

INCORPORATION OF ALKENE HYDROGENATION IN VINYL ACETATE PRODUCTION SYSTEMS AND METHODS

CROSS-REFERENCES TO RELATED APPLICATIONS

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[0001] The present application claims priority to U.S. Provisional Patent Application Serial No. 63/580,797, entitled "INCORPORATION OF ALKENE HYDROGENATION IN VINYL ACETATE PRODUCTION SYSTEMS AND METHODS" and filed on September 6, 2023, the entirety of which is incorporated herein by reference.

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STATEMENT AS TO RIGHTS TO INVENTIONS MADE UNDER FEDERALLY SPONSORED RESEARCH AND DEVELOPMENT

[0002] NOT APPLICABLE

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REFERENCE TO A "SEQUENCE LISTING," A TABLE, OR A COMPUTER PROGRAM LISTING APPENDIX SUBMITTED ON A COMPACT DISK

[0003] NOT APPLICABLE

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BACKGROUND

[0004] Vinyl acetate is conventionally produced via a vapor phase reaction of ethylene, oxygen, and acetic acid where the ethylene is acetoxylation. The rate of acetoxylation increases as the concentration of oxygen in the reactor is increased. However, the amount of oxygen that may be introduced into the reactor is limited by a flammability limit of the reaction mixture. The flammability limit is typically defined as the lowest concentration of oxygen in a mixture that will result in a pressure rise when it contacts an ignition source. If the oxygen concentration exceeds this flammability limit, a fire or explosion could result. Making changes to the reactor and/or the vapor phase components to increase the flammability limit and, consequently, increase the production ability of the reactor is desired.

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BRIEF SUMMARY

[0005] A nonlimiting example method of producing vinyl acetate may include: reacting via a hydrogenation reaction one or more alkenes and hydrogen in the presence of a hydrogenation catalyst to produce one or more alkanes; and reacting via an acetoxylation reaction acetic acid, ethylene, and oxygen in the presence of an acetoxylation catalyst and an alkane diluent to produce vinyl acetate and water, wherein the alkane diluent comprises the one or more alkanes from the hydrogenation reaction.

[0006] Another nonlimiting example method of producing vinyl acetate may include: reacting a feed stream comprising acetic acid, ethylene, oxygen, and alkane diluent in a vinyl acetate reactor to produce a crude vinyl acetate stream comprising vinyl acetate, water, and the alkane diluent; cooling the crude vinyl acetate stream in a heat exchanger; separating the crude vinyl acetate stream into a first tail gas stream, a flash gas stream and a vinyl acetate stream, wherein the first tail gas stream comprises ethylene and the alkane diluent, wherein the flash gas stream comprises ethylene, carbon dioxide, and the alkane diluent, and wherein the vinyl acetate stream comprises vinyl acetate; adding a second tail gas stream from a natural gas enrichment system to the first tail gas stream, wherein the one or more alkanes become part of the alkane diluent; removing at least a portion of the carbon dioxide from the flash gas stream to produce one or more recycle streams comprising ethylene and the alkane diluent; mixing vaporized acetic acid with the first tail gas stream and at least one of the one or more recycle streams in a vaporizer to produce a vaporized stream; and adding oxygen to the vaporized stream to produce the feed stream.

[0007] Yet another nonlimiting example method of producing vinyl acetate may include: reacting a feed stream comprising acetic acid, ethylene, oxygen, and alkane diluent in a vinyl acetate reactor to produce a crude vinyl acetate stream comprising vinyl acetate, water, and the alkane diluent; cooling the crude vinyl acetate stream in a heat exchanger; separating the crude vinyl acetate stream into a tail gas stream, a flash gas stream and a vinyl acetate stream, wherein the tail gas stream comprises ethylene and the alkane diluent, wherein the flash gas stream comprises ethylene, carbon dioxide, and the alkane diluent, and wherein the vinyl acetate stream comprises vinyl acetate; reacting via a hydrogenation reaction one or more alkenes and hydrogen in a hydrogenation reactor in the presence of a hydrogenation catalyst to produce a product stream comprising one or more alkanes and optionally hydrogen; adding at least a portion of the product stream to the tail gas stream, wherein the one or more alkanes become part of the alkane diluent; monitoring a hydrogen concentration in the alkane feed stream, wherein when the hydrogen concentration is greater than 1 mol% based on a total number of moles present in the product stream performing one or both of: (a) reducing an amount of the product stream from the

hydrogenation reactor added to the tail gas stream; and (b) adding a methane feed stream to the tail gas stream to become part of the alkane diluent; removing at least a portion of the carbon dioxide from the flash gas stream to produce one or more recycle streams comprising ethylene and the alkane diluent; mixing vaporized acetic acid with the tail gas stream and at least one of the one or
5 more recycle streams in a vaporizer to produce a vaporized stream; and adding oxygen to the vaporized stream to produce the feed stream.

[0008] Another nonlimiting example method of producing vinyl acetate may include: (i) producing one or more alkanes via a hydrogenation reaction and/or (ii) performing a natural gas enrichment process to produce an enriched natural gas and a tail gas; and producing vinyl acetate
10 via an acetoxylation reaction of acetic acid, ethylene, and oxygen performed in the presence of an alkane diluent comprising (i) the one or more alkanes from the hydrogenation reaction and/or (ii) the tail gas.

BRIEF DESCRIPTION OF THE DRAWINGS

15 [0009] FIG. 1 illustrates a nonlimiting example of a scheme of the present disclosure that integrates a hydrogenation reaction.

[0010] FIG. 2 illustrates a process flow diagram of a nonlimiting example of a method of the present disclosure that implements the scheme of FIG. 1.

20 [0011] FIG. 3 illustrates a nonlimiting example of a scheme of the present disclosure that integrates a natural gas enrichment process.

[0012] FIG. 4 illustrates a process flow diagram of a nonlimiting example method of the present disclosure that implements the scheme of FIG. 3.

[0013] FIG. 5 illustrates a process flow diagram of a nonlimiting example method of the present disclosure that implements a hybrid of the schemes of FIGS. 1 and 3.

25 [0014] FIG. 6 illustrates a process flow diagram of a nonlimiting example vinyl acetate production process of the present disclosure.

DETAILED DESCRIPTION

30 [0015] The present disclosure relates to systems and methods for producing vinyl acetate at higher production rates by increasing the flammability limit of the mixture in the vinyl acetate reactor. More specifically, the systems and methods described herein may utilize methane and/or higher carbon alkanes (e.g., alkanes with two or more carbons, also referred to herein as C2+ alkanes) in a diluent in the vinyl acetate reactor.

[0016] The vapor phase reaction to produce vinyl acetate typically is performed in the presence of methane as a diluent. The source of methane is typically natural gas, which also includes small amounts of ethane and propane. Without being limited by theory, it is believed that increasing the heat of combustion of the alkane diluent would consequently allow for a higher concentration of oxygen that may safely be present in the vinyl acetate reactor. Accordingly, the flammability limit may be increased by increasing the concentration of C2+ alkanes in the vinyl acetate reactor, which each have higher heats of combustion than methane. Methods and systems for ascertaining and monitoring the flammability limit at various points along a vinyl acetate production process and system are described in US Patent App. Pub. No. 2022/0402852, which is incorporated herein by reference.

[0017] The vinyl acetate production systems and methods of the present disclosure can incorporate (a) a hydrogenation reaction that produces one or more C2+ alkanes and/or (b) a tail gas from a natural gas enrichment process with an increased concentration of one or more C2+ alkanes. The higher concentration of one or more C2+ alkanes may be used to increase the flammability limit of the feed stream to the vinyl acetate reactor and allow for operating at higher oxygen concentration in the vinyl acetate reactor. Advantageously, when incorporating the hydrogenation reaction, a portion of the ethylene designated for use as a reactant can be diverted to the hydrogenation reaction to produce ethane, which provides for minimal retrofitting of existing systems.

[0018] Advantageously, the methods and systems of the present disclosure allow for metering alkane diluent from the hydrogenation reactor and from other sources as needed for the effective and safe operation of vinyl acetate production. For example, the cost to produce vinyl acetate may be lower using a traditional methane diluent, but the production capacity may be higher using an alkane diluent with higher concentrations of C2+ alkanes (e.g., ethane, propane, butane, and the like). Therefore, including the hydrogenation reaction and/or the tail gas from a natural gas enrichment process in the systems and methods of the present disclosure allows operators to readily move between lowest cost operation (relative to the alkane diluent) and highest capacity operation, including intermediate positions between the foregoing.

[0019] FIG. 1 illustrates a nonlimiting example reaction scheme of the present disclosure that integrates a hydrogenation reaction 100 with subsequent acetoxylation reaction 104. In a hydrogenation reaction 100, one or more alkenes (e.g., ethylene, propylene, butylene, or a mixture comprising two or more of the foregoing) and hydrogen are reacted in the presence of a hydrogenation catalyst to produce the corresponding one or more alkanes 102 (e.g., ethane, propane, butane, or a mixture comprising two or more of the foregoing). The one or more alkanes

102 are then used as a diluent (or alkane diluent) in a subsequent acetoxylation reaction 104 between acetic acid, ethylene, and oxygen in the presence of an acetoxylation catalyst to produce vinyl acetate and water. As described in more detail herein, the alkane diluent present during the acetoxylation reaction 104 may comprise the one or more alkanes 102 from the hydrogenation
5 reaction 100 as well as optionally alkanes 106 from other sources (e.g., from recycle streams, a methane-containing stream like a natural gas stream, a propane-containing stream, a butane-containing stream, and the like). Further, other chemical species (e.g., carbon dioxide and inert gases like nitrogen and argon) may be present during the acetoxylation reaction 104.

[0020] The reaction conditions, reactant concentrations, and other details of the hydrogenation
10 reaction and the acetoxylation reaction are provided in the description of FIG. 5. Said details are applicable to FIG. 1. For example, the hydrogenation reaction 100 may be carried out at temperature of -50°C to 200°C (or -10°C to 150°C, or 0°C to 100°C); at pressures of 0.5 MPa to 4 MPa (or 1 MPa to 3 MPa); with ethylene alone, propylene alone, butylene alone, or a mixture comprising two or more of the foregoing in the amounts provided in the FIG. 5 description; and
15 with hydrogen amounts provided in the FIG. 5 description. Similarly, the description of the conditions for the acetoxylation reaction relative to FIG. 5 apply to the acetoxylation reaction 104 of FIG. 1.

[0021] FIG. 2 illustrates a flow diagram of a nonlimiting example vinyl acetate production process 200 of the present disclosure. The vinyl acetate production process 200 includes reacting,
20 in a hydrogenation reactor 206, one or more alkenes 202 (e.g., ethylene, propylene, butylene, or a mixture comprising two or more of the foregoing) and hydrogen 204 in the presence of a hydrogenation catalyst to produce the corresponding one or more alkanes 208 (e.g., ethane, propane, butane, or a mixture comprising two or more of the foregoing). The one or more alkanes 208 are then used as at least a portion of the alkane diluent in the subsequent acetoxylation
25 reaction.

[0022] A reaction feed 218 for the acetoxylation reaction may be produced by mixing components thereof. The reaction feed 218 may comprise ethylene 210, acetic acid 212, oxygen 214, and alkane diluent (e.g., the one or more alkanes 208 from the hydrogenation reactor 206, optionally methane 216 (e.g., a purified methane stream or a natural gas stream), and optionally
30 alkanes from other sources including streams comprising ethane, propane, butane, or a mixture thereof). The ethylene, when present, in the one or more alkenes 202 and the ethylene 210 may be from the same source or from different sources.

[0023] The reaction feed 218 is introduced to a vinyl acetate reactor 220 where the acetoxylation reaction produces a crude vinyl acetate product 222 comprising vinyl acetate, water, and the alkane

diluent. The crude vinyl acetate product 222 may then be treated in one or more processes 224 to produce a vinyl acetate product 226. Said processes may separate water, alkane diluent, and other components (e.g., unreacted ethylene) from the crude vinyl acetate product 222. Further, said processes may purify said components after having been separated from the crude vinyl acetate product 222. Accordingly, at least some of the components separated from the crude vinyl acetate product 222, whether purified or as separated, may be recycled back in one or more recycle streams 228 to be a portion of the reaction feed 218.

[0024] As with FIG. 1, the reaction conditions, reactant concentrations, and other details of the hydrogenation reaction and the acetoxylation reaction provided in the description of FIG. 5 are applicable to FIG. 2.

[0025] In any embodiment of the present disclosure, the inclusion of higher concentrations of C₂+ alkanes in the alkane diluent increases the flammability limit for vinyl acetate production. Product streams from the hydrogenation reaction that comprise C₂+ alkanes may also comprise unreacted hydrogen and/or unreacted alkenes that would become incorporated to the reaction feed (e.g., reaction feed 218 of FIG. 2) for the acetoxylation reaction. The unreacted hydrogen may, among other things, reduce the flammability limit. Unreacted alkenes other than ethylene may react in the acetoxylation reaction to produce unwanted products. Accordingly, one or more strategies may be implemented in the methods and systems of the present disclosure to mitigate, or eliminate, hydrogen and/or alkene breakthrough from the hydrogenation reactor.

[0026] In an example to mitigate alkene breakthrough (e.g., when using propylene and/or butylene), a stoichiometric excess of hydrogen relative to alkene may be present in the hydrogenation reactor. For example, the mole ratio of hydrogen to total alkene may be 1.01:1 to 3:1, or 1.1:1 to 2:1, or 1.01:1 to 1.5:1, or 1.01:1 to 1.1:1.

[0027] In an example to mitigate hydrogen breakthrough, a stoichiometric excess of alkene relative to hydrogen may be present in the hydrogenation reactor. For example, the mole ratio of hydrogen to total alkene may be 1:3 to 1:1.01, or 1:2 to 1:1.1, or 1:1.5 to 1:1.01, or 1:1.1 to 1:1.01.

[0028] The stoichiometric excess of unreacted alkene would allow breakthrough of the unreacted alkene from the hydrogenation reactor but mitigate the breakthrough of hydrogen. This strategy may be preferably implemented when ethylene is the alkene or is at least 50 mol% (or 50 mol% to 99 mol%, or 75 mol% to 99 mol%, or 90 mol% to 99 mol%) of the alkene because ethylene is a reactant in the vinyl acetate synthesis.

[0029] In another example, the amount of hydrogenation catalyst and residence time in the hydrogenation reactor may be in excess to provide 100 mol% conversion of the limiting reactant, whether the hydrogenation conditions include an excess of hydrogen, an excess of alkene, or a

stoichiometric balance of hydrogen and alkene. The hydrogenation reaction conditions and hydrogenation catalysts are discussed in more detail herein at FIG. 6.

5 [0030] In yet another example, the hydrogenation reactor may include more than one hydrogenation catalyst bed in series or a catalyst bed with a mixture of two or more hydrogenation catalysts to provide 100 mol% conversion of the limiting reactant, whether the hydrogenation conditions include an excess of hydrogen, an excess of alkene, or a stoichiometric balance of hydrogen and alkene. Said configurations may be advantageous when the one or more alkenes is a mixture of two or more alkenes, where each hydrogenation catalyst may have a high conversion rate for different alkenes in the mixture of two or more alkenes.

10 [0031] In another example to mitigate hydrogen and/or alkene breakthrough, the product from the hydrogenation reaction may be purified to remove unreacted hydrogen and/or unreacted alkene. For example, guard beds, membranes, or other extraction technologies may be used to remove hydrogen and/or alkene from the product stream (e.g., the one or more alkanes 208 of FIG. 2) from hydrogenation reactor.

15 [0032] In an example to mitigate hydrogen buildup, oxygen may be introduced to the system upstream of the vinyl acetate reactor. Reducing buildup of hydrogen may allow for higher hydrogen breakthrough concentrations.

[0033] More than one of the foregoing strategies may be implemented. For example, the hydrogenation catalyst choice (including a mixed catalyst), a molar excess of a reactant (hydrogen
20 or an alkene), and product stream purification may be used in any combination to mitigate hydrogen and/or alkene breakthrough.

[0034] If breakthrough of reactants from the hydrogenation reaction occurs, an ethylene breakthrough is preferred since ethylene is a reactant in the acetoxylation reaction. While hydrogen breakthroughs may reduce the flammability limit in the acetoxylation reactor and produce side
25 products in the acetoxylation reaction, hydrogen breakthrough may be preferable to propylene or butylene breakthrough as the side products of such reactants may require additional downstream separate processes to remove from a vinyl acetate product.

[0035] Without being limited by theory, it is believed that the reaction feed for the acetoxylation reaction may comprise up to 1 mol% of hydrogen without significant effect on the flammability
30 limit and the acetoxylation reaction product. Accordingly, small amounts of hydrogen breakthrough may be allowed but are preferably monitored. For example, the hydrogen concentration in the product stream from the hydrogenation reactor and/or in the reaction feed for the acetoxylation reaction may be monitored. The amount of hydrogen breakthrough that can be tolerated in the methods and systems of the present disclosure will depend on many factors

including, but not limited to, the conditions of the acetoxylation reaction and the chemical composition of the reaction feed for the acetoxylation reaction. In general, the hydrogenation product preferably has 1 mol% or less, 0.5 mol% or less, or 0.1 mol% or less of hydrogen, or is at least substantially free (e.g., 0 mol% to 0.01 mol%) of hydrogen, based on a total number of moles
5 in the product stream from the hydrogenation reaction. However, higher values may be tolerated depending on the foregoing factors.

[0036] The hydrogen concentration in the product stream from the hydrogenation reactor may be monitored using a hydrogen analyzer.

[0037] If the hydrogen concentration in the product stream from the hydrogenation reactor is
10 above a threshold value (e.g., 1 mol% based on a total number of moles in the product stream), one or more actions may be taken.

[0038] In a first example, the amount of product stream from the hydrogenation reactor used to produce the feed stream for the vinyl acetate reactor may be decreased (or even stopped), and an amount of alkane diluent (e.g., methane, ethane, propane, butane, or a mixture comprising two or
15 more of the foregoing) from another source may be used to make up for said decrease or stoppage, each responsive to a determination that the hydrogen concentration is above the threshold value. Examples of other sources may include, but are not limited to, natural gas, natural gas liquids, a petroleum refining by-product, the like, and a combination thereof.

[0039] In another example, the vinyl acetate production method and system may be shut down
20 responsive to a determination that the hydrogen concentration is above the threshold value.

[0040] FIG. 3 illustrates a nonlimiting example of a scheme of the present disclosure that integrates a natural gas enrichment process 300 with subsequent acetoxylation reaction 312. In a natural gas enrichment process 300, a natural gas 302 is processed with a separation system 304 (e.g., a pressure swing absorption system) that produces a methane-enriched natural gas 306 and a
25 tail gas 308. The separation system 304 aims to remove at least a portion of the C2+ alkanes to produce a methane-enriched natural gas 306 that has a higher concentration of methane than the natural gas 302. Separation systems 304 are common in chemical processing plants and facilities where one or more processes requires high-purity methane. The C2+ alkanes removed from the natural gas 302 exit the separation system 304 in the tail gas 308. Accordingly, the tail gas 308 has
30 a higher concentration of C2+ alkanes than the natural gas 302. Typically, the tail gas 308 is used a fuel in other processes or burned as waste.

[0041] Methods of the present disclosure may utilize the tail gas 308 as at least a portion of the alkane diluent in the subsequent acetoxylation reaction 312. As illustrated, the tail gas 308 is then used as a diluent (or alkane diluent) in a subsequent acetoxylation reaction 312 between acetic

acid, ethylene, and oxygen in the presence of an acetoxylation catalyst to produce vinyl acetate and water. As described in more detail herein, the alkane diluent present during the acetoxylation reaction 312 may comprise the one or more alkanes from the tail gas 308 as well as optionally alkanes 310 from other sources (e.g., from recycle streams, a methane-containing stream like a natural gas stream, a propane-containing stream, a butane-containing stream, and the like). Further, other chemical species (e.g., carbon dioxide and inert gases like nitrogen and argon) may be present during the acetoxylation reaction 312.

[0042] The natural gas 302 may comprise 96 vol% to 98 vol% (or 97 vol% to 98 vol%) methane, 1 vol% to 2.5 vol% (or 1 vol% to 2 vol%) C2+ alkanes, and 0.5 vol% to 1.5 vol% (or 0.5 vol% to 1 vol%) other chemical species (e.g., carbon dioxide and inert gases like nitrogen and argon). The methane-enriched natural gas 306 may comprise 98 vol% to 99.8 vol% (or 98.5 vol% to 99.5 vol%) methane, 0.1 vol% to 1.5 vol% (or 0.1 vol% to 1 vol%) C2+ alkanes, and 0.1 vol% to 1 vol% (or 0.1 vol% to 0.5 vol%) other chemical species. The tail gas 308 may comprise 94 vol% to 97 vol% (or 95 vol% to 96.5 vol%) methane, 1.5 vol% to 4 vol% (or 1.5 vol% to 3 vol%) C2+ alkanes, and 1 vol% to 2 vol% (or 1 vol% to 1.5 vol%) other chemical species.

[0043] The reaction conditions, reactant concentrations, and other details of the acetoxylation reaction are provided in the description of FIG. 6. Said details are applicable to FIG. 3.

[0044] FIG. 4 illustrates a flow diagram of a nonlimiting example vinyl acetate production process 400 of the present disclosure. The vinyl acetate production process 400 includes enriching, in a separation system 434 (e.g., a pressure swing absorption system), natural gas 432 to produce methane-enriched 436 and tail gas 438 (e.g., as described in FIG. 3). The tail gas 438 is then used as at least a portion of the alkane diluent in the subsequent acetoxylation reaction.

[0045] A reaction feed 218 for the acetoxylation reaction may be produced by mixing components thereof. The reaction feed 218 may comprise ethylene 210, acetic acid 212, oxygen 214, and alkane diluent (e.g., the tail gas 438, optionally methane 216 (e.g., a purified methane stream or a natural gas stream), and optionally alkanes from other sources including streams comprising ethane, propane, butane, or a mixture thereof). The disclosure of the processing of the reaction feed 218 of FIG. 2 applies to FIG. 4 where the same reference numbers are used.

[0046] As with FIG. 3, the reaction conditions, reactant concentrations, and other details of the hydrogenation reaction and the acetoxylation reaction provided in the description of FIG. 6 are applicable to FIG. 4.

[0047] A hybrid of FIGS. 1 and 2 with FIGS. 3 and 4 are also contemplated. For example, FIG. 5 illustrates a flow diagram of a nonlimiting example vinyl acetate production process 500 of the present disclosure. The vinyl acetate production process 500 includes reacting, in a hydrogenation

reactor 206, one or more alkenes 202 (e.g., ethylene, propylene, butylene, or a mixture comprising two or more of the foregoing) and hydrogen 204 in the presence of a hydrogenation catalyst to produce the corresponding one or more alkanes 208 (e.g., ethane, propane, butane, or a mixture comprising two or more of the foregoing). The one or more alkanes 208 are then used as at least a portion of the alkane diluent in the subsequent acetoxylation reaction.

[0048] The vinyl acetate production process 500 includes enriching, in a separation system 434 (e.g., a pressure swing absorption system), natural gas 432 to produce methane-enriched 406 and tail gas 438. The tail gas 438 is then used as at least a portion of the alkane diluent in the subsequent acetoxylation reaction.

[0049] A reaction feed 218 for the acetoxylation reaction may be produced by mixing components thereof. The reaction feed 218 may comprise ethylene 210, acetic acid 212, oxygen 214, and alkane diluent (e.g., the one or more alkanes 208 from the hydrogenation reactor 206, tail gas 438, optionally methane 216 (e.g., a purified methane stream or a natural gas stream), and optionally alkanes from other sources including streams comprising ethane, propane, butane, or a mixture thereof). The ethylene, when present, in the one or more alkenes 202 and the ethylene 210 may be from the same source or from different sources. The disclosure of the processing of the reaction feed 218 of FIG. 2 applies to FIG. 4 where the same reference numbers are used.

[0050] FIG. 6 illustrates a more detailed process flow diagram of a nonlimiting example vinyl acetate production process 600 of the present disclosure. Additional components and modifications may be made to the process 600 without changing the scope of the present disclosure. Further, as would be recognized by one skilled in the art, the description of the process 600 and related system uses streams to describe the fluids passing through various lines. For each stream, the related system has corresponding lines (e.g., pipes or other pathways through which the corresponding fluids or other materials may pass readily) and optionally valves, pumps, compressors, heat exchangers, or other equipment (not shown) to ensure proper operation of the related system whether explicitly described or not.

[0051] Further, the descriptor used for individual streams does not limit the composition of said streams to consisting of said descriptor. For example, an ethylene stream does not necessarily consist of only ethylene. Rather, the ethylene stream may comprise ethylene and an alkane, and/or contain one or more minor contaminants. Alternatively, the ethylene stream may consist of only ethylene. Alternatively, the ethylene stream may comprise ethylene, another reactant, and optionally an alkane.

[0052] In the illustrated process 600, an acetic acid stream 602 and an ethylene stream 604 are introduced to a vaporizer 606. In addition, one or more recycle streams 630, 658, 668 (each

described further herein) may also be introduced to the vaporizer 606. Optionally, one or more of the recycle streams 630, 658, 668 can be combined (not shown) with each other in any combination and/or with the acetic acid stream 602 before introduction to the vaporizer 606.

[0053] The temperature and pressure of vaporizer 606 may vary over a wide range. The vaporizer 606 preferably operates at a temperature of 100°C to 250° C, or 100°C to 200°C, or 120°C to 150°C. The operating pressure of the vaporizer 606 preferably is at 0.1 MPa to 2 MPa, or 0.25 MPa to 1.75 MPa, or 0.5 MPa to 1.5 MPa. The vaporizer 606 produces a vaporized feed stream 608. The vaporized feed stream 608 exits the vaporizer 606 and combines with an oxygen stream 610 to produce a combined feed stream 612. The combined feed stream 612 is fed to a vinyl acetate reactor 616.

[0054] The operating conditions in the vinyl acetate reactor 616 may be adjusted based on the composition of the combined feed stream 612, which may be used to ascertain a flammability limit of the combined feed stream 612. Example ranges for the operating conditions in the vinyl acetate reactor 616 are provided below.

[0055] The combined feed stream 612 may comprise one or more of: ethylene, acetic acid, oxygen, methane, ethane, propane, butane, water, nitrogen, argon, and carbon dioxide. The combined feed stream 612 may also contain propylene, butylene, and/or hydrogen if breakthrough from the hydrogenation portion of the process 100 occurs. The composition of the combined feed stream 612 is considered at the inlet of the vinyl acetate reactor.

[0056] The concentration of components in the various streams described herein can be measured directly or calculated based on a measurement of a different component. For example, an acetic acid content (accounting for dimerization) in a stream may be calculated based on measurements. Then, the acetic acid content may be derived from the water content. Further, measurements or values derived from measurements need not be at the location of interest. For example, the water content at the reactor inlet may be derived from the water content of a recycle stream coming from purification processes 648. Accordingly, when a condition value (e.g., temperature value, pressure value, or concentration of a component in a stream) is described herein, the condition value is not limited to a direct measurement at said location but encompasses a derived value for said location based on measurements at that location or other locations in the process 600.

[0057] A concentration of ethylene in the combined feed stream 612 may be 30 mol% to 80 mol%, or 35 mol% to 75 mol%, or 40 mol% to 70 mol%, where said mol%s are based on the total moles of the combined feed stream absent the contribution from oxygen and water (or the total moles of an oxygen-free, dry combined feed stream).

- [0058] A concentration of acetic acid in the combined feed stream 612 may be 10 mol% to 40 mol%, or 15 mol% to 35 mol%, or 20 mol% to 30 mol%, where said mol% are based on the total moles of the combined feed stream absent the contribution from oxygen (or the total moles of an oxygen-free combined feed stream).
- 5 [0059] In the combined feed stream 612, the molar ratio of ethylene to oxygen is preferably less than 20:1, or 1:1 to 20:1, or 1:1 to 10:1, or 1.5:1 to 5:1, or 2:1 to 4:1. In the combined feed stream 612, the molar ratio of acetic acid to oxygen is preferably less than 10:1, or 0.5:1 to 10:1, 0.5:1 to 5:1, or 0.5:1 to 3:1. In the combined feed stream 612, the molar ratio of ethylene to acetic acid is preferably less than 10:1, or 1:1 to 10:1, or 1:1 to 5:1, or 2:1 to 3:1.
- 10 [0060] A concentration of water in the combined feed stream 612 may be 0 mol% to 10 mol%, or 0 mol% to 5 mol%, or 1 mol% to 4 mol%, where said mol% are based on the total moles of an oxygen-free combined feed stream.
- [0061] A combined concentration of alkane diluent (i.e., the total concentration of alkane present, which may, for example, include methane, ethane, propane, butane, or any combination thereof) in the combined feed stream 612 may be 10 mol% to 50 mol%, or 20 mol% to 50 mol%, or 30 mol% to 50 mol%, where said mol% are based on the total moles of an oxygen-free, dry combined feed stream. Individually, a concentration of each of the alkanes present in the alkane diluent may be 0.1 mol% to 100 mol%, 0.1 mol% to 99.9 mol%, 0.1 mol% to 5 mol%, or 1 mol% to 10 mol%, or 5 mol% to 25 mol%, or 20 mol% to 60 mol%, or 50 mol% to 80 mol%, or 70
- 15 mol% to 100 mol%, where said mol% are based on the total moles of alkane in the alkane diluent. For example, the combined feed stream 612 may include alkane diluent composed of methane and ethane (i.e., no propane) where the alkane diluent concentration (or a total combined concentration of methane and ethane) is 20 mol% to 50 mol% based on the total moles of an oxygen-free, dry combined feed stream. In said example, methane may make up 0.1 mol% to 10 mol% of the alkane diluent with the balance being ethane. In another example, the combined feed stream 612 may
- 20 comprise ethane, propane, and optionally methane, where the alkane diluent concentration (or a total concentration of the alkanes) may be 10 mol% to 50 mol% based on the total moles of an oxygen-free, dry combined feed stream. In said example, a concentration of ethane may be 0.1 mol% to 99.9 mol% based on the total moles of the alkane diluent, a concentration of propane may
- 25 be 0.1 mol% to 99.9 mol% based on the total moles of the alkane diluent, and a concentration of methane may be 0 mol% to 5 mol% based on the total moles of the alkane diluent. In yet another example, the combined feed stream 612 may comprise ethane, propane, butane, and optionally methane, where the alkane diluent concentration (or a total concentration of the alkanes) may be 10 mol% to 50 mol% based on the total moles of an oxygen-free, dry combined feed stream. In
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said example, a concentration of ethane may be 0.1 mol% to 99.8 mol% based on the total moles of the alkane diluent, a concentration of propane may be 0.1 mol% to 99.8 mol% based on the total moles of the alkane diluent, a concentration of butane may be 0.1 mol% to 99.8 mol% based on the total moles of the alkane diluent, and a concentration of methane may be 0 mol% to 10 mol%

5 based on the total moles of the alkane diluent.

[0062] A concentration of carbon dioxide in the combined feed stream 612 may be 0 mol% to 30 mol%, or 0 mol% to 25 mol%, or 5 mol% to 20 mol%, where said mol% are based on the total moles of an oxygen-free, dry combined feed stream.

[0063] A concentration of inert gases (e.g., nitrogen and/or argon) in the combined feed stream
10 612 may be 0 mol% to 20 mol%, or 1 mol% to 20 mol%, or 2 mol% to 15 mol%, where said mol% are based on the total moles of an oxygen-free, dry combined feed stream. Typically, the concentration of inert gases builds up over time from inert gases being present in streams fed to the system.

[0064] The vinyl acetate reactor 616 may be a shell and tube reactor that is configured, through a
15 heat exchange medium, to absorb heat generated by the exothermic reaction and control the temperature therein within a temperature range of 100°C to 250°C, or 110°C to 200°C, or 120°C to 180°C. The pressure in the vinyl acetate reactor 616 may be maintained at 0.5 MPa to 2.5 MPa, or 0.5 MPa to 2 MPa.

[0065] Further, the vinyl acetate reactor 616 may be a fixed bed reactor or a fluidized bed
20 reactor, preferably a fixed bed reactor that contains a catalyst suitable for acetoxylation of ethylene. Suitable acetoxylation catalysts for the production of vinyl acetate are described, for example, in U.S. Pat. Nos. 3,743,607; 3,775,342; 5,557,014; 5,990,344; 5,998,659; 6,022,823; 6,057,260; and 6,472,556, each of which is incorporated herein by reference. Suitable acetoxylation catalysts may comprise palladium, gold, vanadium, and mixtures thereof. Particular
25 preference is given to the following acetoxylation catalysts: palladium acetate/potassium acetate/cadmium acetate and palladium acetate/barium acetolaurate/potassium acetate. In general, the palladium content of the acetoxylation catalyst may be 0.5 wt % to 5 wt %, or 0.5 wt % to 3 wt %, or 0.6 wt % to 2 wt %. When gold or one of its compounds is used, it is added in a proportion of 0.01 wt % to 4 wt %, or 0.2 wt % to 2 wt %, or 0.3 wt % to 1.5 wt %. The acetoxylation
30 catalysts also preferably contain a refractory support, preferably a metal oxide such as silica, silica-alumina, titania, or zirconia, more preferably silica.

[0066] The acetoxylation reaction in the vinyl acetate reactor 616 produces a crude vinyl acetate stream 618. Depending on conversion and reaction conditions, the crude vinyl acetate stream 618 can comprise 15 wt % to 45 wt % vinyl acetate, 20 wt % to 70 wt % acetic acid, 0.1 wt % to 10 wt

% water, 10 wt % to 80 wt % ethylene, 1 wt % to 40 wt % carbon dioxide, 0.1 wt % to 50 wt % alkanes (e.g., methane, ethane, propane, butane, or mixtures thereof), and 0.1 wt % to 15 wt % oxygen. Optionally, the crude vinyl acetate stream 618 may also comprise 0.01 wt % to 10 wt % ethyl acetate. The crude vinyl acetate stream 618 may comprise other compounds such as methyl acetate, acetaldehyde, acrolein, propane, and inert gases such as nitrogen or argon. Generally, these other compounds, except for inert gases, are present in very low amounts (e.g., 2 wt% or less).

[0067] The crude vinyl acetate stream 618 passes through a heat exchanger 620 to reduce the temperature of the crude vinyl acetate stream 618 and then to a separator 622 (e.g., a distillation column). Preferably, the crude vinyl acetate stream 618 is cooled to a temperature of 80°C to 145°C, or 90°C to 135°C, prior to being introduced into the separator 622. Preferably, no condensation of the liquefiable components occurs and the cooled crude vinyl acetate stream 618 is introduced to the separator 622 as gas.

[0068] The energy to separate the components of the crude vinyl acetate stream 618 may be provided by the heat of reaction in the reactor 616. In some embodiments, there may be an optional reboiler dedicated to increasing the separation energy within the separator 622.

[0069] The separator 622 separates the crude vinyl acetate stream 618 into at least two streams: an overheads stream 624 and a bottoms stream 626. The overheads stream 624 can comprise ethylene, carbon dioxide, water, alkanes (e.g., methane, ethane, propane, butane, or mixtures thereof), oxygen, and vinyl acetate. The bottoms stream can comprise vinyl acetate, acetic acid, water, and potentially ethylene, carbon dioxide, and alkanes.

[0070] The overheads stream 624 is conveyed to a scrubber 628 to remove vinyl acetate in the overheads stream 624. As a result, the scrubber 628 has a tail gas stream 630 and a bottoms stream 632. Vinyl acetate scrubbing can be achieved by passing the overheads stream 624 through a mixture of water and acetic acid.

[0071] The tail gas stream 630 comprises ethylene, carbon dioxide, alkanes, and oxygen. The tail gas stream 630 (also referred to as a recycle stream) is conveyed back to the vaporizer 606 through the heat exchanger 620, where the crude vinyl acetate stream 618 heats the tail gas stream 630. Optionally, the tail gas stream 630 can be augmented with or otherwise have added thereto other streams including other recycle streams (not shown) in the process and feed streams. As illustrated, an alkane feed stream 634 from a hydrogenation reactor 670, an ethylene feed stream 636, a tail gas stream 640 from a natural gas enrichment process (not shown) (e.g., as described in FIGS. 3-5), and a methane feed stream 638 are combined (e.g., mixed with or entrained with) with the tail gas stream 630 from the scrubber 628. While the methane feed stream 638 is illustrated, the

use of methane in the systems and methods described herein is optional. Further, the methane feed stream 638 may, more generally, be an alkane feed stream where said alkane feed stream comprises one or more alkanes not from the hydrogenation reactor but rather from other sources as discussed above. Said alkane feed stream may, in practice, be multiple streams that are combined with the tail gas stream 630.

[0072] Further, while FIG. 6 illustrates the use of both the alkane feed stream 634 from the hydrogenation reactor 670 and the tail gas stream 640 from a natural gas enrichment process. Methods and systems of the present disclosure may include only one of the foregoing rather than both as illustrated.

[0073] Further, while FIG. 6 illustrates the use of both the methane feed stream 638 and the tail gas stream 640 from a natural gas enrichment process. Methods and systems of the present disclosure may include only one of the foregoing rather than both as illustrated. Advantageously, the methane feed stream 638 may be completely replaced with the tail gas stream 640, which as discussed above includes methane but higher concentrations of C2+ alkanes. Further, the hydrogen and/or alkene breakthrough concerns with the hydrogenation process are not present with the tail gas stream 640 from a natural gas enrichment process. As such, the tail gas stream 640 from a natural gas enrichment process may be the primary source of the alkane diluent and/or the backup source for the alkane diluent if a hydrogen and/or alkene breakthrough is observed.

[0074] Regarding the hydrogenation process, a first alkene feed stream 636a (illustrated as ethylene slip stream from the ethylene feed stream 636), a hydrogen feed stream 672, and a second alkene feed stream 674 are conveyed to the hydrogenation reactor 670. As a slip stream of the ethylene feed stream 636, the first alkene feed stream 636a may use up to 5 vol%, or 0.1 vol% to 5 vol%, or 0.5 vol% to 2 vol% of the ethylene feed stream 636, the remainder being directed to and combined with tail gas stream 630.

[0075] The second alkene feed stream 674 may comprise ethylene, propylene, butylene, or any mixture thereof.

[0076] While FIG. 6 illustrates the use of two sources (or feeds) of alkene, the process 600 could be modified to use one or more sources of alkene introduced into the hydrogenation reactor 670.

[0077] When more than one alkene is used as reactants in the hydrogenation reactor 670, an individual alkene may be present at 1 mol% to 99 mol%, or 1 mol% to 50 mol% to 25 mol% to 75 mol%, or 50 mol% to 99 mol%, based on the total combined moles of alkene. For example, when both ethylene and propylene are used as reactants in the hydrogenation reactor 670, the ethylene and the propylene may individually be present at 0.1 mol% to 99.9 mol%, or 1 mol% to 50 mol% to 25 mol% to 75 mol%, or 50 mol% to 99 mol%, based on the total combined moles of ethylene

- and propylene. In another example, when both ethylene, propylene, and butylene are used as reactants in the hydrogenation reactor 670, each alkene may individually be present at 0.1 mol% to 99.9 mol%, or 1 mol% to 50 mol% to 25 mol% to 75 mol%, or 50 mol% to 99 mol%, based on the total combined moles of alkene. In yet another example, the alkene reactants for the hydrogenation reactor 670 may comprise 30 mol% to 99.9 mol% ethylene, 0.1 mol% to 50 mol% propylene, and optionally 0.1 mol% to 50 mol% butylene, based on the total combined moles of alkene. In another example, the alkene reactants for the hydrogenation reactor 670 may comprise 90 mol% to 99.9 mol% ethylene, 0.1 mol% to 10 mol% propylene, and optionally 0.1 mol% to 5 mol% butylene, based on the total combined moles of alkene. In another example, the alkene reactants for the hydrogenation reactor 670 may comprise 0.1 mol% to 70 mol% ethylene, 30 mol% to 99.9 mol% propylene, and optionally 0.1 mol% to 50 mol% butylene, based on the total combined moles of alkene. In another example, the alkene reactants for the hydrogenation reactor 670 may comprise 0.1 mol% to 10 mol% ethylene, 90 mol% to 99.9 mol% propylene, and optionally 0.1 mol% to 5 mol% butylene, based on the total combined moles of alkene.
- [0078]** The hydrogen may be present at any suitable level based on the composition of the alkenes being used. As discussed above, the hydrogen is present to accommodate 100 mol% conversion of all alkenes to alkanes including having an excess of hydrogen present, especially when the alkene includes propylene and/or butylene. Further, to mitigate hydrogen breakthrough from the hydrogenation reactor 670, especially when using ethylene, the hydrogen may be present at a lower concentration, for example, to accommodate 99 mol%, or 98 mol%, or 95 mol%, or 90 mol%, conversion of all alkenes to alkanes.
- [0079]** The mole ratio of hydrogen to total alkene as reactants for the hydrogenation reaction may be 1:3 to 3:1, or 1:1.5 to 1.5:1, or 1:1, 1.01:1 to 3:1, or 1.1:1 to 2:1, or 1.01:1 to 1.5:1, or 1.01:1 to 1.1:1, or 1:3 to 1:1.01, or 1:2 to 1:1.1, or 1:1.5 to 1:1.01, or 1:1.1 to 1:1.01.
- [0080]** The alkane feed stream 634 may comprise 1 mol% or less, 0.5 mol% or less, or 0.1 mol% or less of hydrogen, or is at least substantially free (e.g., 0 mol% to 0.01 mol%) of hydrogen. Further, the alkane feed stream 634 may comprise 1 mol% or less, 0.5 mol% or less, or 0.1 mol% or less of unreacted alkene, or is at least substantially free (e.g., 0 mol% to 0.01 mol%) of unreacted alkene.
- [0081]** The hydrogenation reactor 670 may be operated at a temperature range of -50°C to 200°C, or -10°C to 150°C, or 0°C to 100°C. The pressure in the vinyl acetate reactor 616 may be maintained at 0.5 MPa to 4 MPa, or 1 MPa to 3 MPa.
- [0082]** The hydrogenation reactor 670 may be a fixed bed reactor or a fluidized bed reactor, preferably a fixed bed reactor that contains a hydrogenation catalyst suitable for hydrogenation of

ethylene and/or propylene. Suitable hydrogenation catalysts may comprise iridium, nickel, palladium, platinum, rhodium, ruthenium, and mixtures thereof. In general, the metal content of the hydrogenation catalyst may be 0.5 wt % to 5 wt %, or 0.5 wt % to 3 wt %, or 0.6 wt % to 2 wt %. When gold or one of its compounds is used, it is added in a proportion of 0.01 wt % to 4 wt %, or 0.2 wt % to 2 wt %, or 0.3 wt % to 1.5 wt %. The hydrogenation catalysts also preferably contain a refractory support, preferably a metal oxide such as silica, silica-alumina, titania, or zirconia, more preferably silica.

[0083] Contaminants in the hydrogen feed, like carbon monoxide, may reduce the activity of the hydrogenation catalyst. Accordingly, a carbon monoxide scrubber or other suitable apparatus may be used to treat the hydrogen feed stream 672 before introducing the hydrogen to the hydrogenation reactor 670 to reduce the concentration of the contaminants like carbon monoxide in the hydrogen feed. The hydrogen feed may contain carbon monoxide at a concentration up to 500 ppm, or up to 250 ppm, or up to 200 ppm, or up to 150 ppm, or up to 100 ppm, or up to 50 ppm, or 0 ppm to 500 ppm, or 0 ppm to 250 ppm, or 0 ppm to 200 ppm, or 0 ppm to 150 ppm, or 0 ppm to 100 ppm, or 0 ppm to 50 ppm, or 0 ppm to 25 ppm.

[0084] While the first alkene feed stream 636a, the hydrogen feed stream 672, and the second alkene feed stream 674 are illustrated as being separately introduced to the hydrogenation reactor 670, any combination of the streams may be premixed before introduction to the hydrogenation reactor 670.

[0085] The product of the hydrogenation reaction is the alkane feed stream 634. Along the alkane feed stream 634 may be one or more analyzers 678 for measuring the concentration of hydrogen and/or alkene in the alkane feed stream 634. As discussed herein, hydrogen may reduce the flammability limit in the downstream vinyl acetate reactor 616 and unreacted propylene and/or butylene may yield undesired side products. The methods described herein to reduce reactant breakthrough and/or react to reactant breakthrough are applicable to the vinyl acetate production process 600. Examples of reactant (e.g., hydrogen and/or alkene) breakthrough mitigation are discussed above.

[0086] An example of reacting to reactant breakthrough in the alkane feed stream 634 from the hydrogenation reactor 670, the vinyl acetate production process 600 may be operated such that the methane feed stream 638 (or, more generally, an alkane feed stream from a source other than the hydrogenation reactor 670) is optionally used with little to no addition of the additional alkane to the tail gas stream 630. Then, if a hydrogen breakthrough threshold concentration and/or an alkene breakthrough threshold concentration is exceeded, the amount from the alkane feed stream 634 added to the tail gas stream 630 may be reduced or stopped, and the amount from the methane feed

stream 638 added to the tail gas stream 630 may be increased to compensate for said reduction or stoppage of flow from the alkane feed stream 634.

5 [0087] While the alkane feed stream 634 from a hydrogenation reactor 670, the ethylene feed stream 636, and the methane feed stream 638 (or, more generally, an alkane feed stream from a source other than the hydrogenation reactor 670) are illustrated as being separately introduced to the tail gas stream 630, any combination of the streams may be premixed before introduction to the tail gas stream 630.

10 [0088] Further, between the scrubber 628 and the heat exchanger 620, other processes (not illustrated) may be performed on the tail gas stream 630. For example, the tail gas stream 630 may have at least a portion of the carbon dioxide removed.

[0089] Referring again to the separator 622, the bottoms stream 626 from the separator 622 and the bottoms stream 632 from the scrubber 628 can be combined and fed to a crude tank 642. Generally, the stream(s) coming into the crude tank 642 are depressurized to a pressure of 0.1 Mpa to 0.15 Mpa. In depressurizing the incoming stream, the ethylene, carbon dioxide, inert gases (e.g.,
15 nitrogen and/or argon), and acetic acid flash to produce a flash gas stream 644. The bottoms of the crude tank 642 primarily comprise vinyl acetate, water, and acetic acid with some ethyl acetate byproduct. The bottoms are transported as a vinyl acetate stream 646 to be purified by various processes 648 to produce the purified vinyl acetate product stream 650. Examples of purification processes 648 include, but are not limited to, azeotrope distillation, water stripping, distillation,
20 phase separations, and the like, and any combination thereof. Examples of different processing methods and systems are described in U.S. Pat. Nos. 6,410,817, 8,993,796, and 9,045,413 and US Patent App. Pub. No. 2014/0066649, each of which is incorporated herein by reference.

[0090] Further, the purification processes 648 may produce additional streams that individually or in any combination can be recycled back to the vaporizer 606, the tail gas stream 630, the flash
25 gas stream 644, and/or other streams within the process 600.

[0091] Optionally (not shown), a portion of the tail gas slip stream 630 may be combined with (e.g., mixed with or entrained with) the flash gas stream 644.

[0092] At least a portion of the carbon dioxide in the flash gas stream 644 (optionally having been combined with a portion of the tail gas slip stream 630) may be removed before recycling
30 back into the vaporizer 606. As illustrated, the flash gas stream 644 first passes through a CO₂ scrubber 652 and then a CO₂ absorber 656 to produce a CO₂ depleted overheads stream 658. Between the CO₂ scrubber 652 and the CO₂ absorber 656, ethylene can be added to the flash gas stream 644 (or as illustrated to a slip stream 662 thereof) from ethylene stream 654.

[0093] The CO₂ depleted overheads stream 658 can then be passed through a heat exchanger 660 and fed into the vaporizer 606. Further, a slip stream 662 from the flash gas stream 644 and/or the CO₂ depleted overheads stream 658 may be used to purge nitrogen and argon from the system. This slip stream 662 can be sent through an ethylene recovery process 664. The ethylene recovery process 660 produces an ethylene vent stream 666 and a recycle stream 668.

[0094] Examples of ethylene recovery processes 664 can include, but are not limited to, scrubbing systems, membrane recovery processes, and the like, and any combination thereof.

[0095] The ethylene recovery processes 664 can produce a vent stream 666 and additional stream(s) 668 that take the ethylene recovered to other processes or for recycling back into the vinyl acetate vaporizer 606.

[0096] While FIG. 6 illustrates the vinyl acetate production process 600 in general, one skilled in the art would recognize how to adapt the teachings of the present disclosure to other vinyl acetate production processes that may vary from the illustrated process 600. Examples of different vinyl acetate production processes and systems are described in U.S. Pat. Nos. 6,410,817; 8,993,796; and 9,045,413 and US Patent App. Pub. No. 2014/0066649, each of which is incorporated herein by reference.

[0097] Unless otherwise indicated, all numbers expressing quantities of ingredients, properties (e.g., molecular weight), reaction conditions, and the like used in the present disclosure and associated claims are to be understood as being modified in all instances by the term “about.” At the very least, and not as an attempt to limit the application of the doctrine of equivalents to the scope of the claim, the term “about” relative to each numerical parameter should at least be construed in light of the number of reported significant digits and by applying ordinary rounding techniques.

[0098] A concentration range listed or described as being useful, suitable, or the like, is intended that any and every concentration within the range, including the end points, is to be considered as having been stated. For example, a range “from 1 to 10” or “of 1 to 10” is to be read as indicating each and every possible number along the continuum between about 1 and about 10. Thus, even if specific data points within the range, or even no data points within the range, are explicitly identified or refer to only a few specific data points, it is to be understood that inventors appreciate and understand that any and all data points within the range are to be considered to have been specified, and that inventors possessed knowledge of the entire range and all points within the range.

[0099] The term “and/or” refers to both the inclusive “and” case and the exclusive “or” case, and is used herein for brevity. For example, a mixture comprising acetic acid and/or methyl acetate may comprise acetic acid alone, methyl acetate alone, or both acetic acid and methyl acetate.

[0100] A listing following “one or more of” or “at least one of” using “and” to connect the listing is intended in the alternative or conjunctive rather than the disjunctive. For example, “at least one of: A, B, and C” and “one or more of: A, B, and C” are each considered to disclose embodiments of A alone, B alone, C alone, A and B in combination, A and C in combination, B and C in combination, and all three of A, B, and C in combination.

[0101] Room temperature is 25°C, and atmospheric pressure is 101.325 kPa unless otherwise noted.

[0102] While compositions, systems, and methods are described herein in terms of “comprising” various components or steps, the compositions, systems, and methods can also “consist essentially of” or “consist of” the various components and steps.

[0103] Illustrative embodiments of the invention are described herein. In the interest of clarity, not all features of an actual implementation are described in this specification. It will of course be appreciated that in the development of any such actual embodiment, numerous implementation-specific decisions must be made to achieve the developer’s specific goals, such as compliance with system-related and business-related constraints, which will vary from one implementation to another. Moreover, it will be appreciated that such a development effort might be complex and time-consuming, but would nevertheless be a routine undertaking for those of ordinary skill in the art having the benefit of this disclosure.

[0104] Example Embodiments

[0105] Embodiment 1. A method of producing vinyl acetate, the method comprising: reacting via a hydrogenation reaction one or more alkenes and hydrogen in the presence of a hydrogenation catalyst to produce one or more alkanes; and reacting via an acetoxylation reaction acetic acid, ethylene, and oxygen in the presence of an acetoxylation catalyst and an alkane diluent to produce vinyl acetate and water, wherein the alkane diluent comprises the one or more alkanes from the hydrogenation reaction.

[0106] Embodiment 2. The method of Embodiment 1, wherein the alkane diluent further comprises methane.

[0107] Embodiment 3. The method of Embodiment 2, wherein the methane is present in the alkane diluent at 0.1 mol% to 5 mol% based on the total moles of the alkane diluent.

[0108] Embodiment 4. The method of any of Embodiments 1-3, wherein the one or more alkenes comprises one or more of ethylene, propylene, and butylene.

[0109] Embodiment 5. The method of Embodiment 4, wherein the alkane diluent comprises ethane, propane, and optionally methane, wherein at least a portion of the ethane and propane are from the hydrogenation reaction, and wherein the ethane is present in the alkane diluent at 0.1 mol% to 99.9 mol% based on the total moles of the alkane diluent, the propane is present in the
5 alkane diluent at 0.1 mol% to 99.9 mol% based on the total moles of the alkane diluent, and the methane is present in the alkane diluent at 0 mol% to 5 mol% based on the total moles of the alkane diluent.

[0110] Embodiment 6. The method of Embodiment 4 or 5, wherein the alkane diluent comprises ethane, propane, and optionally methane, wherein at least a portion of the ethane and
10 propane are from the hydrogenation reaction, and wherein the ethane is present in the alkane diluent at 0.1 mol% to 50 mol% based on the total moles of the alkane diluent, the propane is present in the alkane diluent at 50 mol% to 99.9 mol% based on the total moles of the alkane diluent, and the methane is present in the alkane diluent at 0 mol% to 5 mol% based on the total moles of the alkane diluent.

15 [0111] Embodiment 7. The method of any of Embodiments 1-6, wherein the alkane diluent comprises a tail gas from a natural gas enrichment process.

[0112] Embodiment 8. The method of any of Embodiments 1-7, further comprising:
performing the hydrogenation reaction in a hydrogenation reactor; introducing a hydrogen stream to the hydrogenation reactor; and treating the hydrogen stream before introduction to the
20 hydrogenation reactor to reduce a concentration of carbon monoxide from the hydrogen stream.

[0113] Embodiment 9. The method of any of Embodiments 1-8, wherein the acetoxylation reaction produces a crude vinyl acetate stream; wherein the crude vinyl acetate stream further comprises unreacted ethylene; and wherein the method further comprises: processing the crude vinyl acetate stream to recover at least a portion of the unreacted ethylene and at least a portion of
25 the alkane diluent in an ethylene recovery stream; and recycling the ethylene recovery stream to the acetoxylation reaction.

[0114] Embodiment 10. The method of any of Embodiments 1-9, wherein the hydrogenation reaction produces a product stream comprising the one or more alkanes and optionally hydrogen, and wherein the method further comprises: monitoring a hydrogen concentration in the product
30 stream from a hydrogenation reactor; and reducing an amount of the one or more alkanes from the hydrogenation reactor in the alkane diluent and adding methane to the alkane diluent when the hydrogen concentration in the product stream from the hydrogenation reactor is greater than 1 mol% based on a total number of moles present in the product stream.

- [0115] Embodiment 11. A method of producing vinyl acetate, the method comprising: reacting a feed stream comprising acetic acid, ethylene, oxygen, and alkane diluent in a vinyl acetate reactor to produce a crude vinyl acetate stream comprising vinyl acetate, water, and the alkane diluent; cooling the crude vinyl acetate stream in a heat exchanger; separating the crude vinyl acetate stream into a first tail gas stream, a flash gas stream and a vinyl acetate stream, wherein the first tail gas stream comprises ethylene and the alkane diluent, wherein the flash gas stream comprises ethylene, carbon dioxide, and the alkane diluent, and wherein the vinyl acetate stream comprises vinyl acetate; adding a second tail gas stream from a natural gas enrichment system to the first tail gas stream, wherein the one or more alkanes become part of the alkane diluent; removing at least a portion of the carbon dioxide from the flash gas stream to produce one or more recycle streams comprising ethylene and the alkane diluent; mixing vaporized acetic acid with the first tail gas stream and at least one of the one or more recycle streams in a vaporizer to produce a vaporized stream; and adding oxygen to the vaporized stream to produce the feed stream.
- [0116] Embodiment 12. A method of producing vinyl acetate, the method comprising: reacting a feed stream comprising acetic acid, ethylene, oxygen, and alkane diluent in a vinyl acetate reactor to produce a crude vinyl acetate stream comprising vinyl acetate, water, and the alkane diluent; cooling the crude vinyl acetate stream in a heat exchanger; separating the crude vinyl acetate stream into a tail gas stream, a flash gas stream and a vinyl acetate stream, wherein the tail gas stream comprises ethylene and the alkane diluent, wherein the flash gas stream comprises ethylene, carbon dioxide, and the alkane diluent, and wherein the vinyl acetate stream comprises vinyl acetate; reacting via a hydrogenation reaction one or more alkenes and hydrogen in a hydrogenation reactor in the presence of a hydrogenation catalyst to produce a product stream comprising one or more alkanes and optionally hydrogen; adding at least a portion of the product stream to the tail gas stream, wherein the one or more alkanes become part of the alkane diluent; monitoring a hydrogen concentration in the alkane feed stream, wherein when the hydrogen concentration is greater than 1 mol% based on a total number of moles present in the product stream performing one or both of: (a) reducing an amount of the product stream from the hydrogenation reactor added to the tail gas stream; and (b) adding a methane feed stream to the tail gas stream to become part of the alkane diluent; removing at least a portion of the carbon dioxide from the flash gas stream to produce one or more recycle streams comprising ethylene and the alkane diluent; mixing vaporized acetic acid with the tail gas stream and at least one of the one or more recycle streams in a vaporizer to produce a vaporized stream; and adding oxygen to the vaporized stream to produce the feed stream.

- [0117] Embodiment 13. The method of Embodiment 12, wherein the tail gas stream is a first tail gas stream, and the method further comprising: adding a second tail gas stream from a natural gas enrichment system to the first tail gas stream, wherein the one or more alkanes become part of the alkane diluent.
- 5 [0118] Embodiment 14. The method of any of Embodiments 12-13, wherein the alkane diluent of the feed stream comprises methane at 0.1 mol% to 5 mol% based on the total moles of the alkane diluent.
- [0119] Embodiment 15. The method of any of Embodiments 12-14, wherein the alkane diluent of the feed stream comprises methane at 0 mol% to 0.1 mol% based on the total moles of
- 10 the alkane diluent.
- [0120] Embodiment 16. The method of any of Embodiments 12-15, wherein the one or more alkenes comprises one or more of ethylene, propylene, and butylene.
- [0121] Embodiment 17. The method of Embodiment 16, wherein the alkane diluent of the feed stream comprises ethane, propane, and optionally methane, wherein at least a portion of the
- 15 ethane and the propane are from the hydrogenation reaction, and wherein the ethane is present in the alkane diluent of the feed stream at 0.1 mol% to 99.9 mol% based on the total moles of the alkane diluent, the propane is present in the alkane diluent of the feed stream at 0.1 mol% to 99.9 mol% based on the total moles of the alkane diluent, and the methane is present in the alkane diluent of the feed stream at 0 mol% to 5 mol% based on the total moles of the alkane diluent.
- 20 [0122] Embodiment 18. The method of Embodiment 16 or 17, wherein the alkane diluent of the feed stream comprises ethane, propane, and optionally methane, wherein at least a portion of the ethane and the propane are from the hydrogenation reaction, and wherein the ethane is present in the alkane diluent of the feed stream at 0.1 mol% to 50 mol% based on the total moles of the alkane diluent, the propane is present in the alkane diluent of the feed stream at 50 mol% to 99.9
- 25 mol% based on the total moles of the alkane diluent, and the methane is present in the alkane diluent of the feed stream at 0 mol% to 5 mol% based on the total moles of the alkane diluent.
- [0123] Embodiment 19. A method of producing vinyl acetate, the method comprising: (i) producing one or more alkanes via a hydrogenation reaction and/or (ii) performing a natural gas enrichment process to produce an enriched natural gas and a tail gas; and producing vinyl acetate
- 30 via an acetoxylation reaction of acetic acid, ethylene, and oxygen performed in the presence of an alkane diluent comprising (i) the one or more alkanes from the hydrogenation reaction and/or (ii) the tail gas.
- [0124] Embodiment 20. The method of Embodiment 19, wherein the alkane diluent comprises ethane, propane, and optionally methane, wherein at least a portion of the ethane and the

propane are from the hydrogenation reaction and/or the tail gas, and wherein the ethane is present in the alkane diluent at 0.1 mol% to 99.9 mol% based on the total moles of the alkane diluent, the propane is present in the alkane diluent at 0.1 mol% to 99.9 mol% based on the total moles of the alkane diluent, and the methane is present in the alkane diluent at 0 mol% to 5 mol% based on the total moles of the alkane diluent.

[0125] Hereinafter, the present invention will be better understood in view of the following non-limiting example.

[0126] Examples

[0127] A hydrogenation reaction was performed in a lab-scale reactor with a hydrogenation catalyst from the ACTISORB® O series, available from Clariant, with a feed of about 1 mol% H₂ balance C₂H₄, at variety of temperatures from below 0°C up to about 80°C, and at a pressure of about 2.8 MPa. 100% hydrogen consumption was observed across the temperatures tested.

[0128] A hydrogenation reaction was performed in a pilot plant reactor with a hydrogenation catalyst from the ACTISORB® O series, available from Clariant, with a feed of up to about 4 mol% H₂ balance C₂H₄, at a temperature of about 250°C, and at a pressure of about 2.8 MPa. 100% hydrogen consumption was observed. The hydrogenation product was then used as at least a portion of the alkane diluent in a vinyl acetate production process with up to about 10 mol% oxygen in the reaction feed to the vinyl acetate reactor.

WHAT IS CLAIMED IS:

1. A method of producing vinyl acetate, the method comprising:
reacting via a hydrogenation reaction one or more alkenes and hydrogen in the presence of a hydrogenation catalyst to produce one or more alkanes; and
reacting via an acetoxylation reaction acetic acid, ethylene, and oxygen in the presence of an acetoxylation catalyst and an alkane diluent to produce vinyl acetate and water, wherein the alkane diluent comprises the one or more alkanes from the hydrogenation reaction.
2. The method of claim 1, wherein the alkane diluent further comprises methane.
3. The method of claim 2, wherein the methane is present in the alkane diluent at 0.1 mol% to 5 mol% based on total moles of the alkane diluent.
4. The method of claim 1, wherein the one or more alkenes comprises one or more of ethylene, propylene, and butylene.
5. The method of claim 4, wherein the alkane diluent comprises ethane, propane, and optionally methane, wherein at least a portion of the ethane and propane are from the hydrogenation reaction, and wherein the ethane is present in the alkane diluent at 0.1 mol% to 99.9 mol% based on total moles of the alkane diluent, the propane is present in the alkane diluent at 0.1 mol% to 99.9 mol% based on the total moles of the alkane diluent, and the methane is present in the alkane diluent at 0 mol% to 5 mol% based on the total moles of the alkane diluent.
6. The method of claim 4, wherein the alkane diluent comprises ethane, propane, and optionally methane, wherein at least a portion of the ethane and propane are from the hydrogenation reaction, and wherein the ethane is present in the alkane diluent at 0.1 mol% to 50 mol% based on the total moles of the alkane diluent, the propane is present in the alkane diluent at 50 mol% to 99.9 mol% based on the total moles of the alkane diluent, and the methane is present in the alkane diluent at 0 mol% to 5 mol% based on the total moles of the alkane diluent.

7. The method of claim 1, wherein the alkane diluent comprises a tail gas from a natural gas enrichment process.

8. The method of claim 1, further comprising:
5 performing the hydrogenation reaction in a hydrogenation reactor;
introducing a hydrogen stream to the hydrogenation reactor; and
treating the hydrogen stream before introduction to the hydrogenation reactor to reduce a concentration of carbon monoxide from the hydrogen stream.

10 9. The method of claim 1, wherein the acetoxylation reaction produces a crude vinyl acetate stream; wherein the crude vinyl acetate stream further comprises unreacted ethylene; and wherein the method further comprises:
processing the crude vinyl acetate stream to recover at least a portion of the unreacted ethylene and at least a portion of the alkane diluent in an ethylene recovery stream; and
15 recycling the ethylene recovery stream to the acetoxylation reaction.

10. The method of claim 1, wherein the hydrogenation reaction produces a product stream comprising the one or more alkanes and optionally hydrogen, and wherein the method further comprises:
20 monitoring a hydrogen concentration in the product stream from the hydrogenation reaction;
and
reducing an amount of the one or more alkanes from the hydrogenation reaction in the alkane diluent and adding methane to the alkane diluent when the hydrogen concentration in the product stream from the hydrogenation reactor is greater than 1 mol% based on a total number of moles
25 present in the product stream.

11. A method of producing vinyl acetate, the method comprising:
reacting a feed stream comprising acetic acid, ethylene, oxygen, and alkane diluent in a vinyl acetate reactor to produce a crude vinyl acetate stream comprising vinyl acetate, water, and the alkane
30 diluent;
cooling the crude vinyl acetate stream in a heat exchanger;

separating the crude vinyl acetate stream into a first tail gas stream, a flash gas stream and a vinyl acetate stream, wherein the first tail gas stream comprises ethylene and the alkane diluent, wherein the flash gas stream comprises ethylene, carbon dioxide, and the alkane diluent, and wherein the vinyl acetate stream comprises vinyl acetate;

5 adding a second tail gas stream from a natural gas enrichment system to the first tail gas stream, wherein the one or more alkanes become part of the alkane diluent;

removing at least a portion of the carbon dioxide from the flash gas stream to produce one or more recycle streams comprising ethylene and the alkane diluent;

10 mixing vaporized acetic acid with the first tail gas stream and at least one of the one or more recycle streams in a vaporizer to produce a vaporized stream; and

adding oxygen to the vaporized stream to produce the feed stream.

12. A method of producing vinyl acetate, the method comprising:

15 reacting a feed stream comprising acetic acid, ethylene, oxygen, and alkane diluent in a vinyl acetate reactor to produce a crude vinyl acetate stream comprising vinyl acetate, water, and the alkane diluent;

cooling the crude vinyl acetate stream in a heat exchanger;

20 separating the crude vinyl acetate stream into a tail gas stream, a flash gas stream and a vinyl acetate stream, wherein the tail gas stream comprises ethylene and the alkane diluent, wherein the flash gas stream comprises ethylene, carbon dioxide, and the alkane diluent, and wherein the vinyl acetate stream comprises vinyl acetate;

reacting via a hydrogenation reaction one or more alkenes and hydrogen in a hydrogenation reactor in the presence of a hydrogenation catalyst to produce a product stream comprising one or more alkanes and optionally hydrogen;

25 adding at least a portion of the product stream to the tail gas stream, wherein the one or more alkanes become part of the alkane diluent;

monitoring a hydrogen concentration in the product stream, wherein when the hydrogen concentration is greater than 1 mol% based on a total number of moles present in the product stream performing one or both of:

30 (a) reducing an amount of the product stream from the hydrogenation reactor added to the tail gas stream; and

(b) adding a methane feed stream to the tail gas stream to become part of the alkane diluent;

removing at least a portion of the carbon dioxide from the flash gas stream to produce one or more recycle streams comprising ethylene and the alkane diluent;

- 5 mixing vaporized acetic acid with the tail gas stream and at least one of the one or more recycle streams in a vaporizer to produce a vaporized stream; and
 adding oxygen to the vaporized stream to produce the feed stream.

13. The method of claim 12, wherein the tail gas stream is a first tail gas stream, and the
10 method further comprising:

 adding a second tail gas stream from a natural gas enrichment system to the first tail gas stream, wherein the one or more alkanes become part of the alkane diluent.

14. The method of claim 12, wherein the alkane diluent of the feed stream comprises
15 methane at 0.1 mol% to 5 mol% based on total moles of the alkane diluent.

15. The method of claim 12, wherein the alkane diluent of the feed stream comprises methane at 0 mol% to 0.1 mol% based on total moles of the alkane diluent.

20 16. The method of claim 12, wherein the one or more alkenes comprises one or more of ethylene, propylene, and butylene.

17. The method of claim 16, wherein the alkane diluent of the feed stream comprises ethane, propane, and optionally methane, wherein at least a portion of the ethane and the propane are
25 from the hydrogenation reaction, and wherein the ethane is present in the alkane diluent of the feed stream at 0.1 mol% to 99.9 mol% based on total moles of the alkane diluent, the propane is present in the alkane diluent of the feed stream at 0.1 mol% to 99.9 mol% based on the total moles of the alkane diluent, and the methane is present in the alkane diluent of the feed stream at 0 mol% to 5 mol% based on the total moles of the alkane diluent.

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18. The method of claim 16, wherein the alkane diluent of the feed stream comprises ethane, propane, and optionally methane, wherein at least a portion of the ethane and the propane are

from the hydrogenation reaction, and wherein the ethane is present in the alkane diluent of the feed stream at 0.1 mol% to 50 mol% based on total moles of the alkane diluent, the propane is present in the alkane diluent of the feed stream at 50 mol% to 99.9 mol% based on the total moles of the alkane diluent, and the methane is present in the alkane diluent of the feed stream at 0 mol% to 5 mol% based on the total moles of the alkane diluent.

19. A method of producing vinyl acetate, the method comprising:

(i) producing one or more alkanes via a hydrogenation reaction and/or (ii) performing a natural gas enrichment process to produce an enriched natural gas and a tail gas; and
10 producing vinyl acetate via an acetoxylation reaction of acetic acid, ethylene, and oxygen performed in the presence of an alkane diluent comprising (i) the one or more alkanes from the hydrogenation reaction and/or (ii) the tail gas.

20. The method of claim 19, wherein the alkane diluent comprises ethane, propane, and
15 optionally methane, wherein at least a portion of the ethane and the propane are from the hydrogenation reaction and/or the tail gas, and wherein the ethane is present in the alkane diluent at 0.1 mol% to 99.9 mol% based on total moles of the alkane diluent, the propane is present in the alkane diluent at 0.1 mol% to 99.9 mol% based on the total moles of the alkane diluent, and the methane is present in the alkane diluent at 0 mol% to 5 mol% based on the total moles of the alkane diluent.

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