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

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
17 September 2015 (17.09.2015)

WIPO | PCT

(10) International Publication Number
WO 2015/137923 A1

(51) **International Patent Classification**:
C07D 307/02 (2006.01) ***C07D 307/26*** (2006.01)

(21) **International Application Number**:
PCT/US2014/023301

(22) **International Filing Date**:
11 March 2014 (11.03.2014)

(25) **Filing Language**: English

(26) **Publication Language**: English

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(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, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, 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, 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).

Published:

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

WO 2015/137923 A1

(54) **Title**: METHODS AND COMPOUNDS FOR PRODUCING NYLON 12

(57) **Abstract**: Nylon 12 may be produced by dimerization of 6-carbon furan compounds into 12-carbon dimers, and conversion of the dimers into nylon 12. The 6-carbon furan compounds may be produced from biomass. Ester-aldehyde dimers and amino-ester dimers may be produced from the 6-carbon furan compounds as precursors for at least the production of nylon 12, and the components for producing the nylon 12 may be provided as a kit.

METHODS AND COMPOUNDS FOR PRODUCING NYLON 12

BACKGROUND

[0001] Nylon is a designation for a family of synthetic polymers known as aliphatic polyamides, and is one of the most commonly used polymers. The chemical constituents of nylon include carbon, hydrogen, nitrogen, and oxygen. Types of nylons include nylon 6,6, that may be formed by reacting a diamine and a dicarboxylic acid so that amides are formed at both ends of each monomer, nylon 6 that may be made by a ring-opening polymerization of cyclic amides (lactams), and nylon 12 that may be produced from cyclododecatriene.

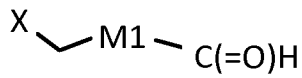
[0002] Nylons are designated by a numerical suffix that specifies the numbers of carbons donated by the monomers. For example, for nylons with a two-number designation, such as nylon 6,6 or nylon 6,12, the first number represents the number of carbons from the diamine monomer, and the second number represents the number of carbons from the diacid monomer. For nylons having a single number designation, such as nylon 12, the number represents the number of carbon atoms in the repeating monomer units.

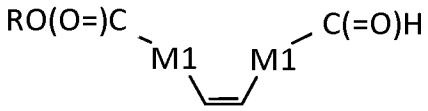
[0003] Nylon 12 (polyamide 12) is a major component of tubings used in automotive brake and fuel lines. Nylon 12 has generally been produced from cyclododecatriene by converting the cyclododecatriene to laurolactam, which is a starting monomer for industrial production of nylon 12. Cyclododecatriene may be produced from butadiene as the raw material. In one method for the production of butadiene that may be considered non-environmentally friendly, the butadiene is derived from petroleum products. Further, an explosion in 2012 at an Evonik Industries plant in Germany that produces a large proportion of the world's supply of cyclododecatriene, resulted in a shortage of the starting materials, and generated concerns over a potential shortage of nylon 12 with the potential of halting of new automobile assembly worldwide.

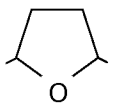
[0004] Thus, there remains a need for environmentally friendly, scalable and cost competitive alternative approaches for producing nylon 12. The alternative approaches should utilize raw materials and methods that are environmentally friendly instead of relying on petrochemically derived raw materials. Such alternative approaches may additionally alleviate concerns over future problems with current production methods, such as that caused by the Evonik Industries explosion.

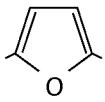
SUMMARY

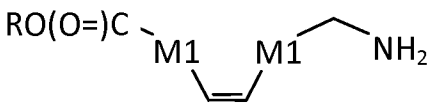
[0005] Nylon 12 may be produced by dimerization of 6-carbon furan compounds into 12-carbon dimers, and conversion of the dimers into nylon 12. The 6-carbon furan compounds may be produced from biomass. Ester-aldehyde dimers and amino-ester dimers may be produced from the 6-carbon furan compounds as precursors for at least the production of nylon 12.

[0006] In an embodiment, a method for producing nylon 12, includes converting alkyl furan compounds of formula 

to an ester-aldehyde dimer of formula 

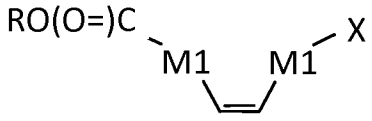
, wherein X is –OH or halogen, R is C_1-C_5 alkyl, and M1 is 

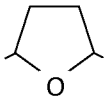
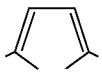
or 

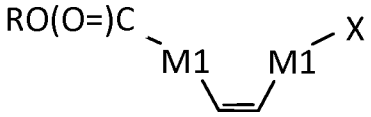
, converting the ester-aldehyde dimer to an amino-ester of formula 

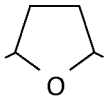
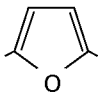
, and converting the amino-ester to nylon 12.

[0007] In an embodiment, a method for producing nylon 12 from waste stream biomass includes converting the biomass to 5-chloromethylfurfural and 5-hydroxymethylfurfural, and using the 5-chloromethylfurfural and 5-hydroxymethylfurfural as reactants for producing the nylon 12.

[0008] In an embodiment, a kit for the production of nylon 12 includes a furan dimer compound of formula 

, wherein R is C_1-C_5 alkyl, M1 is  or  , and X is –CHO or $–CH_2–NH_2$; a halide source; and a catalyst.

[0009] In an embodiment, a furan dimer compound has a formula 

, wherein R is C_1-C_5 alkyl, M1 is  or  , and X is –CHO or $–CH_2–NH_2$.

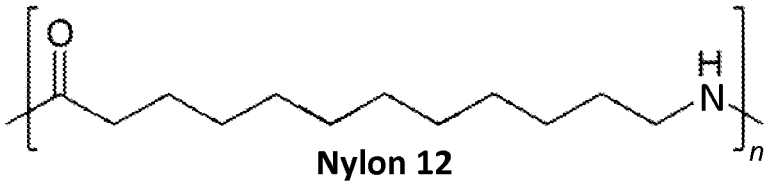
BRIEF DESCRIPTION OF THE FIGURES

[0010] FIG. 1 depicts a general flow diagram for an illustrative method for the production of nylon 12 according to an embodiment.

[0011] FIG. 2 depicts a diagram for an illustrative method for the production of nylon 12 from waste stream products according to an embodiment.

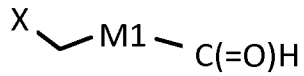
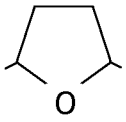
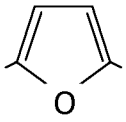
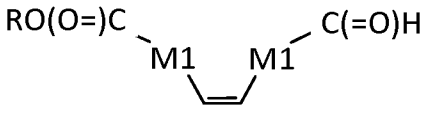
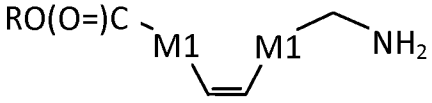
DETAILED DESCRIPTION

[0012] Nylon 12 receives its numerical designation from the number of carbon atoms in its monomer units, wherein each monomer unit has twelve carbons as illustrated,



Nylon 12

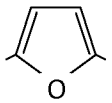
, and n is about 2 to about 1000. In accordance with embodiments as discussed herein, nylon 12 may be produced from 6-carbon compounds by methods that are also environmentally friendly.

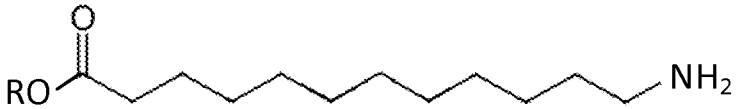
[0013] A representation of a method for producing nylon 12 is depicted in FIG. 1. In an embodiment, alkyl furan compounds **1A** and/or **2A** of formula  , wherein X is –OH or halogen, and M1 is  or  , may be converted to ester-aldehyde dimers **3** of formula  , wherein R is C_1-C_5 alkyl. The dimers **3** may be converted to amino-esters **4** of formula  , and the amino-esters may be converted to nylon 12.

[0014] In an embodiment, the amino-esters **4** may be converted to nylon 12 by a hydrogenation-hydrodeoxygenation-polymerization reaction. One type of hydrogenation-hydrodeoxygenation-polymerization reaction may include treating the amino-ester **4** with a halide source and hydrogen gas in the presence of a catalyst. The halide source may be a hydrogen halide, or combination of hydrogen halides. Hydrogen halides may include hydrogen iodide, hydrogen chloride, and hydrogen bromide, or any combination thereof. The catalyst may include platinum catalysts, palladium catalysts, rhodium catalysts, ruthenium catalysts, nickel catalysts, cobalt catalysts, iron catalysts, molybdenum catalysts, iridium catalysts, rhenium catalysts, or gold catalysts, or any combination thereof. In an embodiment, the catalyst may be mounted on a support.

[0015] The conversion of amino-ester **4** to nylon 12 may proceed via any of the three depicted pathways represented in FIG. 1. In a first possible reaction, the hydrogenation-hydrodeoxygenation may take place prior to polymerization to open the furan rings M1 and produce an amino-acid or amino-ester monomer **5**. Polymerization of the amino-acid or the amino-ester monomer may then occur to produce the nylon 12. In a second

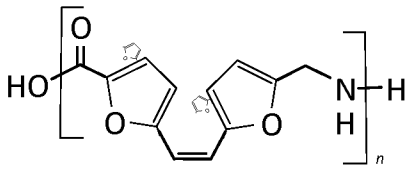
possible reaction, polymerization may take place prior to the hydrogenation-hydrodeoxygenation to form a polymer **6** that contains furan rings M1. Alternatively, the hydrogenation-hydrodeoxygenation and polymerization may occur simultaneously to form nylon 12 directly from the amino-ester **4**.

[0016] For reactions wherein M1 of the amino-ester **4** may be  , the intermediary amino-ester monomer **5** may be represented by

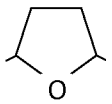


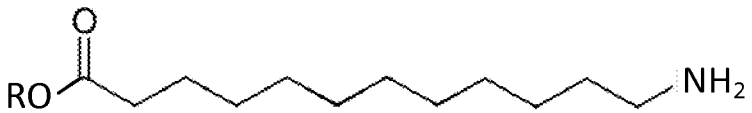
,

and the polymer **6** may be represented by



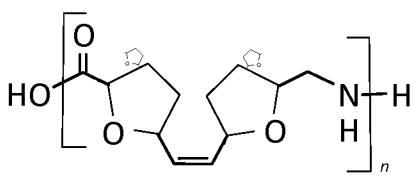
, wherein n is about 2 to about 1000.

[0017] For reactions wherein M1 of the amino-ester **4** may be  , the intermediary amino-ester monomer **5** may be represented by



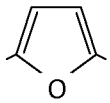
,

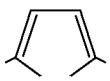
and the polymer **6** may be represented by



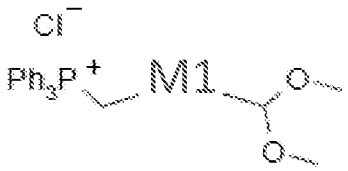
, wherein n is about 2 to about 1000.

[0018] The starting materials for producing nylon 12, alkyl furan compounds **1A** and/or **2A**, may be produced from biomass. In an embodiment, the alkyl furan compounds **1A** and/or **2A** may be produced from biomass by isolating hexoses (glucose and/or fructose), sucrose, cellulose, or corn stover, or any combination thereof from the biomass, and converting the hexoses, sucrose, cellulose, or corn stover, or any combination thereof to the alkyl furan compounds. In an embodiment, nylon 12 may be produced from waste stream biomass. The biomass may be lignocellulosic biomass, and the biomass may be obtained from waste streams of a variety of other processes, such as, for example, waste wood chips and sawdust from lumber and paper production.

[0019] In an embodiment, the alkyl furan compound **1A** may be 5-chloromethylfurfural, wherein M1 is  . The 5-chloromethylfurfural may be produced from biomass by heating the hexoses, sucrose, cellulose, sugarcane bagasse, or corn stover, or any combination thereof in the presence of at least one solvent. Some examples of the solvent may include, but are not limited to, a mixture of 1,2-dichloroethane and hydrochloric acid, or a mixture of dichloromethane and hydrochloric acid. The reaction may be carried out in the presence of an alkaline salt. Some examples of alkaline salts may include, but are not limited to, lithium halide, sodium halide, or potassium halide, or any combination thereof.

[0020] In an embodiment, the alkyl furan compound **2A** may be 5-hydroxymethylfurfural wherein M1 is  . The 5-hydroxymethylfurfural may be produced from biomass by heating the hexoses, or cellulose, or any combination thereof in the presence of at least one of an acid and a metal salt catalyst.

[0021] To prepare reactants for the production of the ester-aldehyde dimers **3**, alkyl furan compounds **1A**, may be converted to dimethylacetal protected Wittig reagents **1**

of formula  . In addition, furan compounds **2A** may be oxidized to produce carboxylic acids of formula HO(O=)C—M1—C(=O)H, and the carboxylic acid may be alkylated to produce carboxylic acid alkyl esters **2** of formula RO(O=)C—M1—C(=O)H. The Wittig reagents **1** may be reacted with the carboxylic acid alkyl esters **2** to produce the ester-aldehyde dimers **3**.

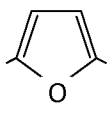
[0022] The 5-chloromethyl furan compounds **1A** may be converted to the dimethylacetal protected Wittig reagents **1** by treating the 5-chloromethyl furan compounds with triphenylphosphine, triarylphosphine, trialkyphosphine, or diarylalkylphosphine, or any combination thereof, followed by reaction with an alcohol in the presence of an acid catalyst. The alcohol may be, but is not limited to, methanol, ethanol, propanol, or ethylene glycol, or any combination thereof. The acid catalyst may be, but is not limited to, hydrochloric acid, sulfuric acid, methanesulfonic acid, or toluenesulfonic acid, or any combination thereof.

[0023] The 5-hydroxymethyl furan compounds **2A** may be oxidized under phase transfer conditions with 4-benzoyloxy-2,2,6,6-tetramethylpiperidin-1-oxyl to produce the intermediary carboxylic acid. Alternatively, the 5-hydroxymethyl furan compounds **2A** may be oxidized by electrochemical oxidation. The carboxylic acid may be alkylated by treating the carboxylic acid with an alkyl alcohol and at least one of toluenesulfonic acid, sulfuric acid, and methanesulfonic acid to produce a corresponding alkyl ester dimethylacetal, that may then be treated with aqueous acid to produce the carboxylic acid alkyl ester **2**.

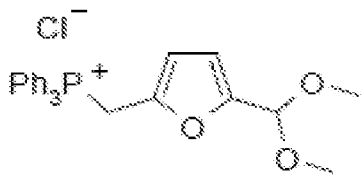
[0024] In an additional reaction sequence, the ester-aldehyde dimer **3** may be converted to the amino-ester **4**. In an embodiment, this may be carried out by aminating the

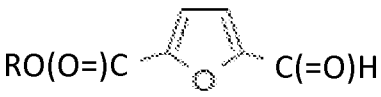
ester-aldehyde dimer **3** with at least one of ammonium hydroxide , ammonia, and hydroxylamine in the presence of hydrogen and a catalyst. The catalyst may include nickel catalysts. In an alternative embodiment, the ester-aldehyde dimer **3** may be converted to the amino-ester **4** by treating the ester-aldehyde with hydroxylamine to produce a corresponding ester-oxime, treating the ester-oxime with hydrogen and a nickel catalyst to produce the amino-ester. In another alternative embodiment, the ester-aldehyde dimer **3** may be converted to the amino-ester **4** by reductive amination of the ester-aldehyde. The reductive amination may include treating the ester –aldehyde with a mixture of sodium cyanoborohydride, ammonium acetate, aqueous ammonium hydroxide and an alcohol. The alcohol may include, but is not limited to, methanol, ethanol, propanol, butanol, or pentanol, or any combination thereof.

[0025] In embodiments, some manufacturers and/or users of nylon 12 for products or portions of articles of manufacture, may want to produce the nylon 12 on site. The ester-aldehyde dimers **3** or the amino-ester dimers **4** may be provided as precursor materials for the production of nylon 12. The components for the production of nylon 12 may be provided as a kit. In an embodiment, a kit for the production of nylon 12 may include the amino-ester dimer and additional reactants for the hydrogenation/hydrodeoxygenation/polycondensation of the amino-ester dimer. The additional reactants may include hydrogen iodide as a halide source, and a platinum catalyst mounted on a support, and the components may be pre-measured and ready for the hydrogenation/hydrodeoxygenation/polycondensation reaction.

[0026] In an embodiment for producing nylon 12, M1 may be 

, and R may be methyl. In preliminary reaction stages, 5-chloromethylfurfural (**CMF** in FIG. 2) may be converted to dimethylacetal protected Wittig reagent **11** of formula



, and 5-hydroxymethylfurfural (**HMF** in FIG. 2) may be oxidized to form 5-formylfuroic acid, that may then be methylated to produce methyl 5-formylfuroate **12** of formula 

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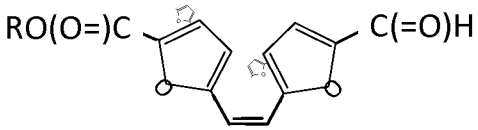
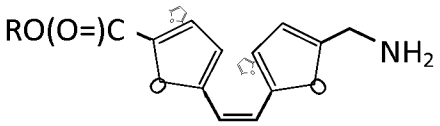
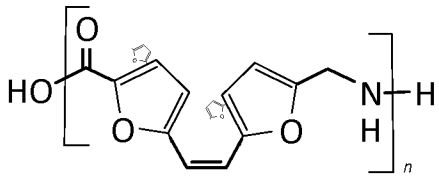
[0027] The Wittig reagent **11** may be reacted with the methyl 5-formylfuroate **12** to produce ester-aldehyde dimers **13** of formula 

. The ester-aldehyde dimers **13** may be converted to amino-esters by amination of the ester-aldehyde to produce amino-esters **14** of formula 

. The amino-esters **14** may be converted to nylon 12 by a single-pot hydrogenation-hydrodeoxygenation-polymerization reaction via intermediary products of the amino-esters **15** of formula 

, and polymers **16** of formula 

, where $n \geq 1$.

[0028] As mentioned herein, nylon 12 may be produced from waste stream biomass, and, as represented in FIG. 2, a method for producing nylon 12 from waste stream biomass may include converting the biomass to 5-chloromethylfurfural and 5-

hydroxymethylfurfural, and using the 5-chloromethylfurfural and 5-hydroxymethylfurfural as reactants for producing nylon 12.

EXAMPLES

EXAMPLE 1: Ester Precursors for Production of Nylon 12

[0029] Ester-aldehyde dimers and amino-ester dimers are produced from 6-carbon furan compounds as precursors for at least the production of nylon 12, as well as other alternative uses.

[0030] A mixture of 5-chloromethyl furfural (CMF, 1 equivalent) and triphenylphosphine (1 equivalent) in dry toluene is heated under reflux for about 2 hours. After cooling, the solid is filtered and rinsed with dry toluene to provide [(5-formyl-2-furanyl)methyl]triphenylphosphonium chloride. A mixture of this phosphonium chloride (1 equivalent), trimethyl orthoformate (1.75 equivalents), and p-toluenesulfonic acid (0.001 equivalent) in dry methanol is heated under reflux for about 3 hours. After cooling, sodium acetate (0.002 equivalent) is added and the mixture is concentrated under reduced pressure. Toluene is added and the precipitate is filtered to yield Wittig reagent **11**.

[0031] A mixture of 5-hydroxymethyl furfural (HMF, 1 equivalent), potassium methoxide (0.25 equivalent), gold on titanium oxide catalyst (0.005 equivalent gold) and methanol is treated with oxygen gas (1 atmosphere) for about 24 hours. The catalyst is removed by filtration and rinsed with methanol. The combined filtrates are concentrated under reduced pressure to yield methyl 5-(hydroxymethyl)-2-furoate. A mixture of methyl 5-(hydroxymethyl)-2-furoate (1 equivalent), o-iodoxybenzoic acid (3 equivalents), and ethyl acetate as solvent, is heated under reflux for about 3 hours. Byproducts are removed by filtration, and the filtrate is concentrated under reduced pressure to yield methyl 5-formyl-2-furoate **12** (R = Me).

[0032] To a solution of Wittig reagent **11** (1 equivalent) and methyl 5-formyl-2-furoate **12** (R = Me) (1 equivalent) in dry methanol is added a solution of lithium methoxide in dry methanol at a rate that maintains the reaction temperature below about 35 °C. After being stirred for about 3 hours, the mixture is concentrated under reduced pressure. The residue is treated with water and extracted with toluene. The extract is dried over magnesium sulfate and concentrated under reduced pressure. Diethyl ether is added to precipitate and triphenylphosphine oxide byproduct is removed by filtration. The filtrate is concentrated under reduced pressure and the residue is treated with 5% hydrochloric acid in 70% aqueous methanol. After being stirred for about 3 hours, the mixture is neutralized by addition of saturated aqueous sodium bicarbonate solution, and then concentrated under reduced pressure to remove the methanol. The aqueous mixture is extracted with toluene. The extract is washed with water, dried over magnesium sulfate, and concentrated under reduced pressure to provide ester-aldehyde dimer **13** as a mixture of cis and trans isomers. The ester-aldehyde dimer **13** may be provided as a precursor for production of nylon 12, as well as other potential uses.

[0033] A mixture of ester-aldehyde dimer **13** (1 equivalent), hydroxylamine hydrochloride (1 equivalents), potassium acetate (1 equivalents) and 50% aqueous ethanol is heated at about 50 °C for about 1 hour. After cooling, the precipitate is filtered, washed with water and dried under reduced pressure to yield the corresponding oxime derivative of ester-aldehyde dimer **13**. The oxime derivative of the ester-aldehyde dimer **13** may be provided as a precursor for production of nylon 12, as well as other potential uses.

[0034] A mixture of the oxime derivative of ester-aldehyde dimer **13**, Raney nickel catalyst, and tetrahydrofuran as solvent is treated with hydrogen gas (50 bar) in an autoclave for about 1 hour. The catalyst is removed by filtration and rinsed with tetrahydrofuran under argon. The combined filtrates are concentrated under reduced pressure

to yield amino-ester dimer **14** (R = Me). The amino-ester dimer **14** (R = Me) may be provided as a precursor for production of nylon 12, as well as other potential uses.

EXAMPLE 2: A KIT FOR THE PRODUCTION OF NYLON 12

[0035] A kit for the production of nylon 12 will include the amino-ester dimer **14** (R = Me) and additional reactants for the hydrogenation/hydrodeoxygenation/polycondensation of the amino-ester dimer **14** (R = Me). The additional reactants will include at least hydrogen iodide as a halide source, and a palladium catalyst mounted on silica. The kit may also include acetic acid and hydrogen gas.

EXAMPLE 3: PRODUCTION OF NYLON 12

The products of the kit of Example 2 will be used to produce nylon 12. A mixture of amino-ester dimer **14** (1 equivalent), 5% palladium on silica (0.01 equivalent palladium), and acetic acid solvent is heated in an autoclave at about 160 °C while treating with hydrogen (about 50 atmospheres pressure) for about 3 hours. The mixture is cooled, hydrogen iodide (1 equivalent) is added, and the mixture is again heated at about 160 °C while treating with hydrogen (about 50 atmospheres) for about 3 hours. The mixture is cooled, and then filtered to remove the catalyst. The solvent is removed by distillation under reduced pressure to yield methyl 12-aminododecanoate. The methyl 12-aminododecanoate is heated at about 270 °C for about 5 hours to provide nylon 12.

EXAMPLE 4: GENERATION OF NYLON 12 REACTANTS FROM WASTE STREAM PRODUCTS

[0036] Nylon 12 may be produced by the process described in Examples 1-3 from 5-hydroxymethylfurfural and 5-chloromethylfurfural derived from waste stream biomass. Lignocellulosic biomass materials, such as corn stover, sugarcane bagasse, wood chips and sawdust will be obtained from a paper mill, or other waste streams. The biomass will be

processed to isolate hexoses, glucose and fructose from the biomass. For 5-hydroxymethylfurfural, the hexoses will be dehydrated by heating the hexoses in the presence of at least one of an acid and a metal salt catalyst to form the 5-hydroxymethylfurfural. For 5-chloromethylfurfural, the hexoses will be chlorinated by heating in the presence of 1,2-dichloroethane and an acid to produce the 5-chloromethyl furfural.

[0037] The examples demonstrate that nylon 12 may be produced from waste products in only a few process steps with high yields, thereby providing an alternative and environmentally friendly method for the production of nylon 12 that does not require petrochemically derived raw materials. The disclosed approach is unlikely to suffer from an explosion risk as is associated with production of the nylon 12 precursor cyclododecatriene.

[0038] This disclosure is not limited to the particular systems, devices and methods described, as these may vary. The terminology used in the description is for the purpose of describing the particular versions or embodiments only, and is not intended to limit the scope.

[0039] In the above detailed description, reference is made to the accompanying drawings, which form a part hereof. In the drawings, similar symbols typically identify similar components, unless context dictates otherwise. The illustrative embodiments described in the detailed description, drawings, and claims are not meant to be limiting. Other embodiments may be used, and other changes may be made, without departing from the spirit or scope of the subject matter presented herein. It will be readily understood that the aspects of the present disclosure, as generally described herein, and illustrated in the Figures, can be arranged, substituted, combined, separated, and designed in a wide variety of different configurations, all of which are explicitly contemplated herein.

[0040] The present disclosure is not to be limited in terms of the particular embodiments described in this application, which are intended as illustrations of various aspects. Many modifications and variations can be made without departing from its spirit and scope, as will be apparent to those skilled in the art. Functionally equivalent methods and apparatuses within the scope of the disclosure, in addition to those enumerated herein, will be apparent to those skilled in the art from the foregoing descriptions. Such modifications and variations are intended to fall within the scope of the appended claims. The present disclosure is to be limited only by the terms of the appended claims, along with the full scope of equivalents to which such claims are entitled. It is to be understood that this disclosure is not limited to particular methods, reagents, compounds, compositions or biological systems, which can, of course, vary. It is also to be understood that the terminology used herein is for the purpose of describing particular embodiments only, and is not intended to be limiting.

[0041] As used in this document, the singular forms "a," "an," and "the" include plural references unless the context clearly dictates otherwise. Unless defined otherwise, all technical and scientific terms used herein have the same meanings as commonly understood by one of ordinary skill in the art. Nothing in this disclosure is to be construed as an admission that the embodiments described in this disclosure are not entitled to antedate such disclosure by virtue of prior invention. As used in this document, the term "comprising" means "including, but not limited to."

[0042] While various compositions, methods, and devices are described in terms of "comprising" various components or steps (interpreted as meaning "including, but not limited to"), the compositions, methods, and devices can also "consist essentially of" or "consist of" the various components and steps, and such terminology should be interpreted as defining essentially closed-member groups.

[0043] With respect to the use of substantially any plural and/or singular terms herein, those having skill in the art can translate from the plural to the singular and/or from the singular to the plural as is appropriate to the context and/or application. The various singular/plural permutations may be expressly set forth herein for sake of clarity.

[0044] It will be understood by those within the art that, in general, terms used herein, and especially in the appended claims (*e.g.*, bodies of the appended claims) are generally intended as "open" terms (*e.g.*, the term "including" should be interpreted as "including but not limited to," the term "having" should be interpreted as "having at least," the term "includes" should be interpreted as "includes but is not limited to," etc.). It will be further understood by those within the art that if a specific number of an introduced claim recitation is intended, such an intent will be explicitly recited in the claim, and in the absence of such recitation no such intent is present. For example, as an aid to understanding, the following appended claims may contain usage of the introductory phrases "at least one" and "one or more" to introduce claim recitations. However, the use of such phrases should not be construed to imply that the introduction of a claim recitation by the indefinite articles "a" or "an" limits any particular claim containing such introduced claim recitation to embodiments containing only one such recitation, even when the same claim includes the introductory phrases "one or more" or "at least one" and indefinite articles such as "a" or "an" (*e.g.*, "a" and/or "an" should be interpreted to mean "at least one" or "one or more"); the same holds true for the use of definite articles used to introduce claim recitations. In addition, even if a specific number of an introduced claim recitation is explicitly recited, those skilled in the art will recognize that such recitation should be interpreted to mean at least the recited number (*e.g.*, the bare recitation of "two recitations," without other modifiers, means at least two recitations, or two or more recitations). Furthermore, in those instances where a convention analogous to "at least one of A, B, and C, etc." is used, in general such a construction is

intended in the sense one having skill in the art would understand the convention (*e.g.*, " a system having at least one of A, B, and C" would include but not be limited to systems that have A alone, B alone, C alone, A and B together, A and C together, B and C together, and/or A, B, and C together, etc.). In those instances where a convention analogous to "at least one of A, B, or C, etc." is used, in general such a construction is intended in the sense one having skill in the art would understand the convention (*e.g.*, " a system having at least one of A, B, or C" would include but not be limited to systems that have A alone, B alone, C alone, A and B together, A and C together, B and C together, and/or A, B, and C together, etc.). It will be further understood by those within the art that virtually any disjunctive word and/or phrase presenting two or more alternative terms, whether in the description, claims, or drawings, should be understood to contemplate the possibilities of including one of the terms, either of the terms, or both terms. For example, the phrase "A or B" will be understood to include the possibilities of "A" or "B" or "A and B."

[0045] In addition, where features or aspects of the disclosure are described in terms of Markush groups, those skilled in the art will recognize that the disclosure is also thereby described in terms of any individual member or subgroup of members of the Markush group.

[0046] As will be understood by one skilled in the art, for any and all purposes, such as in terms of providing a written description, all ranges disclosed herein also encompass any and all possible subranges and combinations of subranges thereof. Any listed range can be easily recognized as sufficiently describing and enabling the same range being broken down into at least equal halves, thirds, quarters, fifths, tenths, etc. As a non-limiting example, each range discussed herein can be readily broken down into a lower third, middle third and upper third, etc. As will also be understood by one skilled in the art all language such as "up to," "at least," and the like include the number recited and refer to ranges which

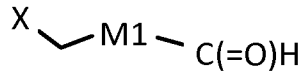
can be subsequently broken down into subranges as discussed above. Finally, as will be understood by one skilled in the art, a range includes each individual member. Thus, for example, a group having 1-3 cells refers to groups having 1, 2, or 3 cells. Similarly, a group having 1-5 cells refers to groups having 1, 2, 3, 4, or 5 cells, and so forth.

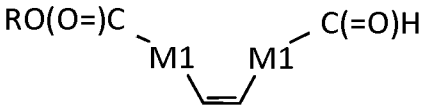
[0047] Various of the above-disclosed and other features and functions, or alternatives thereof, may be combined into many other different systems or applications. Various presently unforeseen or unanticipated alternatives, modifications, variations or improvements therein may be subsequently made by those skilled in the art, each of which is also intended to be encompassed by the disclosed embodiments.

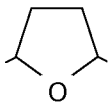
CLAIMS

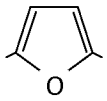
What Is Claimed Is:

1. A method for producing nylon 12, the method comprising:

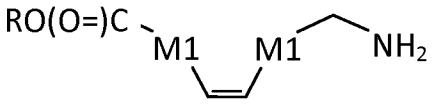
converting alkyl furan compounds of formula 

to an ester- aldehyde dimer of formula 

, wherein X is –OH or halogen, R is C_1-C_5 alkyl, and M1 is 

or 

;

converting the ester-aldehyde dimer to an amino-ester of formula 

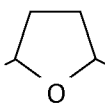
; and

converting the amino-ester to nylon 12.

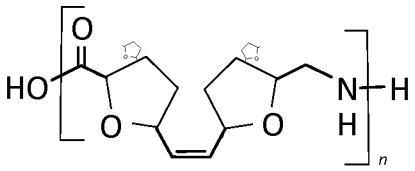
2. The method of claim 1, wherein converting the amino-ester to nylon 12 comprises a hydrogenation-hydrodeoxygenation-polymerization reaction.

3. The method of claim 2, wherein the hydrogenation-hydrodeoxygenation-polymerization reaction comprises treating the amino-ester with a halide source and hydrogen gas in the presence of a catalyst.

4. The method of claim 3, wherein the hydrogenation-hydrodeoxygenation-polymerization reaction comprises a single pot reaction wherein:

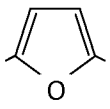
amino esters having M1 of 

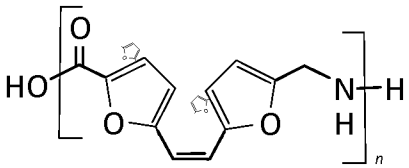
produce intermediary products of



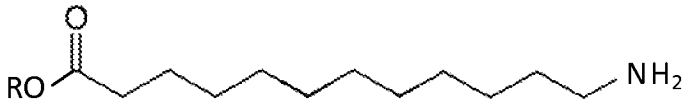
and

; and

amino esters having M1 of  produce intermediary products of



and



, where $n \geq 2$.

5. The method of claim 3, wherein the halide source is at least one hydrogen halide.

6. The method of claim 3, wherein the halide source is hydrogen iodide, hydrogen chloride, hydrogen bromide, or any combination thereof.

7. The method of claim 3, wherein the catalyst comprises platinum, palladium, rhodium, ruthenium, nickel, cobalt, iron, molybdenum, iridium, rhenium, gold, or any combination thereof.

8. The method of claim 3, wherein the catalyst is mounted on a support.

9. The method of claim 1, further comprising producing the alkyl furan compounds from biomass by isolating hexoses, sucrose, cellulose, corn stover, or any

combination thereof from the biomass, and converting the hexoses, sucrose, cellulose, corn stover, or any combination thereof to the alkyl furan compounds.

10. The method of claim 9, wherein the alkyl furan compounds comprise 5-chloromethylfurfural, and producing the 5-chloromethylfurfural from biomass comprises heating the hexoses, sucrose, cellulose, corn stover, or any combination thereof in the presence of 1,2-dichloroethane and hydrochloric acid.

11. The method of claim 9, wherein the alkyl furan compounds comprise 5-chloromethylfurfural, and producing the 5-chloromethylfurfural from biomass comprises heating the hexoses, sucrose, cellulose, corn stover, or any combination thereof in the presence of 1,2-dichloroethane, hydrochloric acid, and an alkaline salt.

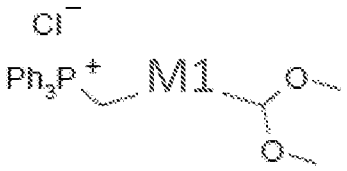
12. The method of claim 11, wherein the alkaline salt comprises lithium halide, sodium halide, potassium halide, or any combination thereof.

13. The method of claim 9, wherein the alkyl furan compounds comprise 5-hydroxymethylfurfural, and producing the 5-hydroxymethylfurfural from biomass comprises heating the hexoses, cellulose, or any combination thereof in the presence of at least one of an acid and a metal salt catalyst.

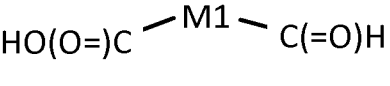
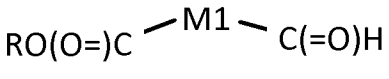
14. The method of claim 1, wherein:

the alkyl furan compounds comprise both 5-chloromethyl furan compounds and 5-hydroxymethyl furan compounds; and

converting the alkyl furan compounds to the ester-aldehyde dimers comprises:

converting the 5-chloromethyl furan compounds to dimethylacetal protected Wittig reagents of formula 

;

oxidizing the 5-hydroxymethyl furan compounds to produce a carboxylic acid  , and alkylating the carboxylic acid to produce a carboxylic acid alkyl ester of formula  ; and

reacting the Wittig reagent with the carboxylic acid alkyl ester to produce the ester-aldehyde dimers.

15. The method of claim 14, wherein converting the 5-chloromethyl furan compounds to dimethylacetal protected Wittig reagents comprises treating the 5-chloromethyl furan compounds with triphenylphosphine, triarylphosphine, trialkyphosphine, diarylalkylphosphine, or any combination thereof, followed by reaction with an alcohol in the presence of an acid catalyst.

16. The method of claim 15, wherein the alcohol comprises methanol, ethanol, propanol, ethylene glycol, or any combination thereof, and the acid catalyst comprises hydrochloric acid, sulfuric acid, methanesulfonic acid, toluenesulfonic acid. or any combination thereof.

17. The method of claim 14, wherein oxidizing the 5-hydroxymethyl furan compounds comprises oxidizing the 5-hydroxymethyl furan compounds under phase transfer conditions with 4-benzoyloxy-2,2,6,6-tetramethylpiperidin-1-oxyl.

18. The method of claim 14, wherein alkylating the carboxylic acid comprises treating the carboxylic acid with an alkyl alcohol and at least one of toluenesulfonic acid, sulfuric acid, and methanesulfonic acid to produce a corresponding alkyl ester

dimethylacetal, and treating the alkyl ester dimethylacetal with aqueous acid to produce the carboxylic acid alkyl ester.

19. The method of claim 1, wherein converting the ester-aldehyde dimer to an amino-ester comprises aminating the ester-aldehyde with at least one of ammonium hydroxide, ammonia, and hydroxylamine in the presence of hydrogen and a catalyst.

20. The method of claim 19, wherein the catalyst comprises a nickel catalyst.

21. The method of claim 1, wherein converting the ester-aldehyde dimer to an amino-ester comprises:

treating the ester-aldehyde with hydroxylamine to produce a corresponding ester-oxime; and

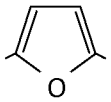
treating the ester-oxime with hydrogen and a nickel catalyst to produce the amino-ester.

22. The method of claim 1, wherein converting the ester-aldehyde dimer to an amino-ester comprises reductive amination of the ester-aldehyde.

23. The method of claim 22, wherein the reductive amination comprises treating the ester –aldehyde with a mixture of sodium cyanoborohydride, ammonium acetate, aqueous ammonium hydroxide and an alcohol.

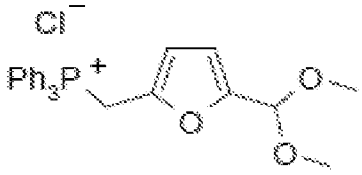
24. The method of claim 23, wherein the alcohol comprises methanol, ethanol, propanol, butanol, pentanol, or any combination thereof.

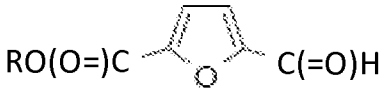
25. The method of claim 1, wherein:

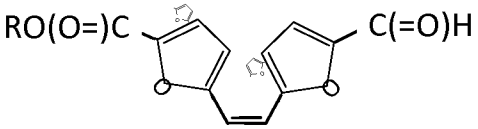
M1 is 

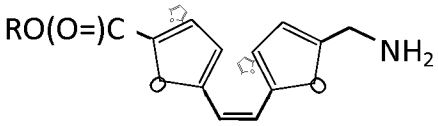
, and R is methyl;

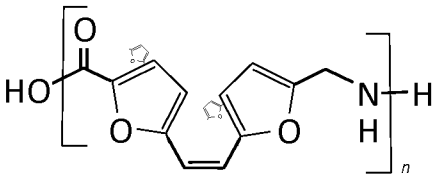
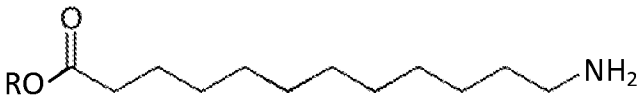
converting the alkyl furan compounds to the ester-aldehyde dimers comprises:

converting 5-chloromethylfurfural to dimethylacetal protected Wittig reagent of formula  ;

oxidizing 5-hydroxymethylfurfural to 5-formylfuroic acid, and methylating the 5-formylfuroic acid to produce methyl 5-formylfuroate of formula  ; and

reacting the Wittig reagent with the methyl 5-formylfuroate to produce ester-aldehyde dimers of formula  ;

converting the ester-aldehyde dimer to an amino-ester comprises amination of the ester-aldehyde to produce amino-esters of formula  ; and

converting the amino-esters to nylon 12 comprises a single-pot hydrogenation-hydrodeoxygenation-polymerization reaction via intermediary products of  and  , where $n \geq 2$.

26. A method for producing nylon 12 from waste stream biomass, the method comprising:

converting the biomass to 5-chloromethylfurfural and 5-hydroxymethylfurfural; and

using the 5-chloromethylfurfural and 5-hydroxymethylfurfural as reactants for producing nylon 12.

27. The method of claim 26, wherein the biomass is lignocellulosic biomass.

28. The method of claim 26, wherein converting the biomass to 5-hydroxymethylfurfural comprises heating biomass derived hexoses, cellulose, or combination thereof in the presence of at least one of an acid and a metal salt catalyst to produce the 5-hydroxymethyl furfural.

29. The method of claim 28, further comprising isolating the hexoses, the cellulose, or the combination thereof from the biomass.

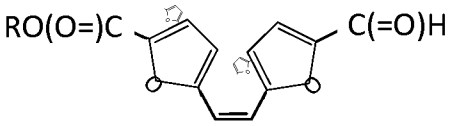
30. The method of claim 26, wherein converting the biomass to 5-chloromethylfurfural comprises heating biomass derived hexoses, sucrose, cellulose, corn stover, or combination thereof in the presence of 1,2-dichloroethane and an acid to produce the 5-chloromethyl furfural.

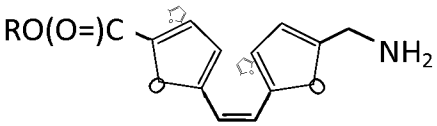
31. The method of claim 26, wherein converting the biomass to 5-chloromethylfurfural comprises heating biomass derived hexoses, sucrose, cellulose, corn stover, or combination thereof in the presence of 1,2-dichloroethane, hydrochloric acid, and an alkaline salt to produce the 5-chloromethyl furfural.

32. The method of claim 31, wherein the alkaline salt comprises lithium halide, sodium halide, potassium halide, or any combination thereof.

33. The method of claim 31, further comprising isolating the hexoses, the sucrose, the cellulose, the corn stover, or the combination thereof from the biomass.

34. The method of claim 26, wherein using the 5-chloromethylfurfural and 5-hydroxymethylfurfural as reactants comprises:

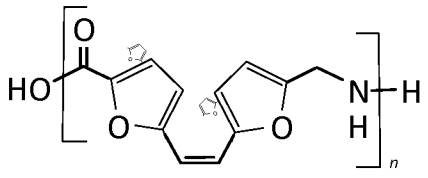
producing an intermediary ester- aldehyde dimer of formula  from the 5-chloromethylf 5-hydroxymethylfurfural, wherein R is C1-C5 alkyl;

converting the ester-aldehyde dimer to an amir ula  ; and

converting the amino-ester to nylon 12.

35. The method of claim 34, wherein converting the amino-ester to nylon 12 comprises a hydrogenation-hydrodeoxygenation-polymerization reaction.

36. The method of claim 35, wherein the hydrogenation-hydrodeoxygenation-polymerization reaction comprises treating the amino-ester with a halide source and hydrogen gas in the presence of a catalyst.

37. The method of claim 36, wherein the hydrogenation-hydrodeoxygenation-polymerization reaction comprises a single pot reaction with intermediary products of  and  , wherein n ≥ 2.

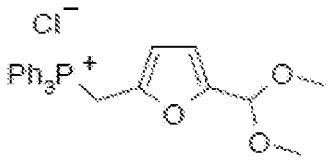
38. The method of claim 36, wherein the halide source is at least one hydrogen halide.

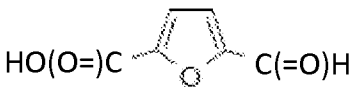
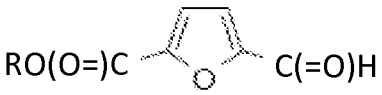
39. The method of claim 36, wherein the halide source is hydrogen iodide, hydrogen chloride, hydrogen bromide, or a combination thereof.

40. The method of claim 36, wherein the catalyst comprises platinum, palladium, rhodium, ruthenium, nickel, cobalt, iron, molybdenum, iridium, rhenium, gold, or any combination thereof.

41. The method of claim 36, wherein the catalyst is mounted on a support.

42. The method of claim 34, wherein producing the intermediary ester- aldehyde dimer comprises:

converting 5-chloromethylfurfural to dimethylacetal protected Wittig reagents of formula  ;

oxidizing 5-hydroxymethylfurfural to produce a carboxylic acid  , and alkylating the carboxylic acid to produce a carboxylic acid alkyl ester of formula  ; and

reacting the Wittig reagent with the carboxylic acid alkyl ester to produce the ester-aldehyde dimers.

43. The method of claim 42, wherein converting 5-chloromethylfurfural compounds to dimethylacetal protected Wittig reagents comprises treating the 5-chloromethyl furan compounds with triphenylphosphine, triarylphosphine, trialkyphosphine,

diarylalkylphosphine, or any combination thereof, followed by reaction with an alcohol in the presence of an acid catalyst.

44. The method of claim 43, wherein the alcohol comprises methanol, ethanol, propanol, ethylene glycol, or any combination thereof, and the acid catalyst comprises hydrochloric acid, sulfuric acid, methanesulfonic acid, toluenesulfonic acid. or any combination thereof.

45. The method of claim 42, wherein oxidizing the 5-hydroxymethylfurfural compounds comprises oxidizing the 5-hydroxymethylfurfural compounds with 4-benzoyloxy-2,2,6,6-tetramethylpiperidin-1-oxyl under phase transfer conditions.

46. The method of claim 42, wherein alkylating the carboxylic acid comprises treating the carboxylic acid with an alkyl alcohol and at least one of toluenesulfonic acid, sulfuric acid, and methanesulfonic acid to produce a corresponding alkyl ester dimethylacetal, and treating the alkyl ester dimethylacetal with aqueous acid to produce the carboxylic acid alkyl ester..

47. The method of claim 34, wherein converting the ester-aldehyde dimer to an amino-ester comprises aminating the ester-aldehyde with at least one of ammonium hydroxide, ammonia, and hydroxylamine in the presence of hydrogen and a catalyst.

48. The method of claim 47, wherein the catalyst comprises a nickel catalyst.

49. The method of claim 47, wherein the aminating comprises treating the ester-aldehyde with ammonium hydroxide in the presence of nickel catalyst.

50. The method of claim 34, wherein converting the ester-aldehyde dimer to an amino-ester comprises:

treating the ester-aldehyde with hydroxylamine to produce a corresponding ester-oxime; and

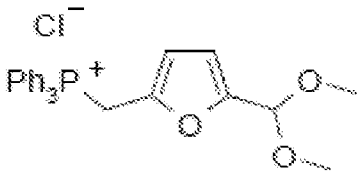
treating the ester-oxime with hydrogen and a nickel catalyst to produce the amino-ester.

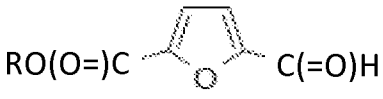
51. The method of claim 34, wherein converting the ester-aldehyde dimer to an amino-ester comprises reductive amination of the ester-aldehyde.

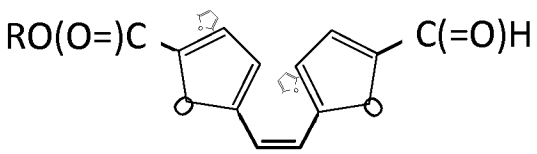
52. The method of claim 51, wherein the reductive amination comprises treating the ester –aldehyde with a mixture of sodium cyanoborohydride, ammonium acetate, aqueous ammonium hydroxide and an alcohol.

53. The method of claim 52, wherein the alcohol comprises methanol, ethanol, a propanol, a butanol, a pentanol, or any combination thereof.

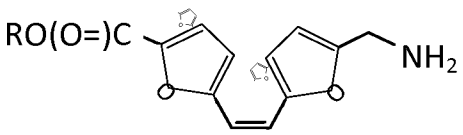
54. The method of claim 26, wherein using the 5-chloromethylfurfural and 5-hydroxymethylfurfural as reactants for producing nylon 12 comprises:

converting the 5-chloromethylfurfural to dimethylacetal protected Wittig reagent of formula  ;

oxidizing the 5-hydroxymethylfurfural to 5-formylfuroic acid, and methylating the 5-formylfuroic acid to produce methyl 5-formylfuroate of formula  , where R is $-CH_3$;

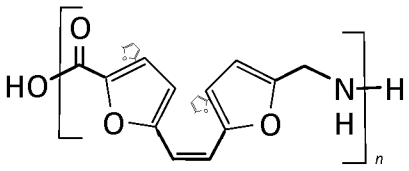
reacting the Wittig reagent with the methyl 5-formylfuroate to produce ester-aldehyde dimers of formula  ;

aminating the ester-aldehyde dimers to produce amino-esters of formula

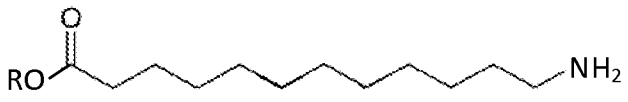


; and

converting the amino-esters to nylon 12 by a hydrogenation-hydrodeoxygenation-polymerization reaction via intermediary products of

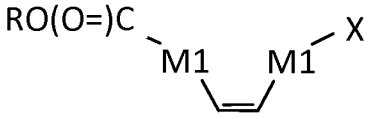
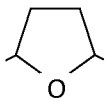
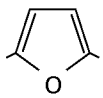


and



.

55. A kit for the production of nylon 12, the kit comprising:

a furan dimer compound of formula  , wherein R is C_1-C_5 alkyl, M1 is  or  , and X is –CHO or $–CH_2–NH_2$;

a halide source; and

a catalyst.

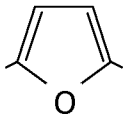
56. The kit of claim 55, wherein the halide source is at least one hydrogen halide.

57. The kit of claim 55, wherein the halide source is hydrogen iodide, hydrogen chloride, hydrogen bromide, or a combination thereof.

58. The kit of claim 55, wherein the catalyst comprises platinum, palladium, rhodium, ruthenium, nickel, cobalt, iron, molybdenum, iridium, rhenium, gold, or any combination thereof.

59. The kit of claim 58, wherein the catalyst is mounted on a support.

60. The kit of claim 55, wherein R is $–CH_3$ and X is $–CH_2–NH_2$.

61. The kit of claim 60, wherein M1 is 

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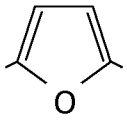
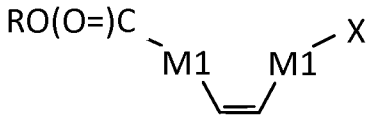
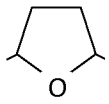
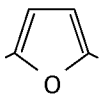
62. The kit of claim 55, wherein M1 is 

.

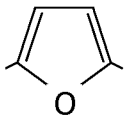
63. A furan dimer compound of formula 

, wherein R is C_1-C_5 alkyl, M1 is 

or 

, and X is –CHO or $–CH_2–NH_2$.

64. The compound of claim 63, wherein R is $–CH_3$ and X is –CHO.

65. The compound of claim 64, wherein M1 is 

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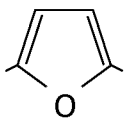
66. The compound of claim 63, wherein R is $–CH_3$ and X is $–CH_2–NH_2$.

67. The compound of claim 66, wherein M1 is 

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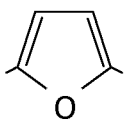
68. The compound of claim 63, wherein M1 is 

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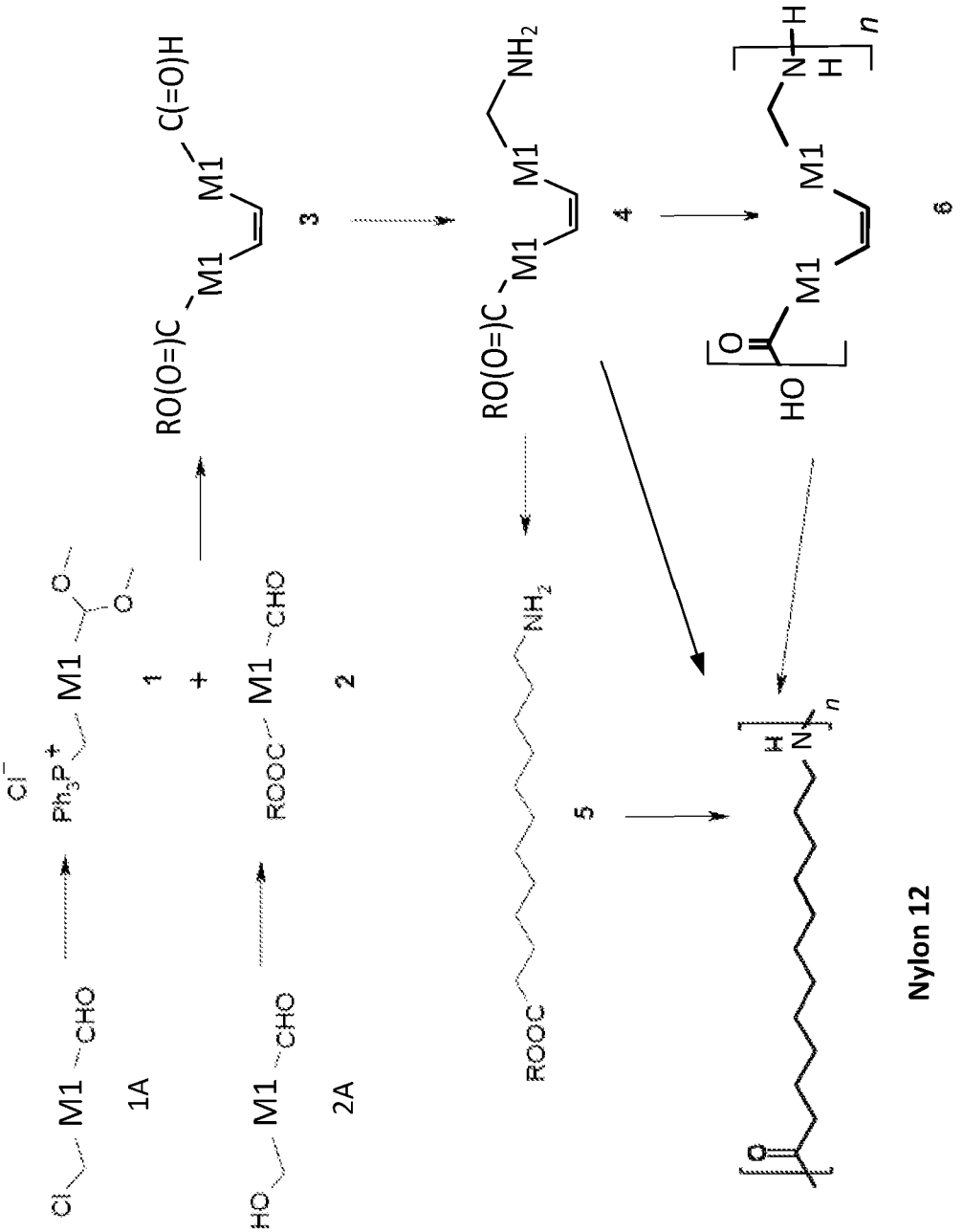
Cl
M1
CHO
1A
Cl⁻
Ph3P+
1
+
M1
CHO
2
HO
M1
CHO
2A
ROOC
RO(O=)C
M1
M1
C(=O)H
3
RO(O=)C
M1
M1
NH2
4
ROOC
NH2
5
HO
O
M1
M1
H
N
n
6
Nylon 12

FIG. 1

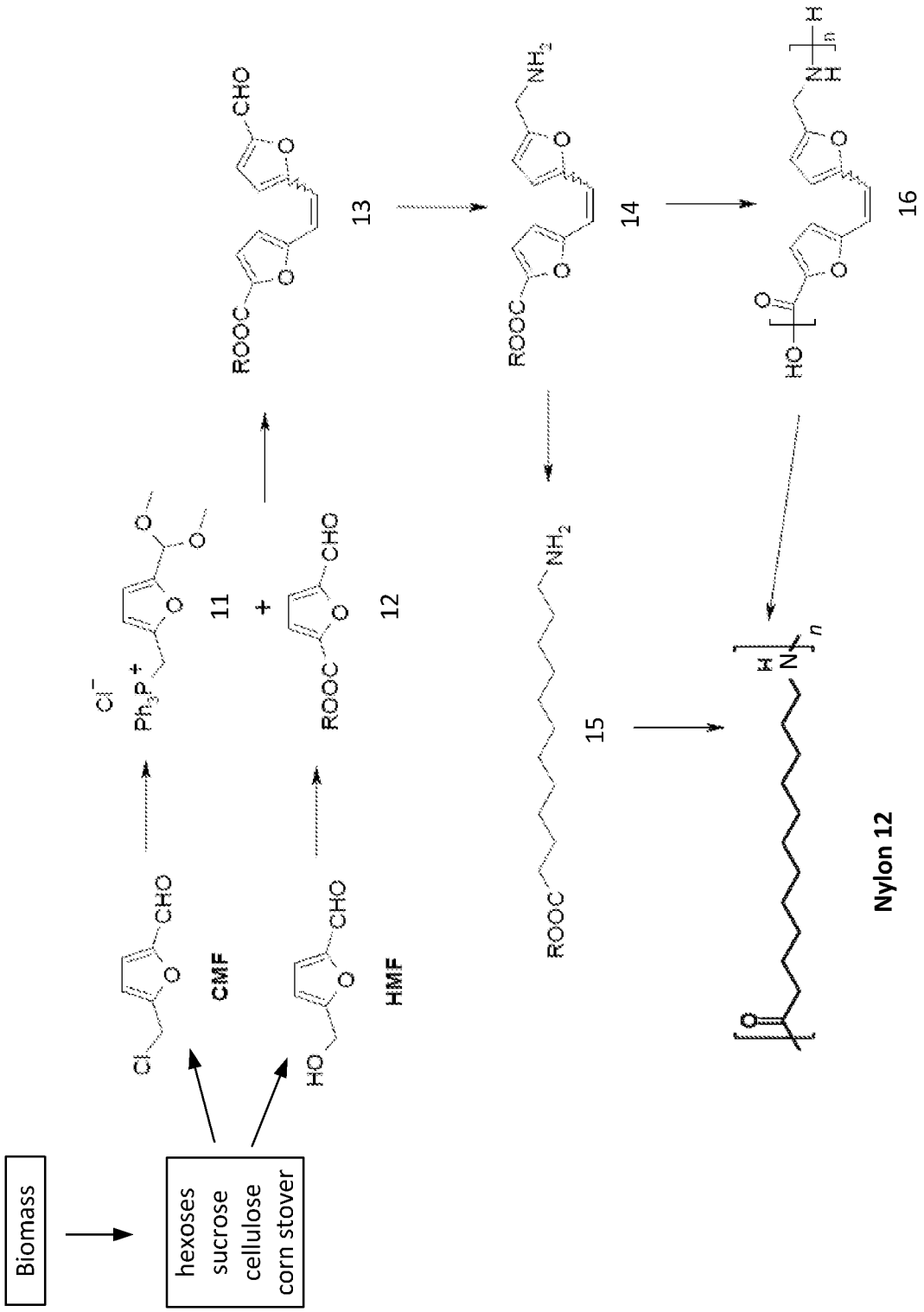
Biomass
hexoses
sucrose
cellulose
corn stover
CMF
HMF
11
12
13
14
15
16
Nylon 12

FIG. 2

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US14/23301

A. CLASSIFICATION OF SUBJECT MATTER
IPC(8) - C07D 307/02, 307/26 (2014.01)
USPC - 540/1; 562/524
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)
IPC(8): C07D 307/02, 307/26 (2014.01)
USPC: 540/1; 562/524

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)
MicroPatent (US-G, US-A, EP-A, EP-B, WO, JP-bib, DE-C,B, DE-A, DE-T, DE-U, GB-A, FR-A); ProQuest; Scifinder; Google/Google Scholar; KEYWORDS: empire, development, dimer, furan, biomass, ester-aldehyde, amino-ester, nylon 12, nylon-12, precursor, alkyl, furan, waste, stream, biomass, lignocellulosic

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5,530,148 A (NWAONICHA, CP et al.) 25 June 1996; abstract	1-68
A	US 2010/0317822 A1 (BOUSSIE, TR et al.) 16 December 2010; formulas I and III; paragraphs [0011]-[0012]	1-68
A	US 8,324,376 B2 (BINDER, JB et al.) 04 December 2012; column 11, lines 10-20	1-68
A	US 8,288,459 B2 (IWAMOTO, T) 16 October 2012; column 2, lines 1-23	1-68
A	US 6,423,768 B1 (KHOURI, FF) 23 July 2002; entire document	1-68
A	US 6,538,099 B2 (ISOBE, N et al.) 25 March 2003; entire document	1-68
A	US 7,776,996 B2 (DEININGER, J et al.) 17 August 2010; entire document	1-68
A	WO 2008/138568 A1 (LORENZ, G) 20 November 2008; entire document	1-68
A	WO 2013/034305 A1 (GOMES, M et al.) 14 March 2013; entire document	1-68

☐ Further documents are listed in the continuation of Box C. ☐

* 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
20 May 2014 (20.05.2014)	02 JUN 2014
Name and mailing address of the ISA/US Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-3201	Authorized officer: Shane Thomas PCT Helpdesk: 571-272-4300 PCT OSP: 571-272-7774

Form PCT/ISA/210 (second sheet) (July 2009)