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(54) Title: ACRYLIC ACID, AND METHODS OF PRODUCING THEREOF

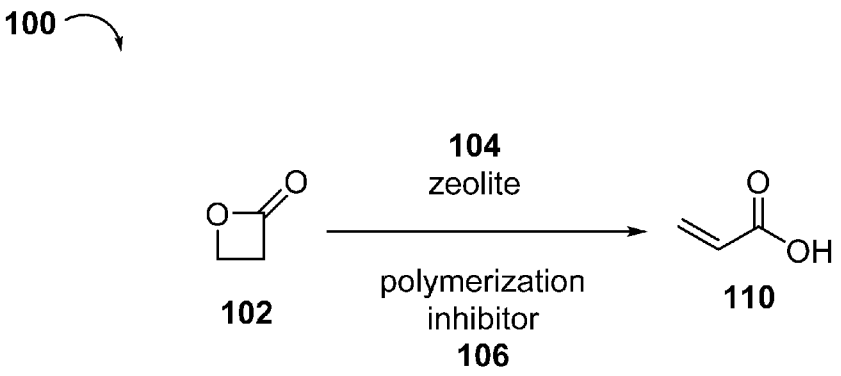

FIG. 1

(57) Abstract: Provided herein are methods of producing acrylic acid from beta-propiolactone. Such methods may involve the use of a heterogeneous catalyst, such as a zeolite.

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ACRYLIC ACID, AND METHODS OF PRODUCING THEREOF

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims priority to U.S. Provisional Patent Application No. 62/311,262, filed March 21, 2016, which is incorporated herein by reference in its entirety.

FIELD

[0001] The present disclosure relates generally to production of acrylic acid, and more specifically to production of acrylic acid from beta-propiolactone.

BACKGROUND

[0002] The production and use of acrylic acid (AA) has grown significantly in recent decades as the demand for polyacrylic acid-based superabsorbent polymers (SAPs) has grown. SAPs are used extensively for the manufacture of diapers, adult incontinence products, and feminine hygiene products, as well as in agricultural applications.

[0003] Currently, commercial acrylic acid is typically derived from propylene oxidation. Propylene is primarily a product of oil refining and its price and availability are closely tied to crude oil prices. Because of this, acrylic acid prices have risen dramatically in recent years. Thus, there exists a need in the art for alternative methods to synthesize acrylic acid.

BRIEF SUMMARY

[0004] Provided herein are methods of producing acrylic acid from beta-propiolactone. In some aspects, provided is a method of producing acrylic acid from beta-propiolactone, by combining beta-propiolactone, a heterogeneous catalyst, a polymerization inhibitor, and optionally a solvent; and producing acrylic acid from at least a portion of the beta-propiolactone. In some embodiments, the heterogeneous catalyst is a zeolite. In some variations, the zeolite is an acidic zeolite.

DESCRIPTION OF THE FIGURES

[0005] The present application can be best understood by reference to the following description taken in conjunction with the accompanying figures, in which like parts may be referred to by like numerals.

[0006] FIG. **1** depicts an exemplary process to produce acrylic acid from beta-propiolactone in the presence of a zeolite and a polymerization inhibitor.

[0007] FIG. **2** depicts an exemplary reaction system to produce acrylic acid from beta-propiolactone according to the methods described herein.

DETAILED DESCRIPTION

[0008] The following description sets forth exemplary methods, parameters and the like. It should be recognized, however, that such description is not intended as a limitation on the scope of the present disclosure but is instead provided as a description of exemplary embodiments.

[0009] Provided herein are methods of producing acrylic acid from beta-propiolactone using heterogeneous catalysts, such as zeolites. Such methods produce acrylic acid from beta-propiolactone in a one-pot reaction. Such methods may also produce acrylic acid in high yields, by minimizing other products that may form, such as polypropiolactone and polyacrylic acid.

[0010] In some aspects, provided is a method of producing acrylic acid from beta-propiolactone, by combining beta-propiolactone, a zeolite, and a polymerization inhibitor; and producing acrylic acid from at least a portion of the beta-propiolactone. For example, with reference to FIG. **1**, process **100** is an exemplary process to produce acrylic acid. Beta-propiolactone **102** is combined with zeolite **104** and polymerization inhibitor **106** to produce acrylic acid **110**. In some variations, process **100** is performed neat. In other variations, process **100** is performed in the presence of a solvent. In some embodiments, the method further includes continuously isolating the acrylic acid produced. In some variations, the acrylic acid is isolated by distillation.

[0011] The beta-propiolactone, catalysts, polymerization inhibitors, solvents and reaction conditions, as well as acrylic acid produced, are described in further detail below.

Beta-propiolactone (BPL)

[0012] In some embodiments, the beta-propiolactone used in the methods described herein may be produced by epoxide carbonylation. For example, the beta-propiolactone may be produced from ethylene oxide and carbon monoxide via a carbonylation reaction. *See e.g.*, WO 2010/118128. In one variation, the beta-propiolactone is produced by reacting ethylene oxide with carbon monoxide in the presence of a carbonylation catalyst and optionally a solvent.

[0013] Suitable carbonylation catalysts are described in, for example, WO 2010/118128. For example, the carbonylation catalyst comprises [(TPP)Al][$Co(CO)_4$], [(ClTPP)Al][$Co(CO)_4$], [(TPP)Cr][$Co(CO)_4$], [(ClTPP)Cr][$Co(CO)_4$], [(salcy)Cr][$Co(CO)_4$], [(salph)Cr][$Co(CO)_4$], or [(salph)Al][$Co(CO)_4$]. It should generally be understood that "TPP" refers to tetraphenylporphyrin; "ClTPP" refers to *meso*-tetra(4-chlorophenyl)porphyrin); "salcy" refers to (*N*, *N'*-bis(3,5-di-*tert*-butylsalicylidene)-1,2-diaminocyclohexane); and "salph" refers to (*N*, *N'*-bis(salicylidene)-*o*-phenylenediamine).

[0014] In some variations, the beta-propiolactone is added to the reaction with an initial pressure of carbon monoxide. In other variations where the method is continuous, no initial pressure is required to add the beta-propiolactone.

Catalysts

[0015] In some embodiments, the catalyst used in the conversion of beta-propiolactone to acrylic acid is a heterogeneous catalyst. In certain variations, the catalyst is a zeolite. In one variation, the catalyst is an acidic zeolite. For example, the zeolite may be Zeolite Y or Zeolite ZSM-5.

[0016] In certain variations, the zeolite is Zeolite Y hydrogen in powder form. In one variation, the Zeolite Y hydrogen has a 80:1 mole ratio SiO_2/Al_2O_3, and has a powder surface area of 780 m^2/g.

[0017] The zeolite may be dried using any suitable methods or techniques known in the art (*e.g.*, using heat and/or vacuum) prior to use.

[0018] A combination of any of the catalysts described herein may also be used.

Polymerization Inhibitors

[0019] In some embodiments, the polymerization inhibitor used in the conversion of beta-propiolactone to acrylic acid is a radical polymerization inhibitor. Suitable polymerization inhibitors may include, for example, phenothiazine.

Solvents

[0020] In some embodiments of the methods described herein, the conversion of beta-propiolactone to acrylic acid is performed neat. In other embodiments, the conversion of beta-propiolactone to acrylic acid is performed in the presence of a solvent.

[0021] In some variations, the solvent selected (i) dissolves, or at least partially dissolves, the beta-propiolactone, but does not react, or minimally reacts, with the beta-propiolactone; or (ii) has a high boiling point so that the acrylic acid produced may be distilled while solvent remains in the reactor, or a combination of (i) and (ii). In certain variations, the solvent is a polar aprotic solvent. For example, the solvent may be a high boiling polar aprotic solvent. In one variation, the solvent includes sulfolane.

[0022] The amount of solvent used may be varied to balance the metering of beta-propiolactone added and the overall concentration of reagents in the reaction mixture. For example, in one variation, the ratio of beta-propiolactone to solvent in the reaction is about 1 : 1.

[0023] The solvent may be dried using any suitable methods or techniques known in the art prior to use.

[0024] A combination of any of the solvents described herein may also be used.

Processing Conditions

[0025] The methods described herein may be carried out batch-wise or continuously. Various factors may affect the conversion of beta-propiolactone to acrylic acid according to the methods described herein.

[0026] For example, the rate of beta-propiolactone addition may affect the yield of acrylic acid. In some variations, the method further includes controlling the rate of addition of beta-propiolactone. A slower rate of beta-propiolactone addition was unexpectedly observed to increase the yield of acrylic acid produced. In some variations of the methods described herein, the beta-propiolactone is provided at a rate of less than 1.5 g/min, less than 1.4 g/min, less than 1.3 g/min, less than 1.2 g/ min, less than 1.1 g/min, less than 1 g/min, less than 0.9 g/min, or less than 0.8 g/ min; or between 0.5 g/min and 1.5 g/min, or between 0.75 g/min and 1.25 g/min; or about 1 g/min.

[0027] A slower rate of beta-propiolactone addition was also unexpectedly observed to reduce the amount of other products formed, such as polypropiolactone and polyacrylic acid. In some variations, the method further includes minimizing or suppressing production of polypropiolactone from at least a portion of the beta-propiolactone. In one variation, little or no polypropiolactone is produced. In other variations that may be combined with the foregoing, the

method further includes minimizing or supressing production of polyacrylic acid from at least a portion of the acrylic acid produced. In one variation, little or no polyacrylic acid is produced.

[0028] The amount of beta-propiolactone added may be metered by any suitable methods or techniques in the art. For example, beta-propiolactone may be metered or slowly added to the reactor via a needle valve.

[0029] The removal of acrylic acid produced may also affect the yield of acrylic acid. Stripping off of the acrylic acid produced was also unexpectedly observed to increase yield of the acrylic acid produced. In some variations, the method further includes stripping off at least a portion of the acrylic acid produced (*e.g.*, by distillation). In certain variations of the foregoing, stripping off at least a portion of the acrylic acid produced minimizes polymerization of the acrylic acid, and thus, formation of polyacrylic acid.

[0030] In some embodiments, the acrylic acid may be produced at a pressure that strips off of at least a portion of the acrylic acid produced. For example, in one variation, the method may be performed at subatmospheric pressure of 100 mm Hg. In other variations, vacuum may be applied in the range of 200 to 20 mm Hg.

[0031] The acrylic acid may be produced at elevated temperatures according to the methods described herein. In some embodiments, the temperature is at least 100°C, at least 105°C, at least 110°C, at least 115°C, at least 120°C, at least 125°C, at least 130°C, at least 135°C, at least 140°C, at least 145°C, at least 150°C, at least 155°C, at least 160°C, at least 165°C, at least 170°C, at least 175°C, at least 180°C, at least 185°C, at least 190°C, at least 195°C, at least 200°C, at least 205°C, at least 210°C, at least 215°C, or at least 220°C; or between 100°C and 220°C, or between 170°C and 200°C. In some variations, the reactor in which the method is performed is heated to the temperatures described herein. In other variations, the beta-propiolactone, polymerization inhibitor, catalyst, and/or solvent is provided to the reactor at the temperatures described herein.

Acrylic Acid

[0032] In some embodiments of the methods described herein, acrylic acid is produced at a yield of at least 50%, at least 55%, at least 60%, at least 65%, at least 70%, at least 75%, at least 80%, at least 85%, at least 90%, or at least 95%.

[0033] In some embodiments of the methods described herein, the acrylic acid produced has a purity of at least 95%, at least 96%, at least 97%, or at least 98%. In some variations where the acrylic acid produced is isolated, *e.g.*, by distillation, the acrylic acid has a purity of at least 98%, at least 98.5%, at least 99%, at least 99.1%, at least 99.2%, at least 99.3%, at least 99.4%, at least 99.5%, at least 99.6%, at least 99.7%, at least 99.8%, or at least 99.9%.

Downstream Products

[0034] The acrylic acid produced according to the methods described herein may be used for various applications. For example, acrylic acid may be used to make polyacrylic acid for superabsorbent polymers (SAPs). The SAPs find use in diapers, adult incontinence products, and feminine hygiene products among other things.

[0035] In some aspects, provided is a method for producing a superabsorbent polymer, by: polymerizing the acrylic acid produced according to any of the methods described herein in the presence of a cross-linker to produce the superabsorbent polymer.

Acrylic Acid Production Systems

[0036] In other aspects, provided herein are systems for production of acrylic acid. For example, with reference to FIG. **2**, an exemplary acrylic acid production system is depicted. System **200** is configured to produce acrylic acid from beta-propiolactone, according to the methods described herein.

[0037] System **200** includes reactor **210**, configured to receive beta-propiolactone, a zeolite, and a polymerization inhibitor, and to produce acrylic acid from at least a portion of the beta-propiolactone according to the methods described herein. Reactor **210** is configured to produce acrylic acid at an elevated temperature. Any of the temperatures described herein for the methods may be employed in the system. For example, in one variation, reactor **210** is configured to produce acrylic acid at a temperature between 170°C and 200°C. Suitable reactors may include, for example, a Parr reactor.

[0038] In some variations, reactor **210** is configured to control the rate of addition of one or more of the beta-propiolactone, the zeolite, and the polymerization inhibitor added. For example, in one variation, a mixture of the beta-propiolactone and the polymerization inhibitor may be slowly added using a needle valve to a mixture of catalyst in a solvent.

[0039] With reference again to FIG. **2**, reactor **210** further includes vapor port **214**. In some variations, reactor **210** is configured to continuously strip off at least a portion of the acrylic acid produced, and vapor port **214** is configured to pass acrylic acid vapors to collection vessel **220**.

[0040] With reference again to FIG. **2**, system **200** further includes acid/base scrubber **230**, configured to receive acrylic acid from collection vessel **220**. In other variations of the system, acid/base scrubber **230** may be omitted. Further, with reference to FIG. **2**, elements **212**, **216** and **222** are dip tubes.

[0041] The systems provided herein may be configured for batch-wise or continuous production of acrylic acid.

EXAMPLES

[0042] The following Examples are merely illustrative and are not meant to limit any aspects of the present disclosure in any way.

Example 1

Conversion of beta-propiolactone to acrylic acid using a zeolite

[0043] This Example demonstrates the production of acrylic acid from beta-propiolactone using a zeolite.

[0044] A mixture of beta-propiolactone (3.0 g) and phenothiazine (9.0 mg) was added using a needle value to a mixture of sulfolane (40.0g) and Zeolite Y hydrogen (20.0 g) at 165°C with 50 psi of carbon monoxide. Zeolite Y hydrogen (80:1 mole ratio SiO_2/Al_2O_3, powder S.A. 780 m^2/g) was dried under vacuum at 100°C for one day before use. Phenothiazine was the polymerization inhibitor used. Sulfolane was the solvent used, and was dried over 3Å molecular sieves prior to use. The beta-propiolactone was added slowly using the needle valve over about 8.6 minutes. The reaction mixture was heated to 170°C to produce acrylic acid.

[0045] The reaction was monitored by infrared spectroscopy (IR). The reaction was observed to be completed after about 3 hours, when no beta-propiolactone was detectable by IR. The zeolite was then filtered off from the reaction mixture, and a sample of the resulting mixture was dissolved in deuterium (D_2O) and chloroform ($CDCl_3$) for nuclear magnetic resonance (NMR) analysis. The observed vinyl peaks between δ 5.80 and 6.47 ppm in the ^1H NMR confirmed the production of acrylic acid.

CLAIMS

What is claimed is:

1. A method of producing acrylic acid from beta-propiolactone, comprising:
combining beta-propiolactone, a zeolite, and a polymerization inhibitor; and
producing acrylic acid from at least a portion of the beta-propiolactone.

2. The method of claim 1, the zeolite is an acidic zeolite.

3. The method of claim 1 or 2, wherein the zeolite is Zeolite Y or Zeolite ZSM-5, or a combination thereof.

4. The method of any one of claims 1 to 3, wherein the polymerization inhibitor is phenothiazine.

5. The method of any one of claims 1 to 4, wherein the beta-propiolactone is provided at a rate of less than 1.5 g/min.

6. The method of claim 5, wherein the beta-propiolactone is provided at a rate of between 0.75 g/min and 1.25 g/min.

7. The method of any one of claims 1 to 6, wherein the acrylic acid produced is continuously isolated.

8. The method of any one of claims 1 to 7, wherein the acrylic acid is produced at a yield of at least 50%.

9. The method of any one of claims 1 to 8, wherein the acrylic acid is produced at a temperature of between 170°C and 200°C.

10. The method of any one of claims 1 to 9, wherein the beta-propiolactone, the polymerization inhibitor, and the zeolite are further combined with a solvent.

11. The method of claim 10, wherein the solvent comprises a polar aprotic solvent.

12. The method of claim 10, wherein the solvent comprises sulfolane.

13. The method of any one of claims 1 to 12, wherein the acrylic acid produced has a purity of greater than 95%.

14. The method of any one of claims 1 to 13, further comprising isolating acrylic acid.

15. The method of claim 14, wherein the acrylic acid is isolated by distillation.

16. The method of any one of claims 1 to 15, wherein the beta-propiolactone is produced from ethylene oxide and carbon monoxide.

17. A method of producing a superabsorbent polymer, comprising:

polymerizing acrylic acid produced according to the method of any one of claims 1 to 16 in the presence of a cross-linker to produce the superabsorbent polymer.

18. A system, comprising:

a reactor, wherien the reactor comprises one or more inlets and a vapor port; and

a collection vessel,

wherein the one or more inlets of the reactor are configured to receive beta-propiolactone, a zeolite, and a polymerization inhibitor,

wherein the reactor is configured to produce acrylic acid vapors from at least a portion of the beta-propiolactone received, and to continuously strip off at least a portion of the acrylic acid vapors produced, and

wherein the vapor port is configured to pass at least a portion of the acrylic acid vapors to the collection vessel.

19. The system of claim 18, further comprising an acid/base scrubber.

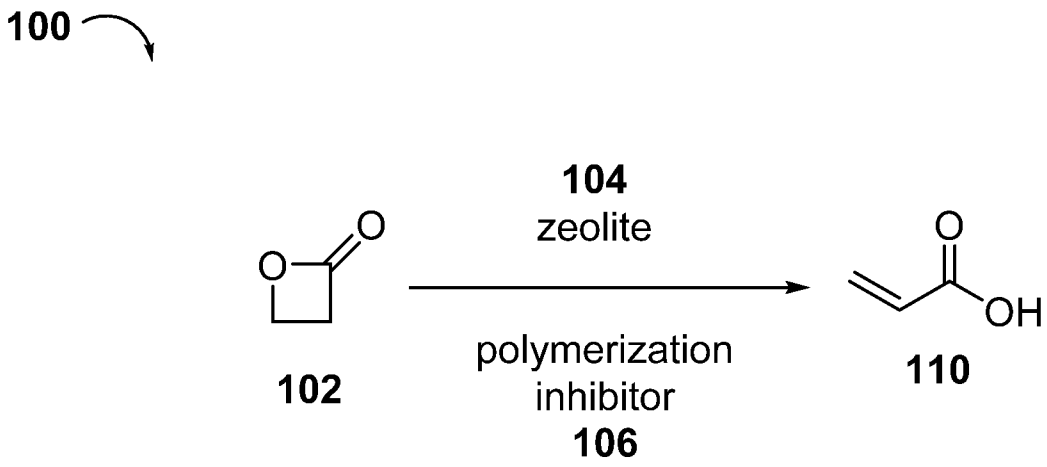
100
104
zeolite
polymerization
inhibitor
106
102
110
O
OH

FIG. 1

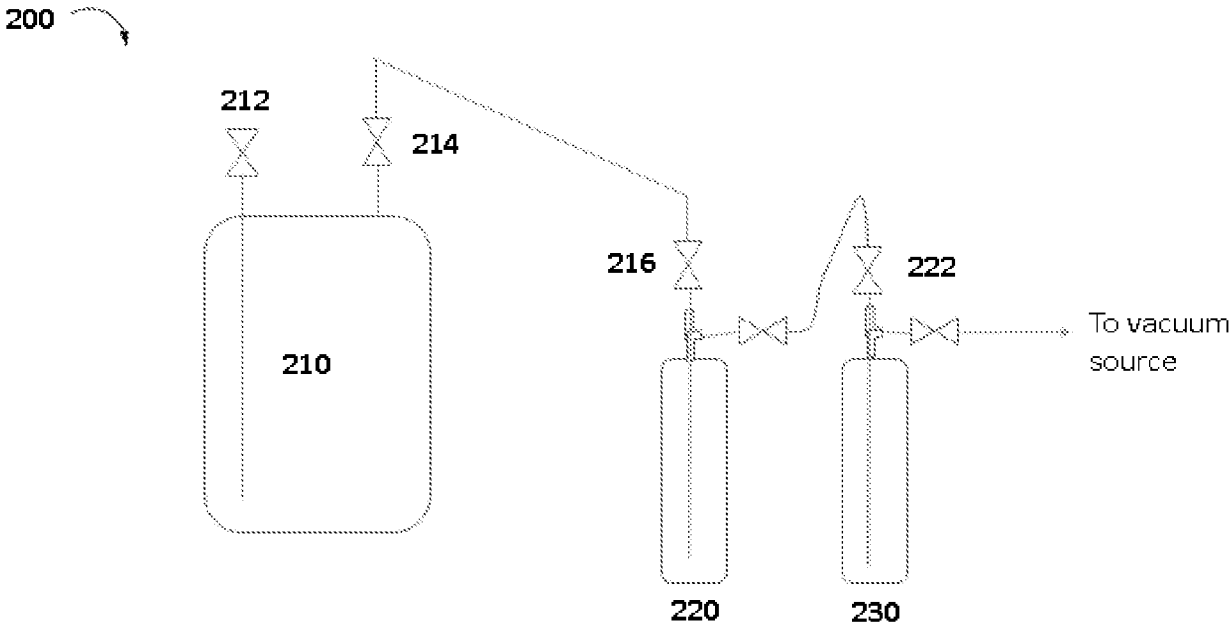
200
212
214
216
222
210
220
230
To vacuum
source

FIG. 2

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US17/23302

A. CLASSIFICATION OF SUBJECT MATTER
IPC - C07B 35/08; C07C 57/04, 51/09 (2017.01)
CPC - C07B 35/08; C07C 57/04, 51/09

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)
See Search History document

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
See Search History document

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2011/0319849 A1 (COLLIAS, DI et al) 29 December 2011; paragraphs [0088], [0120], [0122], [0131]; claims 1, 28	1-2, 3/1-2
X --- Y	WO 2013/063191 A1 (NOVOMER, INC) 2 May 2013; page 41, paragraph 4; page 52, paragraphs 4-5; page 53, paragraph 2; figure 1	18 --- 19
Y	US 5,198,578 A (ETZKORN, WG et al) 30 March 1993; figure 1; column 6, lines 25-30	19
A	WO 2013/185009 A1 (METABOLIX, INC) 12 December 2013; entire publication	1

☐ 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
"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
11 May 2017 (11.05.2017)	05 JUN 2017
Name and mailing address of the ISA/ Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-8300	Authorized officer Shane Thomas PCT Helpdesk: 571-272-4300 PCT OSP: 571-272-7774

Form PCT/ISA/210 (second sheet) (January 2015)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US17/23302

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☒ Claims Nos.: 4-17
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☐ No protest accompanied the payment of additional search fees.