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(54) Title: PRODUCTION OF ALKYL ESTERS OF ACRYLIC ACID

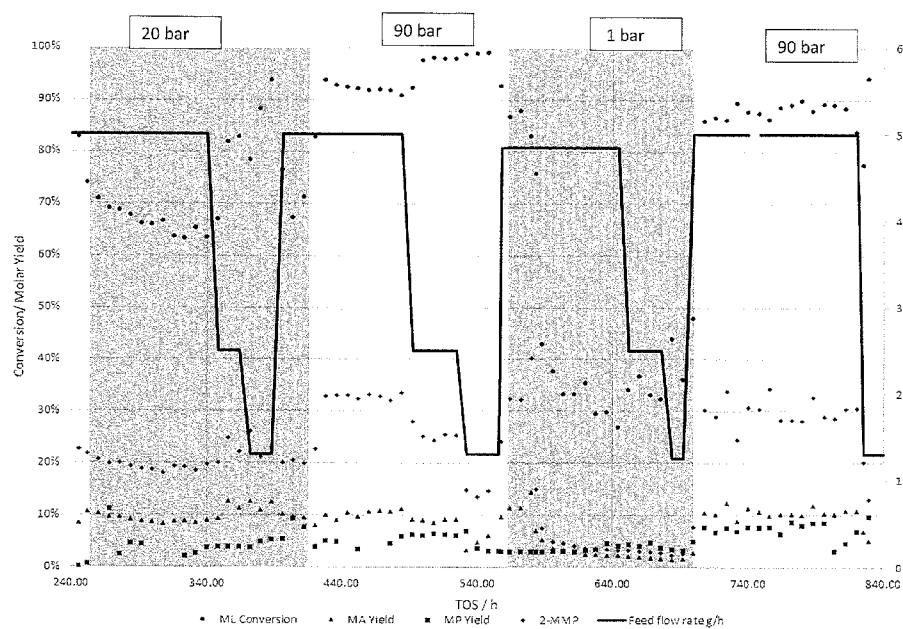


Figure 1 – Conversion/Yield - Time on stream (TOS) showing different operating regimes

(57) Abstract: A process for producing a mixture including acrylic acid or derivatives thereof, the process including the step of contacting a mixture of lactic acid or derivatives thereof and a solvent over a dehydration catalyst to produce the mixture including alkyl esters of acrylic acid, wherein the density of the solvent ranges from about 10 to about 500 kg/m³ under operating conditions.



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,
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- *with international search report (Art. 21(3))*

PRODUCTION OF ALKYL ESTERS OF ACRYLIC ACID

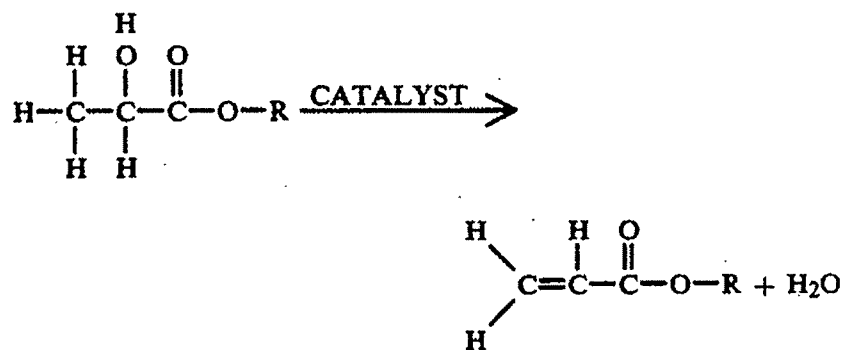
This application claims the benefit of U.S. Provisional Application No. 62/692,916, filed 02 July 2018, which is incorporated herein by reference.

Field of the Invention

The present invention generally relates to a process of producing alkyl esters of acrylic acid from alkyl esters of lactic acid.

Background of the Invention

5 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:



10 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
5 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 Tech., 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,
10 more expensive, and subject to regulations for CO₂ 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
15 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 may be added to reduce the partial pressure by dilution. Suitable catalysts include dehydrogenation catalysts known in the art.

20 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
25 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.

30 Existing processes primarily conduct the dehydration under low pressure (sub atmospheric partial pressure due to dilution) gas phase using alcohol or water. Gas-phase dehydrations require that the reactants are initially converted into the gas phase which often results, for example under the influence of thermal energy on the reactants, in

decomposition of the reactants or products which manifests itself as coking for example. 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.

5 It is therefore an object of the present invention to provide a method for producing alkyl esters of acrylic acid alkyl esters of lactic acid, which avoid the disadvantages of prior art methods.

Summary of the Invention

10 The invention provides a process for producing a mixture of alkyl esters of acrylic acid, the process including the step of contacting a mixture of an alkyl ester of lactic acid and a solvent over a dehydration catalyst to produce the mixture of alkyl esters of acrylic acid, wherein the density of the solvent ranges from about 10 to about 500 kg/m³ under operating conditions.

Brief Description of the Drawings

15 Fig. 1 is a graphical representation of conversion/yields for embodiments of the invention operating at different regimes.

Detailed Description of the Invention

The present invention is directed to a process for manufacturing alkyl esters of acrylic acid from alkyl esters of lactic acid. More preferably, the present invention is 20 directed to a method for manufacturing methyl acrylate from methyl lactate.

Embodiments of the present invention include a 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 25 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 cyclic dimers of lactic acid is 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, 30 lactic acid anhydride, 2-alkoxypropionic acids or their alkyl esters, 2-aryloxypropionic acids or their alkyl esters, 2-acyloxypropionic 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-alkoxypropionic 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.

5 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, or a carbohydrate and their isomers. In still other
10 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
15 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 stream comprising alkyl esters of lactic acid in a liquid stream. The liquid stream can include the alkyl esters of lactic acid and a solvent (diluent). Non-limiting examples of the solvent include water, methanol,
20 ethanol, acetone, C3 to C8 linear and branched alcohols, C3 to C8 esters (e.g. ethyl acetate, methyl propionate), ethers (including dimethyl ether, diethyl ether, diphenyl ether), and mixtures thereof. In some embodiments, the 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 solvent may have a high
25 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 solvent comprises methanol. In some embodiments, high solvency may refer to the solvent being able dissolve >5 w%, >10 w%, >20 w%, >30 w% of methyl lactate.

In one embodiment of the present invention, the liquid stream includes between
30 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.

5 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 95wt%, less than 75wt%, less than 50wt% or less than 25wt%
10 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 13-15 (e.g. oxide of Al, Si, P, S), oxides from Groups 1-3 (e.g. oxide of
15 K, Mg, Ca), 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 13-15 metal oxides. In some embodiments, the mixed oxide may be crystalline or amorphous. Crystalline mixed oxides may include crystalline aluminosilicates also called zeolites. The metal of Groups 1-3 may then be exchanged or deposited in the zeolite.
20 Some examples include catalysts based on calcium sulphate, calcium phosphate, calcium pyrophosphate, and combinations thereof. Suitable promoters 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 Na₂SO₄, Na₃PO₄, NaNO₃,
25 Na₂SiO₃, Na₄P₂O₇, NaH₂PO₄, Na₂HPO₄, Na₂HAsO₄, NaC₃H₅O₃, NaOH, Cs₂SO₄, 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 Na₂CO₃) or a phosphoric acid salt (such as NaH₂PO₄, Na₂HPO₄, LiH₂PO₄, LaPO₄, etc.).

30 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
5 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.

In one embodiment, the operating conditions of the reactor provide a density of the feed solution ranging from about 10 to about 500 kg/m³. In other embodiments, the
10 operating conditions of the reactor provide a density of the feed solution ranging from about 50 to about 400 kg/m³. In still other embodiments, the operating conditions of the reactor provide a density of the feed solution ranging from about 100 to about 300 kg/m³. In some embodiments, the density of the feed solution is greater than 10 kg/m³, greater than 50 kg/m³, greater than 100 kg/m³, or greater than 150 kg/m³. In other embodiments,
15 the density of the feed solution is less than 500 kg/m³, less than 300 kg/m³, or less than 200 kg/m³.

In embodiments of the present invention, the contacting of the stream comprising alkyl esters of lactic acid with the dehydration catalyst may be carried out at supercritical conditions of the solvent, which is defined as above the critical pressure and critical
20 temperature of the solvent.

In one embodiment of the present invention, the stream comprising alkyl esters of lactic acid contacts the dehydration catalyst at a pressure between about 73 psig (5 barg) and about 1305 psig (90 barg). In another embodiment of the present invention, the stream comprising alkyl esters of lactic acid contacts the dehydration catalyst at a pressure of
25 about 290 psig (20 barg). 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
30 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.

Among the benefits attainable by the foregoing embodiments is the increased yield of alkyl esters of acrylic acid and decreased solvent degradation. One of the assumed primary causes of low activity in the prior dehydration systems is poor evaporation of the feed at the reactor inlet. The concentrated substrate when in contact with the hot bed, could likely lead to decomposition reactions, e.g. polymerisation ultimately leading to coke. Not wishing to be bound by theory, it is theorised that the high-density solvent solvates and washes off coke precursors from the surface of the substrate, thereby suppressing further condensation into coke. Applicants have worked to remove the evaporation step. However, for the dehydration to proceed, elevated temperatures are required above the boiling points of the substrate/solvent system. Applicants have theorized, but are not bound by the theory, that by using 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 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 65m²/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, Vol.15, pages1211-1217. 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/m³, at 90 bar about 55 kg/m³ and at 1 bar about 0.62 kg/m³. 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% (Figure 1). As shown in Fig. 1, the MA yield remains 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 appears 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.

CLAIMS

1. A process for producing a mixture comprising acrylic acid or derivatives thereof, the process comprising the step of contacting a mixture of lactic acid or derivatives thereof and a solvent over a dehydration catalyst to produce the mixture comprising acrylic acid or derivatives thereof, wherein the density of the solvent ranges from about 10 to about 500 kg/m³ under operating conditions.

2. 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.

3. The process according to claim 1 or claim 2, wherein lactic acid or derivatives thereof originates from converting a renewable feedstock into the lactic acid or derivatives thereof.

4. The process according to claim 3, wherein the renewable feedstock comprises at least one of a sugar source selected from at least one of sucrose, glucose, xylose or fructose, or polysaccharides.

5. The process according to claims 1 to 4, wherein the acrylic acid or derivatives thereof is at least one of methyl acrylate, ethyl acrylate, butyl acrylate, 2-ethylhexyl acrylate, or mixtures thereof.

6. The process according to claims 1 to 5, wherein the solvent 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.

7. The process according to claims 1 to 6, wherein the solvent is at least one of methanol, ethanol, C₃ to C₈ linear and branched alcohols, or mixtures thereof.

8. The process according to any one of claims 1 to 7, wherein the solvent is at supercritical conditions of temperature and pressure.

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

10. The process according to claim 9, wherein the dehydration catalyst is at least one of a metal oxide from Groups 13-15, oxides from Groups 1-3, or mixtures thereof.

11. The process according to any one of claims 1 to 10, wherein the temperature to produce the mixture comprising acrylic acid or derivatives thereof reaction ranges from about 150 °C to about 450 °C.

12. The process according to any one of claims 1 to 11, wherein the mixture comprising acrylic acid or derivatives thereof further comprises lactic acid or derivatives thereof.

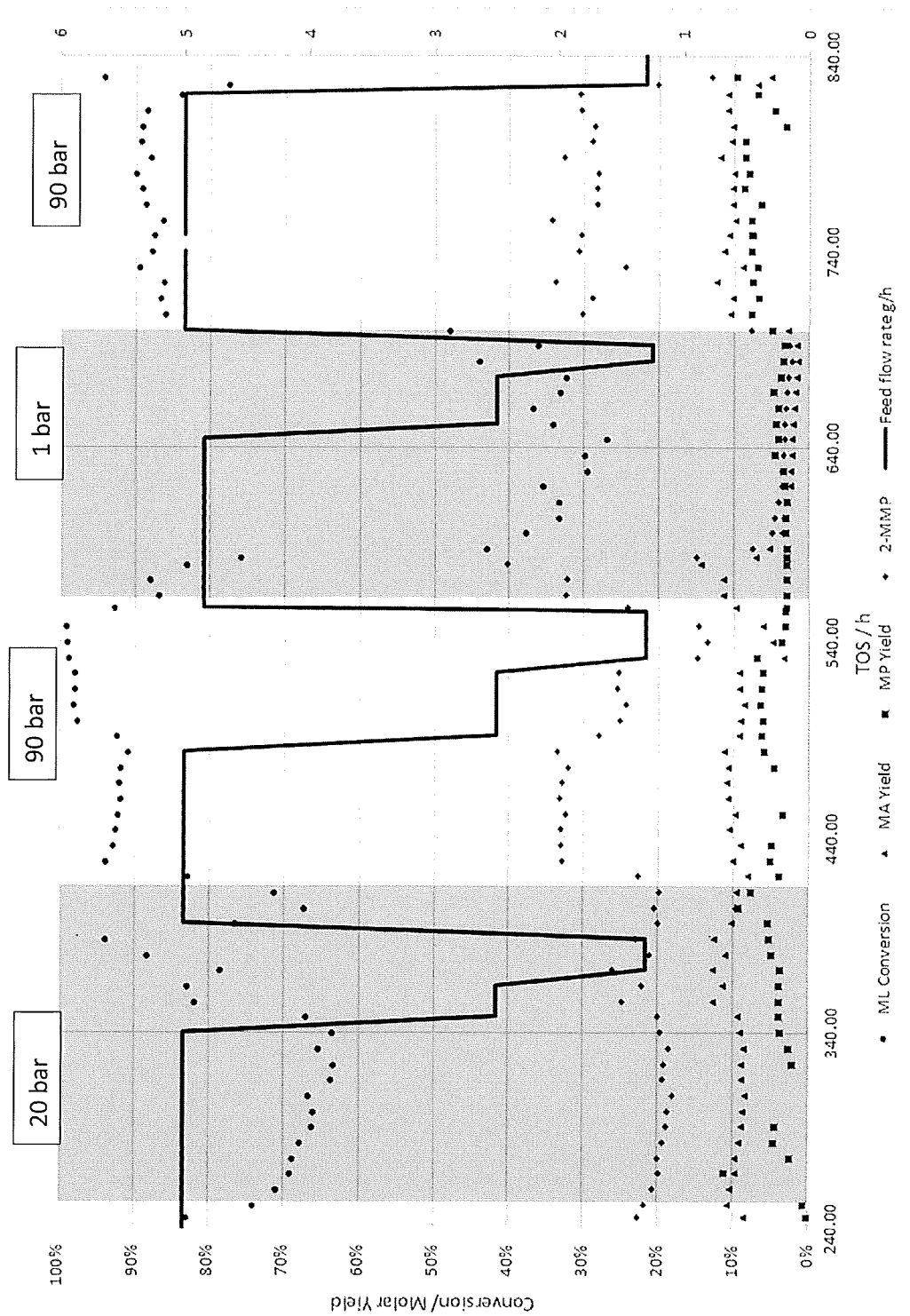


Figure 1 – Conversion/Yield - Time on stream (TOS) showing different operating regimes

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2019/067632

A. CLASSIFICATION OF SUBJECT MATTER
INV. C07C67/327 C07C69/54
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)
C07C

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, CHEM ABS Data, 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	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] abstract; table 1 paragraphs [0001], [02.3] ----- -/-	1-12



Further documents are listed in the continuation of Box C.



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

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"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

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Date of the actual completion of the international search

27 September 2019

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04/10/2019

Name and mailing address of the ISA/

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Authorized officer

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INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2019/067632

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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 abstract; figure 1; table 1 -----	1-12
X	US 2 859 240 A (HOLMEN REYNOLD E) 4 November 1958 (1958-11-04) cited in the application claim 4; examples 1,31 -----	1-12
X	ZHANG J ET AL: "Evaluation of Catalysts and Optimization of Reaction Conditions for the Dehydration of Methyl Lactate to Acrylates", CHINESE JOURNAL OF CHEMICAL ENGINEERING, CHEMICAL INDUSTRY PRESS, BEIJING, CN, vol. 16, no. 2, 1 April 2008 (2008-04-01), pages 263-269, XP022856567, ISSN: 1004-9541, DOI: 10.1016/S1004-9541(08)60073-7 [retrieved on 2008-04-01] abstract; figure 3.2; table 2 -----	1-12

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2019/067632

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2859240	A	04-11-1958	NONE
