(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
22 May 2020 (22.05.2020)

WIPO | PCT

(10) International Publication Number
WO 2020/099430 A1

(51) International Patent Classification:
B01J 23/02 (2006.01) *B01J 38/52* (2006.01)
B01J 27/18 (2006.01) *B01J 38/62* (2006.01)
B01J 27/28 (2006.01)

(21) International Application Number:
PCT/EP2019/081065

(22) International Filing Date:
12 November 2019 (12.11.2019)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
62/767022 14 November 2018 (14.11.2018) US

(71) Applicant *(for all designated States except US)*: **SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V.** [NL/NL]; Carel van Bylandtlaan 30, 2596 HR THE HAGUE (NL).

(71) Applicant *(for US only)*: **SHELL OIL COMPANY** [US/US]; 150 N. Dairy Ashford, HOUSTON, TX 77079 (US).

(72) Inventors: **BISHOPP, Simon, David**; Grasweg 31, 1031 HW Amsterdam (NL). **LANGE, Jean Paul, Andre, Marie, Joseph, Ghislain**; Grasweg 31, 1031 HW AMSTERDAM (NL). **VEERMAN, Johannes, Michael, Maria**; Grasweg 31, 1031 HW Amsterdam (NL).

(74) Agent: **SHELL LEGAL SERVICES IP**; PO Box 384, 2501 CJ THE HAGUE (NL).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:
— *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*

Published:
— *with international search report (Art. 21(3))*

WO 2020/099430 A1

(54) **Title:** REGENERATION OF CATALYST FOR LACTIC ACID DEHYDRATION

(57) **Abstract:** The invention provides a process for regenerating a dehydration catalyst, the process comprises contacting a regeneration agent with the dehydration catalyst under conditions to provide a density of the regeneration agent that ranges from about 10 to about 500 kg/m^3, wherein the regeneration agent is at least one of water, methanol, ethanol, acetone, C3 to C8 linear and branched alcohols, C3 to C8 esters, C3 to C8 ethers, or mixtures thereof.

REGENERATION OF CATALYST FOR LACTIC ACID DEHYDRATION

CROSS REFERENCE TO RELATED APPLICATIONS

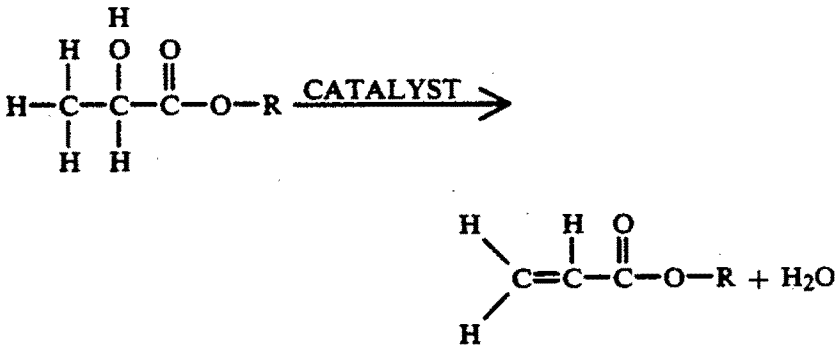
The present application claims the benefit of pending U.S. Provisional Patent Application Serial No. 62/767,022, filed on 14 November 2018, the entire disclosure of which is hereby incorporated by reference.

FIELD OF THE INVENTION

The present invention generally relates to a process of regenerating a catalyst, particularly a dehydration catalyst for producing alkyl esters of acrylic acid from alkyl esters of lactic acid.

BACKGROUND OF THE INVENTION

The production of alkyl esters of acrylic acid from alkyl esters of lactic acid involves the removal of a hydroxyl group from an alpha carbon atom and a hydrogen atom from the adjacent beta carbon atom (forming a water molecule), i.e. a dehydration reaction. The general reaction is indicated by the equation below:



The selection of a catalyst is important because conversion levels, reaction rates, selectivity and catalyst life can each profoundly affect the process economics in terms of plant/equipment costs, as well as related operating costs and raw material consumption.

Alkyl esters of lactic acid, such as methyl lactate, have many uses such as a solvent, a starting material for the manufacture of polylactic acid, or a starting material for numerous other reactions. For example, alkyl esters of lactic acid can be used as an intermediate in lactic acid purification, and as building block in the synthesis of chiral components, e.g., pesticides, and as a starting material for lactide manufacture.

Alkyl esters of lactic acid are also used in the manufacture of alkyl esters of acrylic acid, such as methyl acrylate, which is a starting material for the manufacture of acrylate polymers. Additionally, alkyl esters of acrylic acid are a suitable starting material for acrylic acid and other esters like ethyl acrylate and butyl acrylate.

Acrylic acid, acrylic acid derivatives, or mixtures thereof have a variety of industrial uses, typically in the form of polymers. In turn, these polymers are commonly used in the manufacture of, among other things, adhesives, binders, coatings, paints, polishes, detergents, flocculants, dispersants, thixotropic agents, sequestrants, and superabsorbent polymers (SAP), which are used in disposable absorbent articles, including diapers and hygienic products, for example. Acrylic acid has been commonly made from fossil resources. For example, acrylic acid has long been prepared by catalytic oxidation of propylene. These and other methods of making acrylic acid from fossil sources are described in the Kirk-Othmer Encyclopedia of Chemical Technology, Vol. 1, pgs. 342-369 (5th Ed., John Wiley & Sons, Inc., 2004). Fossil-derived acrylic acid contributes to greenhouse emissions due to its high fossil-derived carbon content. As fossil resources become scarce, more expensive, and subject to regulations for CO_2 emissions, there exists a growing need for bio-based acrylic acid, acrylic acid derivatives, or mixtures thereof that can serve as an alternative to fossil-derived acrylic acid, acrylic acid derivatives, or mixtures thereof.

Known processes for producing of alkyl esters of acrylic acid start with alkyl esters of lactic acid which are subjected to a dehydration reaction in the presence of a catalyst to form alkyl esters of acrylic acid. The process is typically carried out in the gas phase in the presence of excess steam. The reaction temperature is, e.g., 300-500°C. Reaction pressure is, e.g., in the range of 0.5-3 bar, and suitably atmospheric. An inert gas and/or steam may be added to reduce the partial pressure by dilution. Suitable catalysts include dehydration catalysts known in the art.

Prior art techniques describe the use of certain catalysts to promote the direct dehydration from the lactate ester. For example, U.S. Pat. No. 2,859,240 to Holmen disclose a number of catalysts useful in a process conducted at between 250° C to 550° C to produce the acrylate.

Other processes for converting alkyl lactates to alkyl acrylates, such as that disclosed in U.S. Pat. No. 9,422,222 to Godlewski comprise the following steps: a) providing an aqueous solution comprising lactic acid derivatives; b) combining the aqueous solution with an inert gas to form an aqueous solution/gas blend; c) evaporating the aqueous solution/gas blend to

produce a gaseous mixture; and d) dehydrating the gaseous mixture by contacting the mixture with any dehydration catalyst.

Existing processes primarily conduct the dehydration under low pressure (sub atmospheric partial pressure due to dilution) gas phase using alcohol or water. Gas-phase dehydration reaction is generally accompanied by the deposition and subsequent coking of high-boiling by products on the catalyst surface. This coking deactivates the catalyst within a few hours and more frequent decoking may be required, which may necessitate the need for multiple parallel reactors as one is in regeneration, one in operation.

It is therefore an object of the present invention to provide a method for regenerating the catalyst, which avoid the disadvantages of prior art methods.

SUMMARY OF THE INVENTION

The invention provides, in one embodiment, a process for regenerating a dehydration catalyst used to produce a mixture comprising acrylic acid or derivatives thereof. The process includes the steps of: (a) contacting a mixture of lactic acid or derivatives thereof with a dehydration catalyst in a reactor to produce the mixture comprising acrylic acid or derivatives thereof at a first operating condition which provides a gas phase reaction; (b) contacting a regeneration agent with the dehydration catalyst; and (c) changing the first operating condition to a second operating condition, to provide a density of the regeneration agent that ranges from about 10 to about 500 kg/m3.

In another embodiment, the invention provides a process for regenerating a dehydration catalyst, the process comprises contacting a regeneration agent with the dehydration catalyst under conditions to provide a density of the regeneration agent that ranges from about 10 to about 500 kg/m3, wherein the regeneration agent is at least one of water, methanol, ethanol, acetone, C3 to C8 linear and branched alcohols, C3 to C8 esters, C3 to C8 ethers, or mixtures thereof.

DETAILED DESCRIPTION OF THE INVENTION

The present invention is directed to a process for regenerating a dehydration catalyst. More preferably, the present invention is directed to a method for regenerating a catalyst used in the manufacture of alkyl esters of acrylic acid from alkyl esters of lactic acid, for example, manufacturing methyl acrylate from methyl lactate.

All combinations of method or process steps as used herein can be performed in any order, unless otherwise specified or clearly implied to the contrary by the context in which the referenced combination is made. The methods described and claimed herein can comprise, consist of, or consist essentially of the essential elements and limitations of the disclosed methods, as well as any additional or optional ingredients, components, or limitations described herein or otherwise useful in the process.

Embodiments of the present invention include a method of regenerating a catalyst used in the method of making alkyl esters of acrylic acid by contacting alkyl esters of lactic acid with a dehydration catalyst. In some embodiments, the alkyl esters of acrylic acid may also include acrylic acid, acrylic acid derivatives, or mixtures thereof. In some embodiments, the alkyl esters of lactic acid may also include lactic acid, lactic acid derivatives, or mixtures thereof.

Non-limiting examples of alkyl esters of lactic acid are methyl lactate, ethyl lactate, butyl lactate, 2-ethylhexyl lactate, or mixtures thereof. A non-limiting example of dimers of lactic acid is cyclic dilactide. Lactic acid can be L-lactic acid, D-lactic acid, or mixtures thereof. Lactic acid derivatives can be lactic acid oligomers, cyclic dimers of lactic acid, lactic acid anhydride, 2-alkoxypropoanoic acids or their alkyl esters, 2-aryloxypropanoic acids or their alkyl esters, 2-acyloxypropanoic acids or their alkyl esters, or a mixture thereof. Non-limiting examples of metal salts of lactic acid are sodium lactate, potassium lactate, and calcium lactate. Non-limiting examples of 2-alkoxypropoanoic acids are 2-methoxypropanoic acid and 2-ethoxypropanoic acid. A non-limiting example of 2-aryloxypropanoic acid is 2-phenoxypropanoic acid. A non-limiting example of 2-acyloxypropanoic acid is 2-acetoxypropanoic acid.

In some embodiments, the alkyl esters of lactic acid originate from converting a renewable feedstock into the alkyl ester of lactic acid. In still other embodiments, the renewable feedstock may be from at least one of a sugar source selected from at least one of sucrose, glucose, xylose or fructose, and their isomers. In still other embodiments, the renewable feedstock may be from at least one of a sugar source selected from at least one of dimeric and oligomeric sugars such cellobiose, starch, cellulose, hemicellulose, pectin, etc. In some embodiments, the sugars source may be a triose source such as dihydroxyacetone and dihydroxypropanal.

Non-limiting examples of alkyl esters of acrylic acid are methyl acrylate, ethyl acrylate, butyl acrylate, 2-ethylhexyl acrylate, or mixtures thereof. Acrylic acid derivatives can be metal

or ammonium salts of acrylic acid, acrylic acid oligomers, or mixtures thereof. Non-limiting examples of metal salts of acrylic acid are sodium acrylate, potassium acrylate, and calcium acrylate.

Embodiments of the present invention provide a feed stream comprising alkyl esters of lactic acid in a liquid stream. The liquid stream can include the alkyl esters of lactic acid and a reaction solvent (diluent). Non-limiting examples of the reaction solvent include water, methanol, ethanol, acetone, C_3 to C_8 linear and branched alcohols, C_3 to C_8 esters (e.g. ethyl acetate, methyl propionate), ethers (including dimethyl ether, diethyl ether, diphenyl ether), and mixtures thereof. In some embodiments, the reaction solvent may have an atmospheric boiling point below 300°C, below 250°C, or below 200°C and an atmospheric boiling point above 50°C, above 100°C, or above 150°C. In some embodiments, the reaction solvent may have a high solvency for methyl lactate at 150°C, 100°C, 50°C, 25°C, while remaining in the liquid phase. In one embodiment of the present invention, the reaction solvent comprises methanol. In some embodiments, high solvency may refer to the reaction solvent being able to dissolve >5 w%, >10 w%, >20 w%, >30 w% of methyl lactate.

In one embodiment of the present invention, the liquid stream includes between about 2 wt % to about 95 wt % alkyl esters of lactic acid based on the total weight of the liquid stream. In another embodiment of the present invention, the liquid stream includes between about 5 wt % to about 50 wt % alkyl esters of lactic acid, based on the total weight of the liquid stream. In yet another embodiment of the present invention, the liquid stream includes between about 10 wt % to about 25 wt % alkyl esters of lactic acid, based on the total weight of the liquid stream. In even yet another embodiment of the present invention, the liquid stream includes about 20 wt % alkyl esters of lactic acid, based on the total weight of the liquid stream.

In one embodiment of the present invention, the liquid stream comprises a solution of alkyl esters of lactic acid. In some embodiments, the liquid stream includes greater than 5 wt%, greater than 10wt%, greater than 15wt% and greater than 20wt% alkyl esters of lactic acid, based on the total weight of the liquid stream. In some embodiments, the liquid stream includes less than 95 wt%, less than 75 wt%, less than 50 wt% or less than 25 wt% alkyl esters of lactic acid, based on the total weight of the liquid stream.

In some embodiments, suitable dehydration catalysts include catalysts known in the art. In some embodiments, the catalyst may be an oxide or mixed oxide having amphoteric or mildly basic properties. In some embodiments, the mixed oxides may include an acidic oxide from Groups 13-16 (e.g. oxide of Al, Si, P, S), oxides from Groups 1-3 (e.g. oxide of K, Mg,

Ca, Sc), or mixtures. In some embodiments, the mixed oxide can be mixed throughout the bulk of the catalyst or may consist of Groups 1-3 metal oxides deposited on the surface of Groups 13-16 metal oxides. In some embodiments, the mixed oxide may be crystalline or amorphous. Crystalline mixed oxides may include crystalline alumino-silicates also called zeolites. The metal of Groups 1-3 may then be exchanged or deposited in the zeolite. Some examples include catalysts based on calcium sulphate, calcium phosphate, calcium pyrophosphate, and combinations thereof. Suitable promotors include sodium sulphate, copper sulphate, manganese sulphate, iron sulphate, magnesium sulphate, aluminium sulphate, sodium nitrate, sodium phosphate, and potassium phosphate. In other embodiments, the dehydration catalyst may be one or more of Na_2SO_4, Na_3PO_4, $NaNO_3$, Na_2SiO_3, $Na_4P_2O_7$, NaH_2PO_4, Na_2HPO_4, Na_2HAsO_4, $NaC_3H_5O_3$, NaOH, Cs_2SO_4, KOH, CsOH, and LiOH. In still other embodiments, the dehydration catalyst may be selected from one or more of ZSM-5 molecular sieves modified with aqueous alkali (such as NaOH, and Na_2CO_3) or a phosphoric acid salt (such as NaH_2PO_4, Na_2HPO_4, LiH_2PO_4, $LaPO_4$, etc.).

Other catalysts to be considered may include magnesium oxide, nickel oxide, zirconium oxide, calcium phosphates, barium phosphates, magnesium phosphate, bismuth phosphate, cobalt oxide, lithium aluminate, calcium sulfate, calcium carbonate, proprietary commercial molecular sieves, barium sulfate, strontium sulfate, lanthanum phosphate, barium fluoride, barium chloride, aluminum phosphate, zinc sulfate, calcium metasilicate, calcium zirconate, calcium titanate, calcium stannate, calcium aluminate, strontium carbonate, magnesium carbonate, calcium selenite, calcium borates and nickel sulfate, These materials were used alone, or as mixtures with others and promoters, and supported on extended surface materials such as alumina, silica gel, graphite and agents such as sodium and potassium mono and dihydrogen phosphates or organic agents such asphenothiazine.

Prior to contacting the dehydration catalyst, the feed stream is evaporated. In the evaporating step, the aqueous feed stream is heated to provide a gaseous mixture. In one embodiment, the temperature during the evaporating step is from about 165° C. to about 450° C. In another embodiment, the temperature during the evaporating step is from about 250° C. to about 375° C. In one embodiment, the gas hourly space velocity (GHSV) in the evaporating step is from about 720 h−1 to 3,600 h−1. In another embodiment, the gas hourly space velocity (GHSV) in the evaporating step is about 7,200 h−1. The evaporating step can be performed at either atmospheric pressure or higher pressure. In one embodiment, the evaporating step is performed under a pressure from about 5 bar to about 38 bar. In another embodiment, the

evaporating step is performed under a pressure from about 20 bar to about 28 bar. In yet another embodiment, the evaporating step is performed under a pressure from about 24 bar to about 26 bar. At these conditions, the density of the vapour phase for evaporated methanol ranges from 5-40 kg/m^3 (5-38 bar), from 22-35 kg/m^3 (20-28 bar), and from 30-33 kg/m3 (24-26 bar).

In one embodiment, the dehydrating operating conditions of the reactor provide a density of the feed stream of less than about 10 kg/m^3. In other embodiments, the dehydrating operating conditions of the reactor provide a density of the feed solution ranging from about 1 to about 10 kg/m^3. In still other embodiments, the dehydrating operating conditions of the reactor provide a density of the feed solution ranging from about 100 to about 300 kg/m^3. In some embodiments, the density of the feed solution during dehydration is less than 10 kg/m^3, less than 7 kg/m^3, less than 5 kg/m^3, or less than 2 kg/m^3. In other embodiments, the density of the feed solution is greater than 0.5 kg/m^3, greater than 1 kg/m^3, or greater than 0.75 kg/m^3.

In some embodiments, the feed stream may further include inert entraining agents. Non-limiting examples of the inert entraining agents are air, nitrogen, helium, argon, carbon dioxide, carbon monoxide, steam, methane and mixtures thereof. The inert entraining agents can be introduced to the reactor separately or in combination with the feed stream.

In embodiments of the present invention, the contacting of the feed stream comprising alkyl esters of lactic acid with the dehydration catalyst may be carried out in the gas phase, or at conditions below the critical pressure and critical temperature of the reaction solvent.

In one embodiment, the temperature during the dehydrating step is from about 150°C to about 500°C. In another embodiment, the temperature during the dehydrating step is from about 300°C to about 450°C. In one embodiment, the GHSV in the dehydrating step is from about 720 h−1 to about 36,000 h−1. In another embodiment, the GHSV in the dehydrating step is about 3,600 h−1. The dehydrating step can be performed at higher than atmospheric pressure. In one embodiment, the dehydrating step is performed under a pressure of at least about 5 bar. In another embodiment, the dehydrating step is performed under a pressure from about 5 bar to about 38 bar. In another embodiment, the dehydrating step is performed under a pressure from about 10 bar to about 35 bar. In yet another embodiment, the dehydrating step is performed under a pressure from about 20 bar to about 28 bar

In some embodiments of the present invention, the stream comprising alkyl esters of lactic acid contacts the dehydration catalyst at a pressure between about 5 bar and about 90 bar. In another embodiment of the present invention, the stream comprising alkyl esters of lactic acid contacts the dehydration catalyst at a pressure of about 20 bar. In some embodiments, the

pressure is greater than 5 bar, greater than 10 bar, greater than 20 bar, or greater than 30 bar and less than 200 bar, less than 150 bar, less than 100 bar, less than 80 bar, or less than 60 bar.

In some embodiments, the reaction occurs at a temperature between about 80°C and about 700°C. In another embodiment of the present invention, the contacting of the stream comprising alkyl esters of lactic acid with the dehydration catalyst is carried out at a temperature between about 100°C and about 500°C. In yet another embodiment of the present invention, the contacting of the stream comprising alkyl esters of lactic thereof with the dehydration catalyst is carried out at a temperature between about 120°C and about 400°C. In even yet another embodiment of the present invention, the contacting of the stream comprising alkyl esters of lactic acid with the dehydration catalyst is carried out at a temperature between about 180°C and about 250°C. In one embodiment of the present invention, the contacting of the stream comprising alkyl esters of lactic acid with the dehydration catalyst is carried out at a temperature of about 300°C. In some embodiments, the temperature is greater than 200, greater than 250°C, greater than 275°C, greater than 300°C, greater than 325°C or greater than 350°C and less than 500°C, less than 450°C, less than 400°C, or less than 375°C.

Due to poor evaporation of the feed at the reactor inlet, catalyst activity may be reduced. Furthermore, the concentrated substrate when in contact with the hot bed, could likely lead to decomposition reactions, e.g. polymerisation ultimately leading to coke. A reduction in catalyst activity can be improved by regenerating the catalyst and/or changing out the catalyst. Regenerating of the catalyst may be defined as restoring catalyst activity to levels greater than levels recorded prior to regeneration. Regeneration of catalyst typically occurs based on a balance between the cost of shutting down the process versus the benefit of increased yields due to increased activity via regeneration. One of ordinary skill in the art will be able to determine when regeneration should commence based on various operating conditions and costs.

In embodiments of the present invention, regeneration of the dehydration catalyst may be carried out by contacting the catalyst with a regeneration agent at high density conditions of the regeneration agent, which is defined as above the critical pressure and critical temperature of the regeneration agent.

Non-limiting examples of the regeneration agent include methanol, ethanol, acetone, C_3 to C_8 linear and branched alcohols, C_3 to C_8 esters (e.g. ethyl acetate, methyl propionate), ethers (including dimethyl ether, diethyl ether, diphenyl ether), and mixtures thereof. In some embodiments, the regeneration agent may have an atmospheric boiling point below 300°C,

below 250°C, or below 200°C and an atmospheric boiling point above 50°C, above 100°C, or above 150°C. In some embodiments, the regeneration agent may have a high solvency for methyl lactate while remaining in the liquid phase at varying temperatures, for example, 150°C, 100°C, 50°C, 25°C. In one embodiment of the present invention, the regeneration agent comprises methanol.

In some embodiments, the regeneration agent may be the same as the reaction solvent. As such, no additional components are added to the reactor prior to changing the operating conditions from the reaction conditions (gas phase) to the regeneration conditions (high density). In some embodiments, the stream comprising alkyl esters of lactic acid may continue to be fed or may be removed prior to changing the operating conditions, after changing the operating conditions or concurrently with changing the operating conditions.

In some embodiments, the regeneration agent may be different from the reaction solvent. In some embodiments, the stream comprising alkyl esters of lactic acid may continue to be fed along with the regeneration agent. In other embodiments, the stream comprising alkyl esters of lactic acid may be removed from the reactor prior to the regeneration agent being fed to the reactor. In still other embodiments, the stream comprising alkyl esters of lactic acid may be removed from the reactor after the regeneration agent has been fed to the reactor. The stream comprising alkyl esters of lactic acid may be removed from the reactor prior to, after or concurrently with the operating conditions changing from reaction conditions to regenerating conditions.

In some embodiments, the operating conditions may be changed from the reaction conditions to the regeneration conditions prior to, concurrently with or after the regeneration agent is fed to the reactor. The regeneration agent may be fed along with the stream comprising alkyl esters of lactic acid and the reaction solvent. In other embodiments, the stream comprising alkyl esters of lactic acid and the reaction solvent may be removed from the reactor during regeneration of the catalyst. In still other embodiments, the regeneration agent may be fed to the reactor after the stream comprising alkyl esters of lactic acid and the reaction solvent has been removed.

In one embodiment of the present invention, the regeneration agent contacts the dehydration catalyst at a pressure between about 5 bar and about 90 bar. In another embodiment of the present invention, the regeneration agent contacts the dehydration catalyst at a pressure of about 20 bar. In some embodiments, the pressure is greater than 5 bar, greater than 10 bar,

greater than 20 bar, or greater than 30 bar and less than 200 bar, less than 150 bar, less than 100 bar, less than 80 bar, or less than 60 bar.

In some embodiments, the regeneration occurs at a temperature between about 80°C and about 700°C. In another embodiment of the present invention, the contacting of the regeneration agent with the dehydration catalyst is carried out at a temperature between about 100°C and about 500°C. In yet another embodiment of the present invention, the contacting of the regeneration agent with the dehydration catalyst is carried out at a temperature between about 120°C and about 400°C. In even yet another embodiment of the present invention, the contacting of the regeneration agent with the dehydration catalyst is carried out at a temperature between about 180°C and about 250°C. In one embodiment of the present invention, the contacting of the regeneration agent with the dehydration catalyst is carried out at a temperature of about 300°C. In some embodiments, the temperature is greater than 200, greater than 250°C, greater than 275°C, greater than 300°C, greater than 325°C or greater than 350°C and less than 500°C, less than 450°C, less than 400°C, or less than 375°C.

Not wishing to be bound by theory, it is theorised that the high-density regeneration solvent solvates and washes off coke precursors from the surface of the substrate, thereby "restoring" the catalyst activity to levels similar to those achieved at the start of the process. Applicants have theorized, but are not bound by the theory, that by using high density solvents at elevated pressures, either at or near super critical conditions (for example, methanol CP = 240°C, 80 bar), catalyst poisons, i.e. carbon deposition, may be effectively washed off the catalyst to maintain activity and provide an improved process.

The regeneration conditions are maintained for a time sufficient to restore the activity of the catalyst substantially near the original activity. In some embodiments, the time to regenerate the catalyst may be less than 24 hours, less than 12 hours, less than 6 hours or less than 3 hours. In some embodiments, the time to regenerate the catalyst may be more than 0.5 hours, more than 1 hour or more than 2 hours. In some embodiments, the time to regenerate the catalyst may be from about 0.5 hours to about 24 hours, from about 1 hour to about 12 hours, or from about 2 hours to about 6 hours. One of ordinary skill in the art will be able to determine when regeneration should cease based on various operating conditions and costs.

The present invention is further illustrated in the following Examples.

The present invention is further illustrated in the following Examples.

Examples

Applicants investigated increasing the density of the solvent ranges to see if any

performance benefit (yield, selectivity) for the dehydration of methyl lactate in methanol was found.

A 35 ml microflow reactor unit having a packed bed of hydroxyapatite catalyst with a BET surface area of about 65m^2/g was fed a stream of reactants of about 20 wt% methyl lactate and 80 wt% methanol. The hydroxyapatite catalyst was synthesized by the method described in Ghantani et al., *Green Chem.*, 2013,15, 1211-1217. The feed line can optionally be preheated. The reactor itself has a volume of 35mL and is situated in an electrically heated furnace having three separate heating zones. Post reactor there is a condenser followed by a gas-liquid separator. The back pressure in the unit is controlled by use of a standard back pressure regulator on the off-gas line, and additionally via the liquid product sample valve.

The initial reactor pressure was 20 bar. The pressure of the reactor was raised to 90 bar, lowered to 1 bar, and then increased back to 90 bar. The density of the solvent was also increased and decreased in response to the pressure change. The density of the solvent at 20 bar was about 12 kg/m^3, at 90 bar about 55 kg/m^3 and at 1 bar about 0.62 kg/m^3. The density was conservatively calculated using the ideal gas law and adjusting for the molar mass of methanol, for the density of gases is known to increase more steeply than dictated by the ideal gas law when approaching and exceeding the critical pressure (i.e. 80 bar in the case of methanol). The highest pressure applied provided a supercritical atmosphere in the reactor. The resulting product stream included methyl acrylate (MA), methyl propanoate (MP), and 2-methoxy methyl propanoate (2-MMP). Throughout the pressure changes, the catalyst showed moderate activity, with yield to the desired product, methyl acrylate, reaching a maximum of 14%. The MA yield remained stable around 10% for some 150 hours on stream when operating at 90 bar. When the pressure is reduced to 1 bar, the yield of MA immediately drops to 10 % and further decreased to ~ 1 % within a day. However, when the pressure is increased back to 90 bar, the catalyst activity appeared to be restored based on the increase of the methyl acrylate in the product to 10% yield. The catalyst further maintained this high activity for the following 150 hours of operation until the run was interrupted.

Applicants theorize that during low pressure operation (1 bar), deposition on the catalyst may occur, thus reducing product yield. However, when the pressure was increased to 90 bar (supercritical range) it is theorized that the deposits on the catalyst may have been solubilized, thus returning the activity to the catalyst to near previous amounts shown by an increase of the MA product.

It is postulated, without wishing to be bound by theory, that by increasing the density

of the solvent in the dehydration reactor, catalyst activity may be maintained for longer periods of time thus increasing catalyst lifetime and removing the need for separate decoking steps of the catalyst.

Other and further embodiments utilizing one or more aspects of the inventions described above can be devised without departing from the spirit of Applicant's invention. The order of steps can occur in a variety of sequences unless otherwise specifically limited. The various steps described herein can be combined with other steps, interlineated with the stated steps, and/or split into multiple steps. Similarly, elements have been described functionally and can be embodied as separate components or can be combined into components having multiple functions.

While the invention is susceptible to various modifications and alternative forms, specific embodiments thereof are shown by way of examples herein described in detail. It should be understood, that the detailed description thereto are not intended to limit the invention to the particular form disclosed, but on the contrary, the intention is to cover all modifications, equivalents and alternatives falling within the spirit and scope of the present invention as defined by the appended claims.

CLAIMS

1. A process for regenerating a dehydration catalyst used to produce a mixture comprising acrylic acid or derivatives thereof, the process comprising the steps of:

a) contacting a mixture of lactic acid or derivatives thereof with a dehydration catalyst in a reactor to produce the mixture comprising acrylic acid or derivatives thereof at a first operating condition which provides a gas phase reaction;

b) contacting a regeneration agent with the dehydration catalyst;

c) changing the first operating condition to a second operating condition, to provide a density of the regeneration agent that ranges from about 10 to about 500 kg/m^3.

2. The process according to claim 1, wherein prior to the changing the first operating condition to the second operating condition, the lactic acid or derivatives thereof are removed from the reactor feed.

3. The process according to claim 1, wherein at the first operating conditions provide the feed with a density less than 10 kg/m^3.

4. The process according to claim 1, wherein the second operating condition is maintained for at least one hour.

5. The process according to claim 1, wherein the mixture of lactic acid or derivatives thereof further comprises a reaction solvent.

6. The process according to claim 5, wherein the reaction solvent is different from the regeneration agent.

7. The process according to claim 1, wherein steps (a) and (b) occur simultaneously.

8. The process according to claim 1, further comprising changing the second operating condition back to the first operating condition.

9. The process according to claim 8, further comprising removing the regeneration agent from the reactor feed.

10. The process according to claim 1, wherein the lactic acid or derivatives thereof is at least one of methyl lactate, ethyl lactate, butyl lactate, 2-ethylhexyl lactate, or mixtures thereof.

11. The process according to claims 1 to 4, wherein the regeneration agent is at least one of methanol, ethanol, acetone, C_3 to C_8 linear and branched alcohols, C_3 to C_8 esters, C_3 to C_8 ethers, or mixtures thereof.

12. The process of claim 1, wherein the dehydration catalyst is a metal oxide or mixed metal oxide.

13. The process according to claim 12, wherein the dehydration catalyst is at least one of a metal oxide from Groups 13-16, oxides from Groups 1-3, or mixtures thereof.

14. A process for regenerating a dehydration catalyst, the process comprises contacting a regeneration agent with the dehydration catalyst under conditions to provide a density of the regeneration agent that ranges from about 10 to about 500 kg/m^3, wherein the regeneration agent is at least one of methanol, ethanol, acetone, C_3 to C_8 linear and branched alcohols, C_3 to C_8 esters, C_3 to C_8 ethers, or mixtures thereof.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2019/081065

A. CLASSIFICATION OF SUBJECT MATTER
INV. B01J23/02 B01J27/18 B01J27/28 B01J38/52 B01J38/62
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
B01J

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2008/049440 A1 (OUE NORDBIOCHEM [EE]; SHVETS VALERIY [RU] ET AL.) 2 May 2008 (2008-05-02) paragraphs [0036] - [0044]; claims; examples	1-14
E	WO 2020/007808 A1 (SHELL INT RESEARCH [NL]; SHELL OIL CO [US]) 9 January 2020 (2020-01-09) claims; figures; examples; tables	1-14

-/--

[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
29 January 2020	05/02/2020

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	de Cauwer, Robby

2

Form PCT/ISA/210 (second sheet) (April 2005)

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	BO YAN ET AL: "Sustainable Production of Acrylic Acid: Catalytic Performance of Hydroxyapatites for Gas-Phase Dehydration of Lactic Acid", ACS CATALYSIS, vol. 4, no. 6, 6 June 2014 (2014-06-06), pages 1931-1943, XP055659008, US ISSN: 2155-5435, DOI: 10.1021/cs500388x the whole document	1-14
A	AIDA T M ET AL: "Dehydration of lactic acid to acrylic acid in high temperature water at high pressures", THE JOURNAL OF SUPERCRITICAL FLUIDS, ELSEVIER, AMSTERDAM, NL, vol. 50, no. 3, 1 October 2009 (2009-10-01), pages 257-264, XP026395883, ISSN: 0896-8446 [retrieved on 2009-06-23] the whole document	1-14
A	CARL T. LIRA ET AL: "Conversion of lactic acid to acrylic acid in near-critical water", INDUSTRIAL & ENGINEERING CHEMISTRY RESEARCH, vol. 32, no. 11, 1 November 1993 (1993-11-01), pages 2608-2613, XP055271769, ISSN: 0888-5885, DOI: 10.1021/ie00023a025 the whole document	1-14
A	WILLIAM SHU LAI MOK ET AL: "Formation of acrylic acid from lactic acid in supercritical water", JOURNAL OF ORGANIC CHEMISTRY, vol. 54, no. 19, 1 September 1989 (1989-09-01), pages 4596-4602, XP055659343, US ISSN: 0022-3263, DOI: 10.1021/jo00280a027 the whole document	1-14
A	Vom Fachbereich: "On the dehydration of lactic acid in near-and supercritical water", , 1 January 2013 (2013-01-01), XP055659344, Retrieved from the Internet: URL:https://tuprints.ulb.tu-darmstadt.de/3489/1/Dissertation-Szedlacsek.pdf the whole document	1-14

2

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2019/081065

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2008049440 A1	02-05-2008	NONE	
WO 2020007808 A1	09-01-2020	NONE	