process is characterized by an Hourly Catalytic Productivity of at least 0.1 kg vinyl ester product per gm catalyst metal per hour. More preferably, the process is characterized by an Hourly Catalytic Productivity of at least 0.3 or 0.5 kg vinyl ester product per gm catalyst metal per hour. Still

more preferably, the Hourly Catalytic Productivity is at least 0.7 kg vinyl ester product per gm catalyst metal per hour.

In an aspect of the invention, the reaction may carried out in a bubble column. The process is generally operated at a residence time for reactant carboxylic acid of from about 15 minutes or about 4 or 5 hours to about 20 hours. The residence time is preferably from about 10 to about 20 hours and more preferably from about 5 to about 15 hours.

Preferably, the homogeneous transvinylation catalyst comprises a platinum group metal.

A particularly useful commercial embodiment is a continuous process for selective formation of vinyl ester by reactive distillation from its corresponding carboxylic acid. Carboxylic acid and vinyl acetate are fed to a reactor and reacted in the presence of a palladium acetate – bidentate ligand catalyst complex in a reaction mixture to form a vinyl ester product and acetic acid while the acetic acid and vinyl acetate are continuously removed from the reaction mixture. At least a portion of the removed vinyl acetate is separated from the removed acetic acid and recycled to the reaction mixture. The reaction mixture is withdrawn as a crude vinyl ester product mixture which includes residual carboxylic acid, residual vinyl acetate, residual acetic acid, and palladium acetate – bidentate ligand catalyst complex. Residual reactants including carboxylic acid and vinyl acetate; residual acetic acid byproduct; and palladium acetate – bidentate ligand catalyst complex are separated from the crude vinyl ester product mixture to form a purified vinyl ester product.

The process is characterized by a vinyl ester product selectivity of at least 80 mole % and an acetic acid concentration in the crude product mixture of less than 15 weight % as well as a vinyl acetate:carboxylic acid molar ratio of from 1:1 to 6:1 maintained in the reaction mixture. These characteristics are achieved by

catalyst selection and control of the reaction conditions, feed to the reaction mixture, removal of acetic acid from the reaction mixture, and the separation and recycling of vinyl acetate to the reaction mixture.

The catalyst concentration provided is typically from about 50 or 150 parts palladium per million to about 2325 or about 3000 parts palladium per million parts of carboxylic acid provided. Preferably, the catalyst concentration provided is from about 500 to about 1500 parts palladium per million parts of carboxylic acid.

Generally, the process is characterized by an initial turnover number of more than about 10 kg of vinyl ester per gram of palladium contained in the palladium acetate – bidentate ligand catalyst complex utilized. In one embodiment, the initial turnover number is more than about 20 kg of vinyl ester per gram of palladium. In another embodiment, the turnover number is more than 30 kg of vinyl ester per gram of palladium. In a further embodiment, the initial turnover number is more than 40 kg of vinyl ester per gram of palladium

Typically, the process is operated in a continuous mode, wherein vinyl ester product is continuously withdrawn from the reaction mixture.

The palladium acetate – bidentate ligand catalyst complex is characterized by a mole ratio of palladium acetate to bidentate ligand of from about 1:1 to about 1:1.5 or about 1:2. The bidentate ligand is selected from the group consisting of 2,2'-bipyridyl, 1,10-phenanthroline, N,N,N',N'-tetramethylethylenediamine and P,P,P',P'-tetraphenyl-1,2-diphosphinoethane.

In an aspect of the invention, the carboxylic acid may be purified prior to reaction. A purified carboxylic acid is generally evidenced by a bromine value of less than 20 mmoles of $Br_2$/g, a peroxide value of less than 200 ppm, or a permanganate time of at least 30 minutes.

One embodiment provides for a continuous process for selective formation of vinyl ester from neodecanoic acid. Raw neodecanoic acid is purified and then reacted with vinyl acetate in the presence of a homogeneous transvinylation catalyst to form a vinyl neodecanoate product and acetic acid. Acetic acid and vinyl acetate are preferably continuously removed from the reaction mixture and at least a portion of the vinyl acetate is separated from the acetic acid and recycled to the reaction mixture. The reaction mixture may be continuously withdrawn and vinyl neodecanoate product may be separated from residual neodecanoic acid, residual vinyl acetate, residual acetic acid, and homogeneous transvinylation catalyst. The process is generally characterized by a conversion of neodecanoic acid to vinyl ester product with a selectivity of at least 80 mole %, and a crude product mixture containing less than 15 weight % acetic acid. A molar ratio of vinyl acetate:carboxylic acid of from 1:1 to 9:1 is generally maintained in the reaction mixture.

More specifically, one embodiment provides for a process for purifying a carboxylic acid. In this embodiment, a raw carboxylic acid is purified using a method selected from the group consisting of flash distillation; fractionation; extraction; hydrogenation; and combinations thereof. The purification process is characterized by a purified carboxylic acid containing less than 1 weight % impurities selected from the group consisting of compounds having alcohol functional groups; compounds having ester functional groups; compounds having alkene functional groups; compounds having peroxide functional groups; sulfur; and other electropositive metals.

The purification method may include at least hydrogenation. The hydrogenation may be performed with a palladium catalyst supported on carbon or another suitable catalyst that remains active for several cycles of hydrogenation; such as for at least about 25 cycles and up to about 50 cycles of hydrogenation or for at least 50 cycles of hydrogenation; in any case, the catalyst preferably remains active for more than about 30 cycles of hydrogenation. The

conditions may include a temperature in the range of about 50-150°C and a pressusre in the range of about 5-25 kg/cm$^2$.

Alternatively, the purification method may include at least multistage extraction with water. In the extraction step, the carboxylic acid is agitated with water for from about ½ hour to about 6 hours, such as for about 2 hours. The carboxylic acid is subsequently recovered by phase separation, for which the carboxylic acid-water mixture is allowed to settle for from about 10 minutes to about 2 hours.

In another embodiment, a process is provided for selective formation of a vinyl ester from a corresponding carboxylic acid of suitable purity to ameliorate catalyst poisoning. In this process, a carboxylic acid, vinyl acetate, and a homogeneous transvinylation platinum-group metal catalyst are provided to a reaction mixture. The carboxylic acid is generally characterized by at least one of the following parameters: a bromine value of less than 20 mmoles of $Br_2$/g; a peroxide value of less than 200 ppm; or permanganate time of at least 30 minutes. The carboxylic acid and vinyl acetate are reacted in the presence of the homogeneous transvinylation catalyst in the reaction mixture to form a vinyl ester product and acetic acid. Acetic acid and vinyl acetate are removed from the reaction mixture and at least a portion of the vinyl acetate is separated and recycled to the reaction mixture. Residual carboxylic acid and vinyl acetate reactants, acetic acid, and catalyst are separated from the crude vinyl ester product mixture to form a purified vinyl ester product. The process is characterized by a selectivity of at least 80 mole %, less than 15 weight % acetic acid in the crude product mixture, and a molar ratio of vinyl acetate:carboxylic acid of from 1:1 to 9:1 maintained in the reaction mixture. In one aspect of the invention, the carboxylic acid is neodecanoic acid.

Preferably, the carboxylic acid is characterized by at least one of: a bromine value of 18 mmoles of $Br_2$/g or less, a peroxide value of less than 100 ppm, or a

permanganate time of more than 60 minutes. More preferably, the carboxylic acid is characterized by at least one of: a bromine value of less than 10 mmoles of $Br_2$/g, a peroxide value of less than 20 ppm, or a permanganate time of more than 120 minutes.

What is claimed is:

1. A continuous process for selective formation of a vinyl ester from its corresponding carboxylic acid, the process comprising: (a) providing a carboxylic acid, vinyl acetate, and a homogeneous transvinylation catalyst comprising palladium to a reaction mixture; (b) reacting the carboxylic acid and vinyl acetate in the presence of the homogeneous transvinylation catalyst comprising palladium in the reaction mixture to form a vinyl ester product and acetic acid; (c) continuously removing acetic acid and vinyl acetate from the reaction mixture wherein vinyl acetate and acetic acid are continuously removed from the reaction mixture and the vinyl acetate:acetic acid molar ratio is from about 5:1 to about 25:1; (d) separating at least a portion of the removed vinyl acetate from the removed acetic acid and recycling the separated vinyl acetate to the reaction mixture; (e) continuously withdrawing reaction mixture as a crude vinyl ester product mixture which includes residual carboxylic acid, residual vinyl acetate, residual acetic acid, and homogeneous transvinylation catalyst; and (f) separating residual carboxylic acid, residual vinyl acetate, residual acetic acid, and homogeneous transvinylation catalyst from the crude vinyl ester product mixture to form a purified vinyl ester product; wherein the reaction conditions, feed to the reaction mixture, removal of acetic acid from the reaction mixture, and the separation and recycling of vinyl acetate to the reaction mixture are controlled and the catalyst is selected such that carboxylic acid is converted to vinyl ester product with a selectivity of at least 80 mole %, and there is less than 15 weight % acetic acid in the crude product mixture as well as a molar ratio of vinyl acetate:carboxylic acid of from more than 2:1 to 10:1 maintained in the reaction mixture.

2. The process according to claim 1, wherein the reaction conditions, feed to the reaction mixture, removal of acetic acid from the reaction mixture, and the separation and recycling of vinyl acetate to the reaction mixture are controlled and the catalyst is selected such that carboxylic acid is converted to vinyl ester product with a selectivity of at least 80 mole %, and there is less than 10 weight % acetic acid in the crude product mixture as well as a molar ratio of vinyl acetate:carboxylic acid of from more than 2:1 to 6:1 maintained in the reaction mixture.

3. The process according to claim 1, wherein the reaction conditions, feed to the reaction mixture, removal of acetic acid from the reaction mixture, and the separation and recycling of vinyl acetate to the reaction mixture are controlled and the catalyst is selected such that carboxylic acid is converted to vinyl ester product with a selectivity of at least 80 mole %, and there is less than 5 weight % acetic acid in the crude product mixture as well as a molar ratio of vinyl acetate:carboxylic acid of from more than 2:1 to 4:1 maintained in the reaction mixture.

4. The process according to claim 1, wherein the reaction conditions, feed to the reaction mixture, removal of acetic acid from the reaction mixture, and the separation and recycling of vinyl acetate to the reaction mixture are controlled and the catalyst is selected such that carboxylic acid is converted to vinyl ester product with a selectivity of at least 80 mole %, and there is less than 15 weight % acetic acid in the crude product mixture as well as a molar ratio of vinyl acetate:carboxylic acid of from more than 2:1 up to about 3:1 maintained in the reaction mixture.

5. The process according to claim 4, wherein the reaction conditions, feed to the reaction mixture, removal of acetic acid from the reaction mixture, and the separation and recycling of vinyl acetate to the reaction mixture are controlled and the catalyst is selected such that carboxylic acid is converted to vinyl ester product with a selectivity of at least 80 mole %, and there is less than 15 weight % acetic acid in the crude product mixture.

6. The process according to claim 1, wherein the process further comprises separating residual carboxylic acid from the crude vinyl ester product mixture and recycling the residual carboxylic acid to the reaction mixture.

7. The process according to claim 1, wherein the process further comprises separating the homogeneous transvinylation catalyst from the crude vinyl ester product mixture and recycling the catalyst to the reaction mixture.

8. The process according to claim 1, wherein the separated vinyl acetate is recycled at a rate of less than about 8 kg of vinyl acetate for every kg of vinyl ester produced.

9. The process according to claim 1, wherein more than 60 weight % of the carboxylic acid provided is converted to vinyl ester.

10. The process according to claim 1, wherein the carboxylic acid is selected from the group consisting of 2-ethylhexanoic acid, benzoic acid, neodecanoic acid, propionic acid, butyric acid, valeric acid, heptanoic acid, acrylic acid, methacrylic acid, stearic acid, and palmitic acid.

11. The process according to claim 1, wherein the temperature of the reaction (b) is maintained at from about 80° C. up to about 120° C.

12. The process according to claim 1, wherein unreacted vinyl acetate and acetic acid are continuously removed from the reaction mixture in a vinyl acetate:acetic acid molar ratio of from about 6:1 to about 10:1.

13. A continuous process for selective formation of vinyl ester by reactive distillation from its corresponding carboxylic acid, the process comprising: (a) providing carboxylic acid, vinyl acetate, and a palladium acetate-bidentate ligand catalyst complex to a reaction mixture; (b) reacting the carboxylic acid and vinyl acetate in the presence of the palladium acetate—bidentate ligand catalyst complex in the reaction mixture to form a vinyl ester product and acetic acid; (c) continuously removing acetic acid and vinyl acetate from the reaction mixture in a vinyl acetate:acetic acid molar ratio of from about 6:1 to about 10:1; (d) separating at least a portion of the removed vinyl acetate from the removed acetic acid and recycling the separated vinyl acetate to the reaction mixture; (e) withdrawing reaction mixture as a crude vinyl ester product mixture which includes residual carboxylic acid, residual vinyl acetate, residual acetic acid, and palladium acetate—bidentate ligand catalyst complex; and (f) separating residual carboxylic acid, residual vinyl acetate, residual acetic acid, and palladium acetate—bidentate ligand catalyst complex from the crude vinyl ester product mixture to form a purified vinyl ester product; wherein the reaction conditions, feed to the reaction mixture, removal of acetic acid from the reaction mixture, and the separation and recycling of vinyl acetate to the reaction mixture are controlled and the catalyst is selected such that carboxylic acid is converted to vinyl ester product with a selectivity of at least 80 mole %, and there is less than 15 weight % acetic acid in the crude product mixture as well as a molar ratio of vinyl acetate:carboxylic acid of from more than 2:1 to 6:1 maintained in the reaction mixture.

14. The process according to claim 13, wherein the catalyst concentration provided is from about 50 parts palladium per million parts of carboxylic acid provided to about 3,000 parts palladium per million parts of carboxylic acid provided.

15. A continuous process for selective formation of vinyl ester from neodecanoic acid, the process comprising: (a) purifying raw neodecanoic acid; (b) providing the neodecanoic acid, vinyl acetate, and a homogeneous transvinylation catalyst comprising palladium to a reaction mixture; (c) reacting the neodecanoic acid and vinyl acetate in the presence of the homogeneous transvinylation catalyst comprising palladium in the reaction mixture to form a vinyl ester product and acetic acid; (d) continuously removing acetic acid and vinyl acetate from the reaction mixture in a vinyl acetate:acetic acid molar ratio of from about 5:1 to about 25:1; (e) separating at least a portion of the removed vinyl acetate from the removed acetic acid and recycling the separated vinyl acetate to the reaction mixture; (f) continuously withdrawing reaction mixture as a crude vinyl ester product mixture which includes residual carboxylic acid, residual vinyl acetate, residual acetic acid, and homogeneous transvinylation catalyst; and (g) separating residual carboxylic acid, residual vinyl acetate, residual acetic acid, and homogeneous transvinylation catalyst from the crude vinyl ester product mixture to form a purified vinyl ester product; wherein the reaction conditions, feed to the reaction mixture, removal of acetic acid from the reaction mixture, and the separation and recycling of vinyl acetate to the reaction mixture are controlled and the catalyst is selected such that carboxylic acid is converted to vinyl ester product with a selectivity of at least 80 mole %, and there is less than 15 weight % acetic acid in the crude product mixture as well as a molar ratio of vinyl acetate:carboxylic acid of from more than 2:1 to 9:1 maintained in the reaction mixture.

16. A process for selective formation of a vinyl ester from its corresponding carboxylic acid, the process comprising: (a) providing a carboxylic acid, vinyl acetate, and a homogeneous transvinylation platinum-group metal catalyst to a reaction mixture; wherein the carboxylic acid is of suitable purity to ameliorate catalyst poisoning, the carboxylic acid being characterized by at least one of: (i) a bromine value of less than 20 mmoles of $Br_2$/g; (ii) a peroxide value of less than 200 ppm; or (iii) permanganate time of at least 30 minutes; (b) reacting the carboxylic acid and vinyl acetate in the presence of the homogeneous transvinylation catalyst in the reaction mixture to form a vinyl ester product and acetic acid; (c) removing acetic acid and vinyl acetate from the reaction mixture; (d) separating at least a portion of the removed vinyl acetate from the removed acetic acid and recycling the separated vinyl acetate to the reaction mixture; and (e) separating residual carboxylic acid, residual vinyl acetate, residual acetic acid, and homogeneous transvinylation catalyst from the crude vinyl ester product mixture to form a purified vinyl ester product; wherein the reaction conditions, feed to the reaction mixture, removal of acetic acid from the reaction mixture, and the separation and recycling of vinyl acetate to the reaction mixture are controlled and the catalyst is selected such that carboxylic acid is converted to vinyl ester product with a selectivity of at least 80 mole %, and there is less than 15 weight % acetic acid in the crude product mixture as well as a molar ratio of vinyl acetate:carboxylic acid of from 1:1 to 9:1 maintained in the reaction mixture.

17. The process according to claim 16, wherein the carboxylic acid is neodecanoic acid.

18. The process according to claim 16, wherein the carboxylic acid is 2-ethylhexanoic acid.

19. The process according to claim 16, wherein the platinum group metal is palladium.