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(54) **Title**: COMPOUNDS AND METHODS FOR PRODUCING NYLON 6

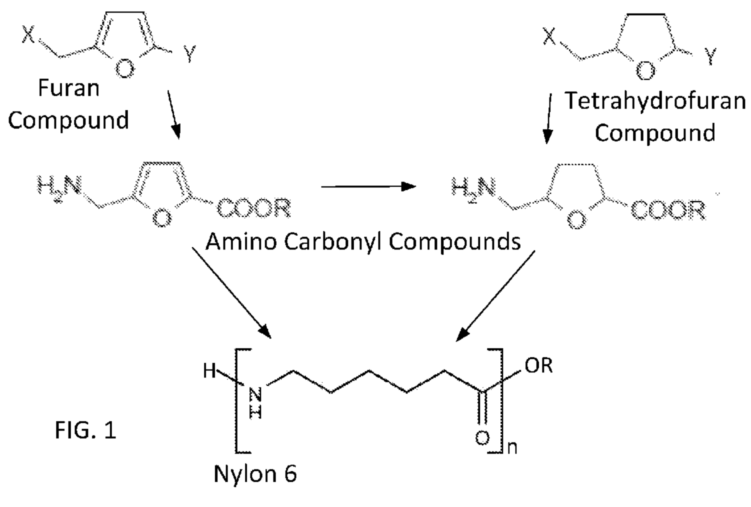


FIG. 1

(57) **Abstract**: Methods and compounds for producing nylon 6 are disclosed. Di-substituted furanic compounds may be used as the raw material for producing precursor compounds for nylon 6, and the precursor compounds are convertible to nylon 6.

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# COMPOUNDS AND METHODS FOR PRODUCING NYLON 6

## BACKGROUND

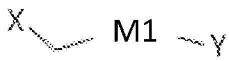
**[0001]** Nylon is a designation for a family of synthetic polymers known as aliphatic polyamides, and is one of the most commonly used polymers. The chemical constituents of nylon include carbon, hydrogen, nitrogen, and oxygen. Nylons may include condensation copolymers, such as nylon 6,6, that may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

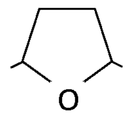
**[0002]** Types of nylons are distinguished by a numerical suffix that specifies the numbers of carbons donated by the monomers. For example, for nylons with a two-number designation, such as nylon 6,6 or nylon 6,12, the first number represents the number of carbons from the diamine monomer, and the second number represents the number of carbons from the diacid monomer. For nylons having a single number designation, such as nylon 4 or nylon 6, the number represents the number of carbon atoms in the repeating monomer units.

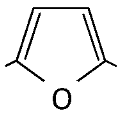
**[0003]** The 6 carbon commodity chemical caprolactam has global production on the order of 2 million metric tons per year. A major use of this commodity chemical is as a monomer in the manufacture of nylon 6. Current industrial processes for the manufacture of caprolactam use petrochemically derived benzene as the raw material. Efforts are being made to replace this petrochemically derived raw material with alternative raw materials, such as those that may be derived from biomass. Replacing current petrochemically derived caprolactam with biomass derived compounds may contribute to reducing greenhouse gas emissions. There remains a need to provide alternative scalable approaches for commercial production of nylon 6 from alternative raw materials.

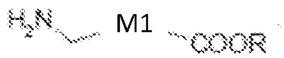
## SUMMARY

**[0004]** Nylon 6 may be produced from di-substituted furanic compounds as the raw material, wherein the furanic compounds may include furans or tetrahydrofurans. The di-substituted furanic compounds may be converted to amino carbonyl compounds, and the amino carbonyl compounds may be converted into nylon 6. In an embodiment, the di-substituted furanic compounds may be derived from biomass.

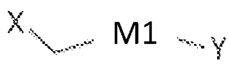
**[0005]** In an embodiment, a method for producing nylon 6 includes converting at least one furanic compound of formula 

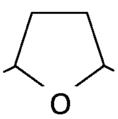
, wherein M1 is 

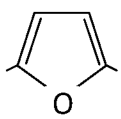
or 

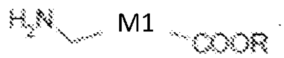
, X is -F, -Cl, -Br, -I, -OH, -$N_3$, an acetate, or sulfonate, and Y is -C(O)R or -C(O)OR, to an amino carbonyl compound of formula 

, wherein R is -H, alkyl, or substituted alkyl, and converting the amino carbonyl compound to nylon 6.

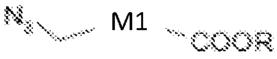
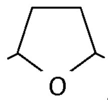
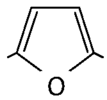
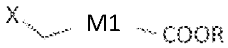
**[0006]** In an embodiment, a method for producing caprolactam includes converting at least one furanic compound of formula 

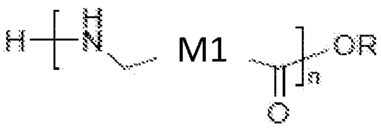
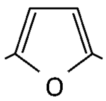
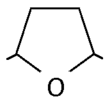
, wherein M1 is 

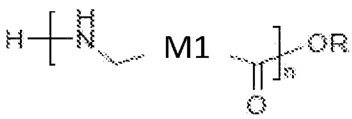
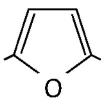
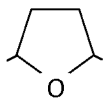
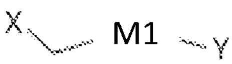
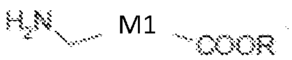
or 

, X is -F, -Cl, -Br, -I, -OH, -$N_3$, an acetate, or sulfonate, and Y is -C(O)R or -C(O)OR, to an amino carbonyl compound of formula 

, wherein R is -H, alkyl, or substituted alkyl, and converting the amino carbonyl compound to caprolactam.

**[0007]** In an embodiment, a method for producing a compound having a structure as represented by , wherein M1 is  or , R is –H, alkyl, or substituted alkyl, includes contacting at least one furanic compound having a structure , wherein X is -F, -Cl, -Br, -I, -OH, $-N_3$, an acetate, or a sulfonate, with at least one of an alkali metal azide and tetraalkylammonium azide.

**[0008]** In an embodiment, a polyamide may have a structure as represented by , wherein M1 is  or  and R is –H, alkyl, or substituted alkyl.

**[0009]** In an embodiment, a method for producing a polyamide having a structure as represented by , wherein M1 is  or  and R is –H, alkyl, or substituted alkyl, includes converting at least one furanic compound having a structure , wherein X is -F, -Cl, -Br, -I, -OH, $-N_3$, an acetate, or sulfonate, and Y comprises -C(O)R or -C(O)OR, to an amino carbonyl compound having a structure , wherein R is –H, an alkyl, or a substituted alkyl, and converting the amino carbonyl compound to the polyamide.

## BRIEF DESCRIPTION OF THE FIGURES

**[0010]** FIG. 1 generally depicts the production of nylon 6 from furanic compounds according to an embodiment.

**[0011]** FIG. 2 generally depicts the production of furfurals from biomass according to an embodiment.

**[0012]** FIG. 3A and 3B depict the conversion of furfurals to an amino carbonyl compound according to an embodiment.

**[0013]** FIG. 4 depicts the conversion of an amino carbonyl compound to nylon 6 according to an embodiment.

**[0014]** FIG. 5 illustrates a more detailed production of nylon 6 from a furan azidoacid precursor according to an embodiment.

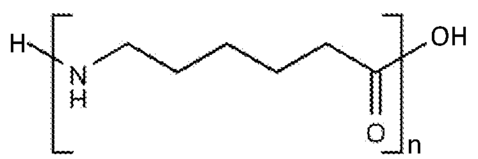
**[0015]** FIG. 6 illustrate a general reaction for production of nylon 6 via a polyamide route according to an embodiment.

**[0016]** FIGS. 7A and 7B illustrate detailed reactions for producing Nylon 6 from furan polyamides.

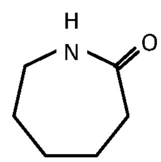
**[0017]** FIG. 8 illustrates an alternate method for producing nylon 6 from a tetrahydrofuran polyamide.

## DETAILED DESCRIPTION

**[0018]** Nylon 6, as indicated above, receives its numerical designation from the number of carbon atoms in its monomer units, wherein each monomer unit has 6 carbons.

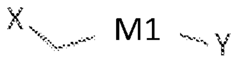
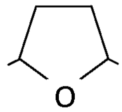
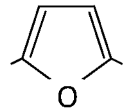
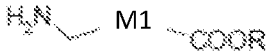



Nylon 6




Caprolactam

The 6-carbon monomers that form nylon 6 may be designated as derivatives of caprolactam.

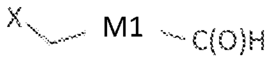
**[0019]** As generally represented in FIG. 1, Nylon 6 may be produced from furanic compounds of formula , where M1 is  or , X is -F, -Cl, -Br, -I, -OH, $-N_3$, an acetate, or a sulfonate, and Y is -C(O)R or -C(O)OR, with R being -H, an alkyl, or a substituted alkyl. The furanic compounds may be converted to amino carbonyl compounds of formula , and the carbonyl compounds may be converted to nylon 6.

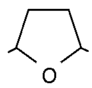
**[0020]** By using furanic compounds as raw materials for nylon 6, the use of petrochemically derived raw materials may be diminished or eliminated. Furanic compounds of the indicated formula may be derived from biomass. In an embodiment, when Y is –C(O)H and X is –OH (5-hydroxymethylfurfural, HMF) or –Cl (5-chloromethylmethylfurfural, CMF) the HMF or CMF may be directly derived from biomass or cellulose. In an alternative embodiment, hexoses may be isolated from biomass, and the hexoses converted to the furanic compounds. Hexoses may also be obtained from other sources.

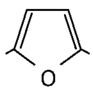
**[0021]** As an example, as represented in FIG. 2, the furanic compound may be 5-chloromethylfurfural (where X is –Cl and Y is –C(O)H in the above formula). Hexoses may be converted to 5-chloromethylfurfural by heating the hexoses with HCl, and 1,2-dichloroethane, with or without an alkaline salt. The alkaline salt may be lithium halide, sodium halide, potassium halide, or any combination thereof.

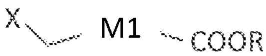
**[0022]** As an alternative example, as represented in FIG. 2, the furanic compound may be 5-hydroxymethylfurfural (where X is –OH and Y is –C(O)H in the above formula). Hexoses may be converted to 5-hydroxymethylfurfural by heating the hexoses with metal, and/or a salt or metal salt catalyst, with or without an acid. The salt/metal salt catalyst may be lithium chloride, lithium bromide, magnesium chloride, lanthanum (III) chloride, chromium (III) chloride, chromium (III) bromide, chromium (II) chloride, iron (III) chloride, copper (II) chloride, gold (III) chloride, tin (IV) chloride, aluminum (III) chloride, iridium (III) chloride, germanium (IV) chloride, ammonium chloride, ammonium bromide, tetraalkylammonium chloride, ammonium hydrosulfate, scandium (III) triflate, ytterbium (III) triflate, zirconium (IV) oxide, titanium (IV) oxide, tungsten (VI) oxide, or any combination thereof.

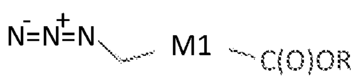
**[0023]** The furanic compound may be converted to the amino carbonyl compound, as generally represented in FIG. 1, by an oxidation reaction (converting a portion of the molecule to a carboxylic acid) and an amination (introducing an amine group onto the molecule).

**[0024]** In an embodiment as generally depicted in FIG. 3A, a halogenated methyl furanic compound of structural formula 

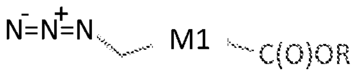
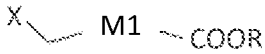
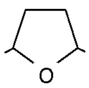
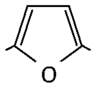
, where M1 is 

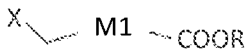
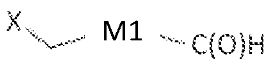
or 

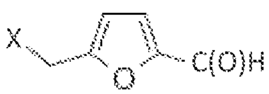
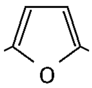
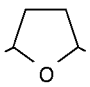
, and X is a halogen, may be oxidized to form a halogenated methyl furanic compound of formula 

, where R is –H, alkyl, or substituted alkyl. The furanic compound may be treated with an azide to replace the halogen and produce 5-(azidomethyl) furanic compounds of formula 

. In an embodiment, the 5-(azidomethyl) furanic compounds may be produced and sold as a precursor for producing nylon 6, or for other uses.

**[0025]** In an embodiment, the 5-(azidomethyl) furanic compounds of formula , where R is –H, alkyl, or substituted alkyl, may be produced by contacting at least one furanic compound of structure , where M1 is  or , X is -F, -Cl, -Br, -I, -OH, an acetate, or a sulfonate, with a solvent and at least one of an alkali metal azide and tetraalkylammonium azide. The alkali metal azide may be sodium azide, and the tetraalkylammonium azide may be tetrabutylammonium azide. The solvent selected may be a function of the azide salt used. For example, if an alkali metal azide is used then the solvent may be dimethylformamide or dimethyl sulfoxide, whereas if tetraalkyammonium azide is used then the solvent may be less polar, such as tetrahydrofuran or 2-methyltetrahydrofuran.

**[0026]** Furanic compounds having the structure  may be produced by oxidizing furanic compounds having a structure  that may be derived directly from biomass, such as cellulose, or produced from biomass by isolating hexoses from the biomass, and converting the hexoses to the furfural compound. If X is -Cl, the hexoses may be converted by heating the hexoses with HCl and 1,2-dichloroethane to produce 5-chloromethylfurfural as the furfural compound.

**[0027]** In an embodiment, where X may be -Cl and R may be -H, the furfural compound having the structure  is 5-chloromethylfurfural as shown in FIG. 3B. While this example, and any examples below may be provided, illustrated and discussed for components having furan rings , the same may generally also apply for similarly structured components wherein the furan ring is replaced with a tetrahydrofuran ring . As shown in FIG. 3B, oxidation of the 5-chloromethylfurfural produces 5-(chloromethyl)-2-furoic acid. The 5-(chloromethyl)-2-furoic acid may then be contacted with a solvent, such as 2-methyltetrahydrofuran and at least one of an alkali metal azide and tetraalkylammonium azide to produce 5-(azidomethyl)-2-furoic acid. The 5-(azidomethyl)-2-furoic acid may be converted to an amino carbonyl compound 5-(aminomethyl)-2-furoic acid. In an embodiment, the 5-chloromethylfurfural may be oxidized with Jones reagent or chromic acid and at least one co-oxidant. In an embodiment, the co-oxidant may be periodic acid.

**[0028]** In a variant of the above reaction procedure, the 5-(chloromethyl)furoic acid may be converted into an ester by reacting the 5-(chloromethyl)furoic acid with diazomethane to produce methyl 5-(chloromethyl)-2-furoate. The methyl 5-(chloromethyl)-2-furoate may then be contacted with a solvent, such as 2-methyltetrahydrofuran, and at least one of an alkali metal azide and tetraalkylammonium azide to produce methyl 5-(azidomethyl)-2-furoate.

**[0029]** The methyl 5-(azidomethyl)-2-furoate may be converted to the amino carbonyl compound methyl 5-(aminomethyl)-2-furoate. In an embodiment, the azide that is reacted with the methyl 5-(chloromethyl)-2-furoate may include at least one of an alkali metal azide and tetraalkylammonium azide. In an embodiment the alkali metal azide may be sodium azide. In an embodiment, the methyl 5-(azidomethyl)-2-furoate may be converted to methyl 5-(aminomethyl)-2-furoate by catalytic hydrogenation of methyl 5-(azidomethyl)-2-

furoate at room temperature in the presence of a hydrogenation catalyst. In an embodiment, the hydrogenation catalyst may be palladium, platinum, rhodium, or combinations thereof.

**[0030]** In an embodiment, as shown in FIG. 3B, if the furanic compound is 5-hydroxymethylfurfural, the 5-hydroxymethylfurfural may be oxidized to produce 5-formyl-2-furoic acid (5-formylfuran-2-carboxylic acid) or methyl 5-(hydroxymethyl)-2-furoate. The methyl 5-(hydroxymethyl)-2-furoate may be converted to methyl 5-(formyl)-2-furoate. The 5-formyl-2-furoic acid or methyl 5-(formyl)-2-furoate may be reacted with an ammonia source to respectively produce 5-(aminomethyl)-2-furoic acid or methyl 5-(aminomethyl)-2-furoate. In an embodiment, the 5-hydroxymethylfurfural may be oxidized with 4-benzoyloxy-2,2,6,6-tetramethylpiperidine-1-oxyl under phase transfer conditions to produce 5-formyl-2-furoic acid. In an embodiment, the ammonia source may include an ammonia equivalent in a solvent, and reacting the 5-formyl-2-furoic acid with the ammonia source may produce an intermediate imine that may be reduced with a reducing agent in a solvent to produce 5-(aminomethyl)-2-furoic acid. In an embodiment, the ammonia equivalent may be ammonia, ammonium acetate, hydroxylamine, or a combination thereof, and the reducing agent may be hydrogen, sodium borohydride, sodium cyanoborohydride, sodium acetoxyborohydride, or a combination thereof. In an embodiment, the reduction of the imine may be done in the presence of a reduction catalyst. The reduction catalyst may be nickel, palladium, platinum, rhodium, or a combination thereof. Alternatively, reductive amination of 5-formyl-2-furoic acid using a mixture of sodium cyanoborohydride, ammonium acetate, aqueous ammonium hydroxide and ethanol may also produce the amino carbonyl compound.

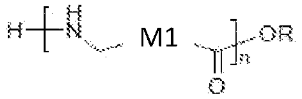
**[0031]** Referring back to FIG. 1, the amino carbonyl compounds produced from the furanic compounds may be converted to nylon 6. This conversion may be done by various routes as illustrated in FIG. 4. In an embodiment, nylon 6 may be produced by a series of reactions involving hydrogenation, hydrodeoxygenation, and polymerization. In a first reaction, the amino acid or ester may be hydrogenated to reduce the furan double bonds, if present, and hydrodeoxygenated to open the ring and produce an aminocaproic acid. The aminocaproic acid may be converted to caprolactam, and, via a ring-opening polymerization, the caprolactam may be polymerized to produce nylon 6. During polymerization, the amide bond within each caprolactam molecule is broken, with the active groups on each side re-forming two new bonds as the monomer becomes part of the polymer backbone.

**[0032]** The hydrogenation, hydrodeoxygenation, and polymerization may be done in a single-vessel reaction sequence. A mixture of the amino carbonyl compound (amino acid or amino ester), at least one metal catalyst, at least one halide source, and hydrogen gas may be heated in stages to conduct the various reactions. In a first stage, the mixture may be heated to a first temperature of about 140 °C to about 160 °C for a period of time sufficient to convert the aminocarbonyl compound to aminocaproic acid. The temperature may then be increased to a second temperature of about 190 °C to about 210 °C for an additional period of time sufficient to convert the aminocaproic acid to caprolactam. The temperature may then be increased to a third temperature of about 240 °C to about 270 °C for another period of time sufficient to convert the caprolactam to nylon 6.

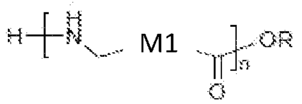
**[0033]** In embodiments, the metal catalyst may be platinum, palladium, rhodium, ruthenium, nickel, cobalt, iron, molybdenum, iridium, rhenium, gold, or any combination thereof. The metal catalyst may be mounted on a support. The halide source may be at least one hydrogen halide, which may be, for example, hydrogen iodide, hydrogen bromide, or a combination thereof.

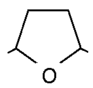
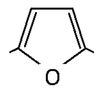
**[0034]** In a variant of this reaction sequence, as depicted in FIG. 4, the aminocaproic acid or aminocaproic ester may be polymerized directly to nylon 6 via a polycondensation reaction.

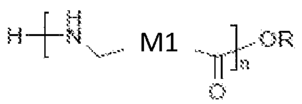
**[0035]** In an embodiment, as also generally represented in FIG. 4, the amino acids or amino esters may be polymerized to produce polyamides of structure

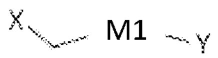


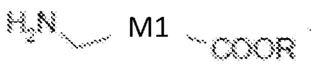
, where R is –H, alkyl, or substituted alkyl. Additional hydrogenation/hydrodeoxygenation of the polyamide may produce nylon 6.

**[0036]** In an embodiment, a polyamide may have a structure as represented by 

, wherein M1 is  or , and R is –H, alkyl, or substituted alkyl. In an embodiment R may be –H or –$CH_3$. A polyamide having such a structure may be used as a precursor for producing nylon 6. The polyamide may be converted to nylon 6 by hydrogenating and hydrodeoxygenating the polyamide.

**[0037]** In a reaction based on FIG. 6, a polyamide having a structure as represented by 

, may be produced by converting at least one furanic compound having a structure 

, wherein X may be -F, -Cl, -Br, -I, -OH, -$N_3$, an acetate, or sulfonate, and Y may be -C(O)R or -C(O)OR, to an amino acid or amino ester having a structure 

, where R may be -H, an alkyl, or a substituted alkyl. The amino acids or amino esters may then be converting to the polyamide. The amino acids or amino esters may be converted to polyamides by polymerization of the amino acids or amino esters. In an embodiment, Y may be -C(O)H and X may be -Cl or -OH.

**[0038]** As mentioned previously, the furanic compound may be derived directly from biomass, or may be produced from biomass by isolating hexoses or cellulose from the biomass, and converting the hexoses or cellulose to the furanic compound. In an embodiment, where X is –Cl and Y is –C(O)H, converting the hexoses or cellulose may be converted to the furanic compound by heating the hexoses or cellulose with HCl and 1,2-dichloroethane to produce 5-chloromethylfurfural as the furanic compound. In a variant, an alkaline salt may be heated with the hexoses, HCl and 1,2-dichloroethane to produce the 5-chloromethylfurfural. The alkaline salt may be lithium halide, sodium halide, potassium halide, or any combination thereof.

**[0039]** In an embodiment for furan compounds, which, as mentioned above, may also be applicable for tetrahdrofuran compounds, where X is –Cl and Y is –C(O)H, conversion of the at least one furan compound to the amino acid may include oxidizing 5-chloromethylfurfural to produce 5-(chloromethyl)-2-furoic acid, contacting the 5-(chloromethyl)-2-furoic acid with a solvent, such as 2-methyltetrahydrofuran, and at least one of an alkali metal azide and tetraalkylammonium azide to produce 5-(azidomethyl)-2-furoic acid, and converting the 5-(azidomethyl)-2-furoic acid to the amino acid 5-(aminomethyl)-2-furoic acid. In embodiments, the alkali metal azide may be sodium azide, and the tetraalkylammonium azide may be tetrabutylammonium azide.

**[0040]** The 5-(azidomethyl)-2-furoic acid may be converted to 5-(aminomethyl)-2-furoic acid by catalytic hydrogenation of 5-(azidomethyl)-2-furoic acid at room temperature in the presence of a hydrogenation catalyst. The hydrogenation catalyst may be palladium, platinum, rhodium, or any combination thereof. The 5-chloromethylfurfural may be oxidized with at least one of: Jones reagent, and chromic acid and at least one co-oxidant. The co-oxidant may be periodic acid.

**[0041]** For furanic compounds where X is –OH and Y is –C(O)H, converting hexoses or cellulose to the furanic compound may include heating the hexoses or cellulose with at least one of an acid and a metal salt catalyst to produce 5-hydroxymethylfurfural as the furanic compound. The step of converting the at least one furanic compound to the amino carbonyl compound may then include oxidizing the 5-hydroxymethylfurfural to produce 5-

formyl-2-furoic acid or methyl 5-formyl-2-furoate, and contacting the 5-formyl-2-furoic acid or methyl 5-formyl-2-furoate with an ammonia source to produce the amino carbonyl compound 5-(aminomethyl)-2-furoic acid or the amino ester methyl 5-(aminomethyl)-2-furoate. In an embodiment, the 5-hydroxymethylfurfural may be oxidized with 4-benzoyloxy-2,2,6,6-tetramethylpiperidine-1-oxyl under phase transfer conditions.

**[0042]** In an embodiment, the ammonia source may be an ammonia equivalent in an appropriate solvent, and upon contacting the 5-formyl-2-furoic acid or methyl 5-formyl-2-furoate with the ammonia source, an intermediate imine may be produced. The intermediate imine may be reduced with a reducing agent in a solvent to produce 5-(aminomethyl)-2-furoic acid or methyl 5-(aminomethyl)-2-furoate. In an embodiment, the intermediate imine may be reduced with the reducing agent in the presence of a reduction catalyst. In various embodiments, the ammonia equivalent may be ammonia, ammonium acetate, hydroxylamine, or a combination thereof, and the reducing agent may be hydrogen, sodium borohydride, sodium cyanoborohydride, sodium acetoxyborohydride, or a combination thereof.

## EXAMPLES

EXAMPLE 1: Method for Producing a Furanazido Acid or Furanazido Ester from 5-Chloromethylfurfural – and Conversion to an Amino Acid or Amino Ester

**[0043]** Furanazido acids or Furanazido esters are provided as precursor compounds for producing nylon 6. FIG. 3B depicts a representation of a method for producing 5-(azidomethyl)-2-furoic acid and methyl 5-(azidomethyl)-2-furoate from furanic compounds. One furanic compounds that is usable for producing 5-(azidomethyl)-2-furoic acid and methyl 5-(azidomethyl)-2-furoate is 5-chloromethylfurfural. As discussed previously, 5-chloromethylfurfural is commercially available (such as from Toronto Research Chemicals, Inc.; Toronto, Canada) or obtainable from biomass and other sources.

**[0044]** A solution of 5-(chloromethyl)furfural (1 equivalent) in isopropanol free acetone is cooled in an ice bath. Jones reagent is added slowly until the yellow color persists.

The reaction is quenched with isopropanol, the mixture is concentrated under reduced pressure, and the residue is extracted with ethyl acetate. The extract is washed with 1 M hydrochloric acid, washed with water, dried over magnesium sulfate, and concentrated under reduced pressure to yield 5-(chloromethyl)-2-furoic acid.

**[0045]** A solution of 5-(chloromethyl)-2-furoic acid in diethyl ether is cooled in an ice bath. A diethyl ether solution of diazomethane is added slowly until the yellow color persists. After being stirred for about 10 minutes, the ether is removed under reduced pressure to yield methyl 5-(chloromethyl)-2-furoate.

**[0046]** A mixture of methyl 5-(chloromethyl)-2-furoate (1 equivalent), tetrabutylammonium azide (1 equivalent) and 2-methyltetrahydrofuran as solvent is stirred for about 1.5 hours. After being washed twice with a 1:1 mixture of brine and 1 M hydrochloric acid, the solution is dried over magnesium sulfate and concentrated under reduced pressure to yield methyl 5-(azidomethyl)-2-furoate.

**[0047]** In a similar manner, 5-(azidomethyl)-2-furoic acid is also synthesized from 5-(chloromethyl)-2-furoic acid.

**[0048]** Methyl 5-(azidomethyl)-2-furoate is converted to methyl 5-(aminomethyl)-2-furoate by treating a mixture of methyl 5-(azidomethyl)-2-furoate (1 equivalent), 10% palladium on carbon (0.03 equivalent palladium), concentrated hydrochloric acid (1.1 equivalents), and methanol as solvent, with hydrogen gas (about 30 psi) for about 3 hours. The catalyst is removed by filtration and rinsed with methanol. The combined filtrates are concentrated under reduced pressure. Trituration of the residue with diethyl ether yields methyl 5-(aminomethyl)-2-furoate hydrochloride salt.

<u>EXAMPLE 2: Method for Producing Furan Acid or Furan Ester from 5-Hydroxymethylfurfural – and Conversion to an Amino Acid or Amino Ester</u>

**[0049]** Furan acids or furan esters are provided as precursor compounds for producing nylon 6. FIG. 3B depicts a representation of a method for producing 5-formyl-2-

furoic acid and methyl 5-(hydroxymethyl)-2-furoate from furanic compounds. One furanic compound that is usable for producing 5-formyl-2-furoic acid and methyl 5-(hydroxymethyl)-2-furoate is 5-hydroxymethylfurfural.

**[0050]** In one process, as shown in FIG. 7A, methyl 5-(hydroxymethyl)-2-furoate is synthesized from 5-(hydroxymethyl)furfural by treating a mixture of 5-(hydroxymethyl)furfural (1 equivalent), potassium methoxide (0.25 equivalent), gold on titanium oxide catalyst (0.005 equivalent gold) and methanol as solvent, 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. A mixture of methyl 5-formyl-2-furoate (1 equivalent), hydroxylamine hydrochloride (1 equivalents), potassium acetate (1 equivalents) and 50% aqueous ethanol is heated at 50 °C for 1 hour. After cooling, the precipitate is filtered, washed with water and dried under reduced pressure to yield methyl 5-formyl-2-furoate oxime.

**[0051]** In an alternative process, as shown in FIG. 7B, 5-formyl-2-furoic acid is synthesized from 5-(hydroxymethyl)furfural by vigorously stirring a two phase mixture of 5-(hydroxymethyl)furfural (1 equivalent), 4-benzoyloxy-2,2,6,6-tetramethylpiperidine-1-oxyl (0.1 equivalent), acetylcholine chloride (0.1 equivalent), saturated aqueous sodium bicarbonate solution, and tetrahydropyran. Pyridinium tribromide (3 equivalents) is added to the mixture in portions. After being stirred for about 5 hours, the reaction is quenched by addition of 5% aqueous sodium thiosulfate solution, acidified by addition of aqueous tartaric acid, and extracted with tetrahydropyran. The extract is concentrated under reduced pressure to yield 5-formyl-2-furoic acid. A mixture of 5-formyl-2-furoic acid (1 equivalent), hydroxylamine hydrochloride (1 equivalent), 10% aqueous sodium hydroxide solution (2.1 equivalents sodium hydroxide) and ethanol is heated at 50 °C. After 1 hour, the mixture is treated with 10% hydrochloric acid (1.2 equivalents) and the solid is filtered to yield 5-formyl-2-furoic acid oxime.

**[0052]** The oximes (FIGS 7A, 7B) are then converted to amino acids or amino esters. For example, a mixture of 5-formyl-2-furoic acid oxime, Raney nickel catalyst, and tetrahydrofuran as solvent is treated with hydrogen gas (50 bar) in an autoclave for 1 hour. The catalyst is removed by filtration and rinsed with tetrahydrofuran under argon. The combined filtrates are concentrated under reduced pressure to yield 5-(aminomethyl)-2-furoic acid. Similarly, methyl 5-formyl-2-furoate oxime may yield methyl 5-(aminomethyl)-2-furoate.

EXAMPLE 3: Methods for Producing Caprolactam

**[0053]** Any of the synthesized amino ester, amino acid, azido ester or azido acid monomers of Examples 1 and 2 may be used for producing caprolactam. A mixture of any, or a combination of, the monomers (1 equivalent), 5% palladium on silica (0.01 equivalent palladium) and acetic acid solvent is heated in an autoclave at 160 °C while treating with hydrogen gas (50 atmospheres) 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 gas (about 50 atmospheres) for about 3 additional hours. After cooling, the mixture is filtered to remove the catalyst. The solvent is removed by distillation under reduced pressure to yield 6-aminocaproic acid.

**[0054]** A mixture of 6-aminocaproic acid and ethanol as solvent is heated at about 200 °C while being stirred vigorously in an autoclave for about 20 minutes. Removal of the solvent under reduced pressure yields caprolactam.

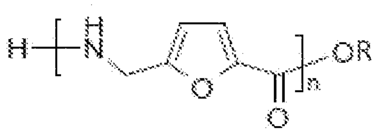
EXAMPLE 4: Method for Producing Nylon 6

**[0055]** Caprolactam is isolated and sold as a precursor for producing nylon 6 or other possible uses. Nylon 6 is also produced as a continuation of the method presented in Example 3 to provide a two-vessel conversion of 5-(aminomethyl)-2-furoic acid, methyl 5-(aminomethyl)-2-furoate, 5-(azidomethyl)-2-furoic acid or methyl 5-(azidomethyl)-2-furoate to nylon 6. After the formation of caprolactam in Example 3, the reaction mixture is heated to a third higher temperature of about 260 ºC for a period of time of about 12 hours to open the caprolactam rings, whereby the amine ends of the molecules will react with the carboxyl end of other molecules to polymerize into nylon 6.

**[0056]** Nylon 6 may also be produced from any of the synthesized amino ester, amino acid, azido ester or azido acid monomers of Examples 1 and 2. A mixture of any, or a combination of, the synthesized amino ester, amino acid, azido ester or azido acid monomers (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 gas (about 50 atmospheres) for about 3 hours. The mixture is cooled, hydrogen iodide (1 equivalent) is added and heated again at 160 °C while treating with hydrogen gas (50 atmospheres) for another 3 hours. The contents of the autoclave are pumped into a second autoclave with removal of the catalyst by filtration. After removal of acetic acid by distillation, ethanol is added to the autoclave. The mixture is heated at about 200 °C while being stirred vigorously for about 20 minutes. After removal of the solvent by distillation, water (5% by weight) is added to the autoclave and the mixture is heated at about 260 °C while maintaining the steam pressure at about 15 atmospheres for about 12 hours. Removal of water by distillation yields nylon 6.

EXAMPLE 5: A Furan-based Polyamide and Method for Producing

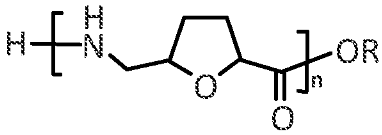
**[0057]** A furan based polyamide having the structure



is produced from furanic compounds according to a method as represented in FIG. 7A. Such a polyamide is usable as a precursor for the production of nylon 6. One furanic compound that is usable for producing the polyamide is 5-hydroxymethylfurfural. As discussed previously, 5-hydroxymethylfurfural is obtained from biomass or other sources. 5-hydroxymethylfurfural is oxidized to produce methyl 5-hydroxymethyl-2-furoate by reacting the 5-hydroxymethylfurfural with oxygen, potassium methoxide, gold on titanium oxide catalyst, and methanol as a solvent. The methyl 5-hydroxymethylfuroate is oxidized to produce methyl 5-formylfuroate with o-iodoxybenzoic acid. The methyl 5-formylfuroate is reacted with hydroxylamine to produce an intermediate oxime that is reduced with hydrogen in the presence of a nickel catalyst to produce methyl 5-(aminomethyl)-2-furoate. The methyl 5-(aminomethyl)-2-furoate is polymerized to produce the polyamide.

EXAMPLE 6: A Tetrahydrofuran-based Polyamide and Method for Producing

**[0058]** A tetrahydrofuran based polyamide having the structure



is produced from furanic compounds. Such a polyamide is usable as a precursor for the production of nylon 6. One furanic compound that is usable for producing the polyamide is 5-hydroxymethylfurfural. As discussed previously, 5-hydroxymethylfurfural is obtained from biomass or other sources. As shown in the upper portion of FIG. 7A, 5-hydroxymethylfurfural is oxidized to produce methyl 5-hydroxymethyl-2-furoate by reacting the 5-hydroxymethylfurfural with oxygen, potassium methoxide, gold on titanium oxide catalyst, and methanol as a solvent. The methyl 5-hydroxymethyl-2-furoate is oxidized to produce methyl 5-formyl-2-furoate with o-iodoxybenzoic acid. The methyl 5-formyl-2-furoate is reacted with hydroxylamine to produce an intermediate oxime that is reduced with hydrogen in the presence of a nickel catalyst to produce methyl 5-(aminomethyl)-2-furoate.

**[0059]** As shown in FIG. 10, the methyl 5-(aminomethyl)-2-furoate is catalytically hydrogenated in the presence of a halide source (HI or HBr) to produce methyl 5-(aminomethyl)-2-tetrahydrofuroate. Via a polycondensation, the methyl 5-(aminomethyl)-2-tetrahydrofuroate is polymerized to form a polyamide.

**[0060]** Therefore, the Examples above demonstrate that nylon 6, and precursors for making nylon 6, such as caprolactam from Example 3 and polyamide from Example 5, can be produced from furanic compounds that are derived from biomass, thereby reducing the need for petrochemically derived raw materials.

**[0061]** 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.

**[0062]** 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.

**[0063]** 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.

**[0064]** 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.”

**[0065]** 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.

**[0066]** 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.

**[0067]** It will be understood by those within the art that, in general, terms used herein, and especially in the appended claims (for example, bodies of the appended claims) are generally intended as “open” terms (for example., 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" (for example, “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 (for example, 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 (for example, “ 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 (for example, “ 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.”

**[0068]** 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.

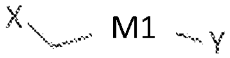
**[0069]** As will be understood by one skilled in the art, for any and all purposes, such as in terms of providing a written description, all ranges disclosed herein also encompass any and all possible subranges and combinations of subranges thereof. Any listed range can be easily recognized as sufficiently 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.

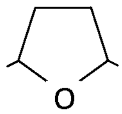
**[0070]** Various of the above-disclosed and other features and functions, or alternatives thereof, may be combined into many other different systems or applications. Various presently unforeseen or unanticipated alternatives, modifications, variations or improvements therein may be subsequently made by those skilled in the art, each of which is also intended to be encompassed by the disclosed embodiments.

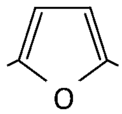
## CLAIMS

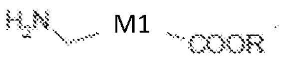
*What Is Claimed Is:*

1. A method for producing nylon 6, the method comprising:

converting at least one furanic compound of formula 

, wherein M1 is 

or 

, X is -F, -Cl, -Br, -I, -OH, -$N_3$, an acetate, or sulfonate, and Y is -C(O)R or -C(O)OR, to an amino carbonyl compound of formula 

, wherein R is -H, alkyl, or substituted alkyl; and

converting the amino carbonyl compound to nylon 6.

2. The method of claim 1, wherein converting the amino carbonyl compound to nylon 6 comprises a two-pot reaction, the two-pot reaction comprising catalytic hydrogenation, catalytic hydrodeoxygenation, polycondensation, or any combination thereof.

3. The method of claim 1, wherein converting the amino carbonyl compound to nylon 6 comprises heating a mixture of the amino carbonyl compound, at least one metal catalyst, at least one halide source, and hydrogen gas, to hydrogenate, hydrodeoxygenate, and polymerize the amino carbonyl compound to form the nylon 6.

4. The method of claim 3, wherein heating the mixture comprises:

heating the mixture to a first temperature of about 120 °C to about 160 °C for a period of time sufficient to convert the amino carbonyl compound to aminocaproic acid to form a second mixture;

heating the second mixture to a second temperature of about 190 ºC to about 210 ºC for a period of time sufficient to convert the aminocaproic acid to caprolactam to form a third mixture; and

heating the third mixture to a third temperature of about 240 ºC to about 270 ºC for a period of time sufficient to convert the caprolactam to the nylon 6.

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

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

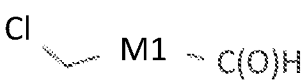
7. The method of claim 3, wherein the halide source is at least one hydrogen halide.

8. The method of claim 3, wherein the halide source is hydrogen iodide, hydrogen bromide, or a combination thereof.

9. The method of claim 1, wherein Y is –C(O)H and X is –Cl or –OH.

10. The method of claim 1, further comprising producing the furanic compound from biomass by isolating hexoses, cellulose, or a combination thereof from the biomass, and converting the hexoses, cellulose, or combination thereof to the furanic compound.

11. The method of claim 10, wherein X is –Cl and Y is –C(O)H, and converting the hexoses, cellulose, or combination thereof to the furanic compound comprises converting the hexoses, cellulose, or combination thereof to the furanic compound

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12. The method of claim 10, wherein X is –OH and Y is –C(O)H, and converting the hexoses, cellulose, or combination thereof to the furanic compound comprises converting the hexoses, cellulose, or combination thereof to the furanic compound


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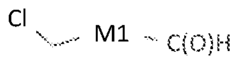
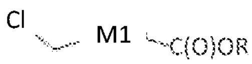
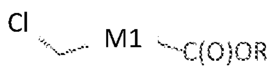
13. The method of claim 1, wherein X is –Cl and Y is –C(O)H, and converting the at least one furanic compound to the amino carbonyl compound comprises:

oxidizing the furanic compound 

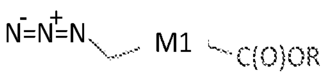
to produce



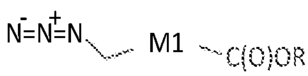

, wherein R is –H, alkyl, or substituted alkyl;

contacting the 

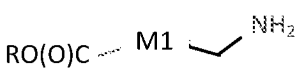
with a solvent and at least one of an alkali metal azide and tetraalkylammonium azide to produce




; and

converting the 

to the amino carbonyl compound

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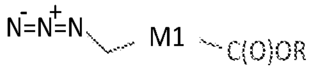
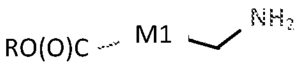
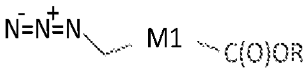
14. The method of claim 13, wherein the alkali metal azide is sodium azide and the tetraalkylammonium azide is tetrabutylammonium azide.

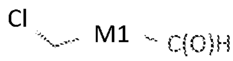
15. The method of claim 13, wherein converting 

to 

comprises catalytically hydrogenating 

at room temperature in the presence of a hydrogenation catalyst.

16. The method of claim 15, wherein the hydrogenation catalyst comprises palladium, platinum, rhodium, or any combination thereof.

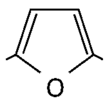
17. The method of claim 13, wherein oxidizing the 

comprises oxidizing with at least one of:

Jones reagent; and

chromic acid and at least one co-oxidant.

18. The method of claim 17, wherein the co-oxidant is periodic acid.

19. The method of claim 13, wherein M1 is 

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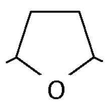
20. The method of claim 13, wherein M1 is 

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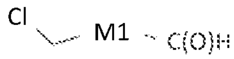
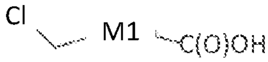
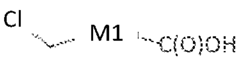
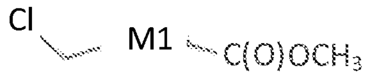
21. The method of claim 13, wherein R is C1 to C5 alkyl.

22. The method of claim 21, wherein oxidizing the 

produces 

, and the method further comprises contacting the 

with diazomethane to produce 

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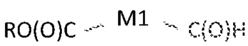
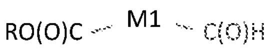
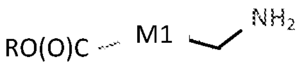
23. The method of claim 1, wherein X is –OH and Y is –C(O)H and converting the at least one furanic compound to the amino carbonyl compound comprises:

oxidizing the furanic compound 

to produce 

, wherein R is –H, alkyl, or substituted alkyl; and

contacting the 

with an ammonia source to produce the amino carbonyl compound 

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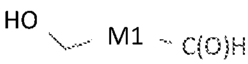
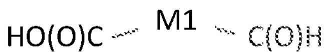
24. The method of claim 23, wherein R is –H and oxidizing the 

comprises oxidizing with 4-benzoyloxy-2,2,6,6-tetramethylpiperidine-1-oxyl under phase transfer conditions to produce 

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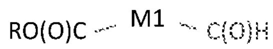
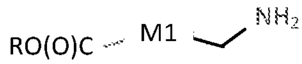
25. The method of claim 23, wherein:

the ammonia source comprises an ammonia equivalent in a solvent;

contacting the  with the ammonia source produces an intermediate imine; and

the contacting further comprises contacting the intermediate imine with a reducing agent in a solvent to produce the .

26. The method of claim 25, wherein:

the ammonia equivalent comprises ammonia, ammonium acetate, hydroxylamine, or a combination thereof; and

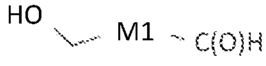
the reducing agent comprises hydrogen, sodium borohydride, sodium cyanoborohydride, sodium acetoxyborohydride, or a combination thereof.

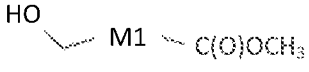
27. The method of claim 25, wherein contacting the intermediate imine further comprises contacting in the presence of a reduction catalyst.

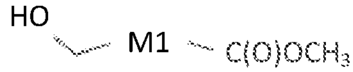
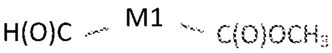
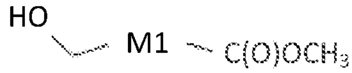
28. The method of claim 27, wherein the reduction catalyst comprises nickel, palladium, platinum, rhodium, or a combination thereof.

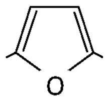
29. The method of claim 23, wherein R is C1 to C5 alkyl.

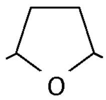
30. The method of claim 23, wherein:

R is $-CH_3$ and oxidizing the  comprises oxidizing with oxygen in the presence of a gold catalyst and a solvent to produce

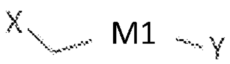
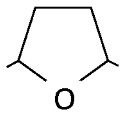
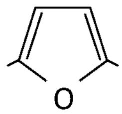
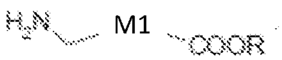
; and

the method further comprises converting  to  by heating the  under reflux with o-iodoxybenzoic acid in the presence of a solvent.

31. The method of claim 23, wherein M1 is .

32. The method of claim 23, wherein M1 is .

33. A method for producing caprolactam, the method comprising:

converting at least one furanic compound of formula , wherein M1 is  or , X is -F, -Cl, -Br, -I, -OH, -$N_3$, an acetate, or sulfonate, and Y is -C(O)R or -C(O)OR, to an amino carbonyl compound of formula , wherein R is -H, alkyl, or substituted alkyl; and

converting the amino carbonyl compound to caprolactam.

34. The method of claim 33, wherein Y is –C(O)H and X is –Cl or –OH.

35. The method of claim 33, wherein converting the amino carbonyl compound to caprolactam comprises heating a mixture of the amino carbonyl compound, at least one metal catalyst, at least one halide source, and hydrogen gas.

36. The method of claim 35, wherein the metal catalyst comprises platinum, palladium, rhodium, ruthenium, nickel, cobalt, iron, molybdenum, iridium, rhenium, gold, or any combination thereof.

37. The method of claim 35, wherein the metal catalyst is mounted on a support.

38. The method of claim 35, wherein the halide source comprises at least one hydrogen halide.

39. The method of claim 35, wherein the halide source is hydrogen iodide, hydrogen bromide, or a combination thereof.

40. The method of claim 35, wherein heating the mixture comprises:

heating the mixture to a first temperature of about 120 ºC to about 160 ºC for a period of time sufficient to convert the amino carbonyl compound to 6-aminocaproic acid in a second mixture; and

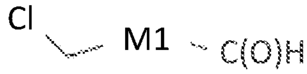
heating the second mixture to a second temperature of about 190 ºC to about 210 ºC for a period of time sufficient to convert the 6-aminocaproic acid to caprolactam.

41. The method of claim 33, wherein Y is –C(O)H and X is –Cl or –OH.

42. The method of claim 33, further comprising producing the furanic compound from biomass by isolating hexoses, cellulose, or a combination thereof from the biomass, and converting the hexoses, cellulose, or combination thereof to the furanic compound.

43. The method of claim 42, wherein X is –Cl and Y is –C(O)H, and converting the hexoses, cellulose, or combination thereof to the furanic compound comprises converting

the hexoses, cellulose, or combination thereof to the furanic compound

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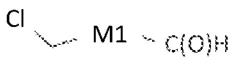
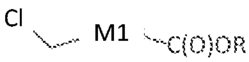
44. The method of claim 42, wherein X is –OH and Y is –C(O)H, and converting the hexoses, cellulose, or combination thereof to the furanic compound comprises converting the hexoses, cellulose, or combination thereof to the furanic compound


.

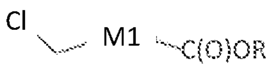
45. The method of claim 33, wherein X is –Cl and Y is –C(O)H, and converting the at least one furanic compound to the amino carbonyl compound comprises:

oxidizing the furanic compound 

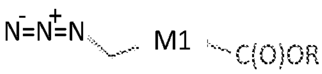
to produce



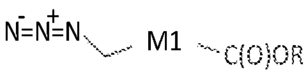

, wherein R is –H, alkyl, or substituted alkyl;

contacting the 

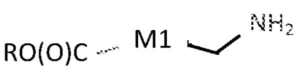
with a solvent and at least one of an alkali metal azide and tetraalkylammonium azide to produce




; and

converting the 

to the amino carbonyl compound

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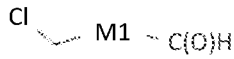
46. The method of claim 45, wherein oxidizing the 

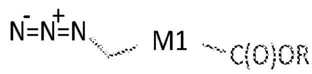
comprises oxidizing the 5-chloromethylfurfural with at least one of:

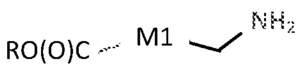
Jones reagent; and

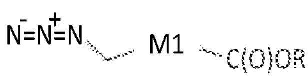
chromic acid and at least one co-oxidant.

47. The method of claim 46, wherein the co-oxidant is periodic acid.

48. The method of claim 45, wherein the alkali metal azide is sodium azide and the tetraalkylammonium azide is tetrabutylammonium azide.

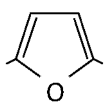
49. The method of claim 45, wherein converting 

to 

comprises catalytically hydrogenating 

at room temperature in the presence of a hydrogenation catalyst.

50. The method of claim 49, wherein the hydrogenation catalyst comprises palladium, platinum, rhodium, or any combination thereof.

51. The method of claim 45, wherein M1 is 

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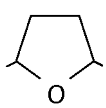
52. The method of claim 45, wherein M1 is 

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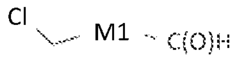
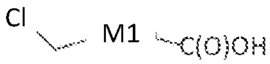
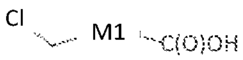
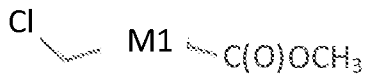
53. The method of claim 45, wherein R is C1 to C5 alkyl.

54. The method of claim 53, wherein oxidizing the 

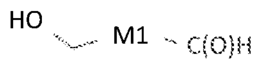
produces 

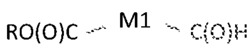
, and the method further comprises contacting the 

with diazomethane to produce 

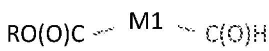
.

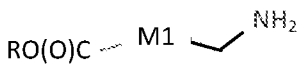
55. The method of claim 33, wherein X is –OH and Y is –C(O)H, and converting the at least one furanic compound to the amino carbonyl compound comprises:

oxidizing the furanic compound 

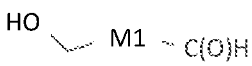
to produce 

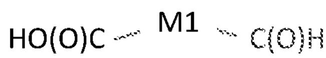
, wherein R is –H, alkyl, or substituted alkyl; and

contacting the 

with an ammonia source to produce the amino carbonyl compound 

.

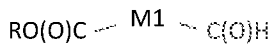
56. The method of claim 55, wherein R is –H and oxidizing the 

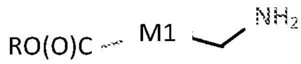
comprises oxidizing with 4-benzoyloxy-2,2,6,6-tetramethylpiperidine-1-oxyl under phase transfer conditions to produce 

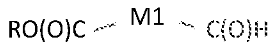
.

57. The method of claim 55, wherein:

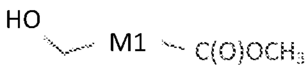
the ammonia source comprises an ammonia equivalent in a solvent;

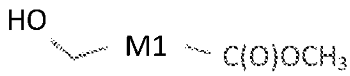
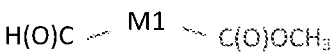
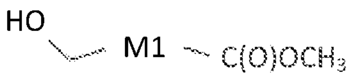
contacting the  with the ammonia source produces an intermediate imine; and

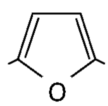
the contacting comprises contacting the intermediate imine with a reducing agent in a solvent to produce the .

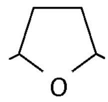
58. The method of claim 57, wherein contacting the  with an ammonia source comprises contacting with hydroxylamine hydrochloride in a solvent.

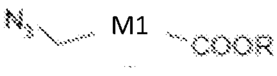
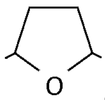
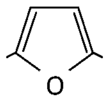
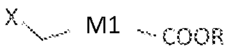
59. The method of claim 55, wherein:

R is –CH3 and oxidizing the  comprises oxidizing with oxygen in the presence of a gold catalyst and a solvent to produce ; and

the method further comprises converting  to  by heating the  under reflux with o-iodoxybenzoic acid in the presence of a solvent.

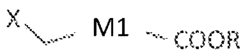
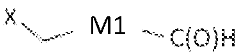
60. The method of claim 55, wherein M1 is .

61. The method of claim 55, wherein M1 is .

62. A method for producing a compound having a structure as represented by , wherein M1 is  or , R is –H, alkyl, or substituted alkyl, the method comprising contacting at least one furanic compound having a structure , wherein X is -F, -Cl, -Br, -I, -OH, an acetate, or a sulfonate, with at least one of an alkali metal azide and tetraalkylammonium azide.

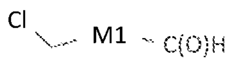
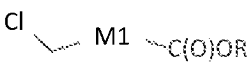
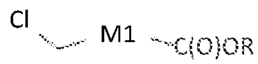
63. The method of claim 62, wherein the alkali metal azide is sodium azide.

64. The method of claim 62, wherein the tetraalkylammonium azide is tetrabutylammonium azide.

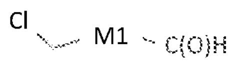
65. The method of claim 62, further comprising producing the at least one furanic compound having the structure  by oxidizing a compound having a structure .

66. The method of claim 65, wherein:

X is -Cl and R is –H;

the oxidizing comprises oxidizing  to produce ; and the contacting comprises contacting the 

with the at least one of an alkali metal azide and tetraalkylammonium azide.

67. The method of claim 66, wherein oxidizing 

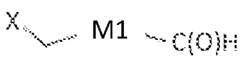
comprises oxidizing with at least one of:

Jones reagent; and

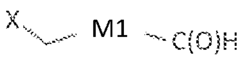
chromic acid and at least one co-oxidant.

68. The method of claim 67, wherein the co-oxidant is periodic acid.

69. The method of claim 65, further comprising producing the

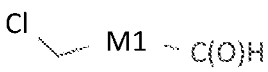


from biomass by isolating hexoses, cellulose, or a combination thereof from the biomass, and converting the hexoses, cellulose, or combination thereof to the



.

70. The method of claim 69, wherein X is –Cl and R is –H, and converting hexoses comprises heating hexoses with HCl and 1,2-dichloroethane to produce



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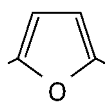
71. The method of claim 65, wherein M1 is 

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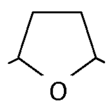
72. The method of claim 65, wherein M1 is 

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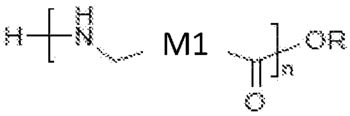
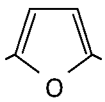
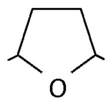
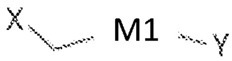
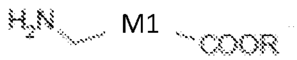
73. A method for producing a polyamide having a structure as represented by




, wherein M1 is  or  and R is –H, alkyl, or substituted alkyl, the method comprising:

converting at least one furanic compound having a structure




, wherein X comprises -F, -Cl, -Br, -I, -OH, $-N_3$, an acetate, or sulfonate, and Y comprises -C(O)R or -C(O)OR, to an amino carbonyl compound having a structure 

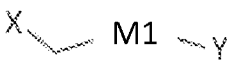
, wherein R comprises –H, a alkyl, or a substituted alkyl; and

converting the amino carbonyl compound to the polyamide.

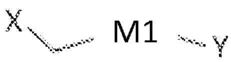
74. The method of claim 73, wherein converting the amino carbonyl compound comprises polymerization of the amino carbonyl compound.

75. The method of claim 73, wherein Y is –C(O)H and X is –Cl or –OH.

76. The method of claim 73, further comprising producing the




from biomass by isolating hexoses, cellulose, or a combination thereof from the biomass, and converting the hexoses, cellulose, or combination thereof to the

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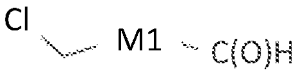
77. The method of claim 73, wherein X is –Cl and Y is –C(O)H, and the furanic compound is 

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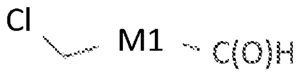
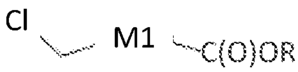
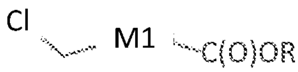
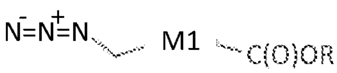
78. The method of claim 77, wherein converting the at least one furanic compound to the amino carbonyl compound comprises:

oxidizing the 

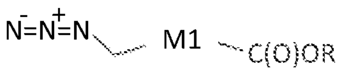
to produce 

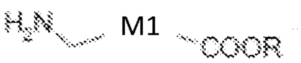
;

contacting the 

and at least one of an alkali metal azide and tetraalkylammonium azide in a solvent to produce 

; and

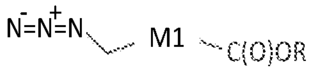
converting the 

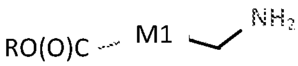
to the amino carbonyl compound 

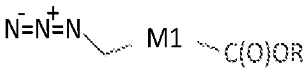
.

79. The method of claim 78, wherein the alkali metal azide is sodium azide.

80. The method of claim 78, wherein the tetraalkylammonium azide is tetrabutylammonium azide.

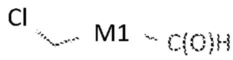
81. The method of claim 78, wherein converting 

to 

comprises catalytically hydrogenating 

at room temperature in the presence of a hydrogenation catalyst.

82. The method of claim 81, wherein the hydrogenation catalyst comprises palladium, platinum, rhodium, or any combination thereof.

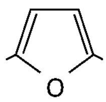
83. The method of claim 78, wherein oxidizing the 

comprises oxidizing with at least one of:

Jones reagent; and

chromic acid and at least one co-oxidant.

84. The method of claim 83, wherein the co-oxidant is periodic acid.

85. The method of claim 78, wherein M1 is 

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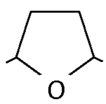
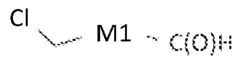
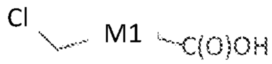
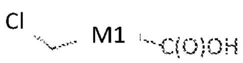
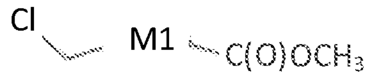
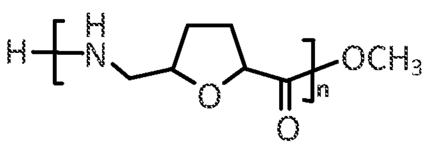
86. The method of claim 78, wherein M1 is 

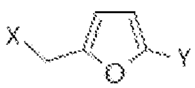
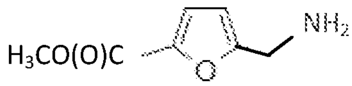
.

87. The method of claim 78, wherein R is C1 to C5 alkyl.

88. The method of claim 87, wherein oxidizing the  produces , and the method further comprises contacting the  with diazomethane to produce .

89. The method of claim 73, wherein the method is a method for producing

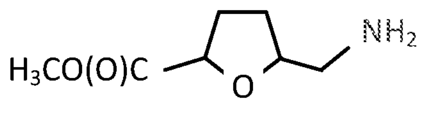
, the method comprising:

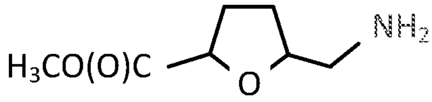
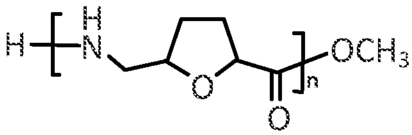
converting at least one furanic compound having a structure , wherein X comprises -F, -Cl, -Br, -I, -OH, $-N_3$, an acetate, or sulfonate, and Y comprises -C(O)R or -C(O)OR, to an amino carbonyl compound having a structure ; and

converting the amino carbonyl compound to the polyamide.

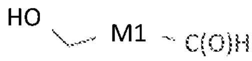
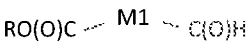
90. The method of claim 89, wherein converting the aminocarbonyl compound to the polyamide comprises:

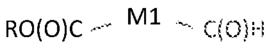
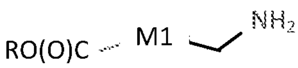
hydrogenating the amino carbonyl to produce

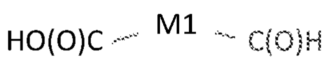
; and

polymerizing the  to produce a polyamide having the structure .

91. The method of claim 73, wherein X is –OH and Y is –C(O)H and converting the at least one furanic compound to the amino carbonyl compound comprises:

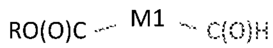
oxidizing the furanic compound  to produce , wherein R is –H, alkyl, or substituted alkyl; and

contacting the  with an ammonia source to produce the amino carbonyl compound .

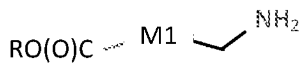
92. The method of claim 91, wherein R is –H and oxidizing the  comprises oxidizing with 4-benzoyloxy-2,2,6,6-tetramethylpiperidine-1-oxyl under phase transfer conditions to produce .

93. The method of claim 91, wherein:

the ammonia source comprises an ammonia equivalent in a solvent;

contacting the 

with the ammonia source produces an intermediate oxime; and

the contacting further comprises contacting the intermediate oxime with a reducing agent in a solvent to produce the 

.

94. The method of claim 93, wherein:

the ammonia equivalent comprises ammonia, ammonium acetate, hydroxylamine, or a combination thereof; and

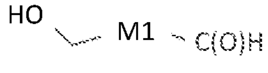
the reducing agent comprises hydrogen, sodium borohydride, sodium cyanoborohydride, sodium acetoxyborohydride, or a combination thereof.

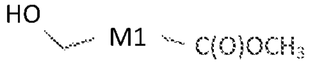
95. The method of claim 93, wherein contacting the intermediate oxime further comprises contacting in the presence of a reduction catalyst.

96. The method of claim 95, wherein the reduction catalyst comprises nickel, palladium, platinum, rhodium, or a combination thereof.

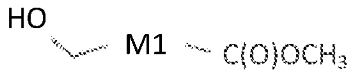
97. The method of claim 91, wherein R is C1 to C5 alkyl.

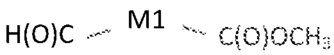
98. The method of claim 91, wherein:

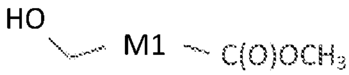
R is –CH3 and oxidizing the 

comprises oxidizing with oxygen in the presence of potassium methoxide and a solvent to produce 

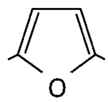
; and

the method further comprises converting 

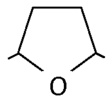
to 

by heating the 

under reflux with o-iodoxybenzoic acid in the presence of a solvent.

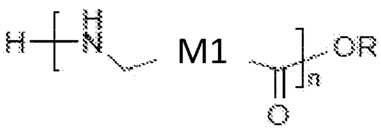
99. The method of claim 91, wherein M1 is 

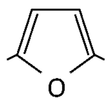
.

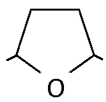
100. The method of claim 91, wherein M1 is 

.

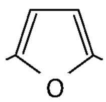
101. A polyamide having a structure as represented by



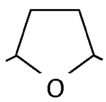
, wherein M1 is 

or 

and R is –H, alkyl, or substituted alkyl.

102. The compound of claim 101, wherein M1 is 

.

103. The compound of claim 101, wherein M1 is 

.

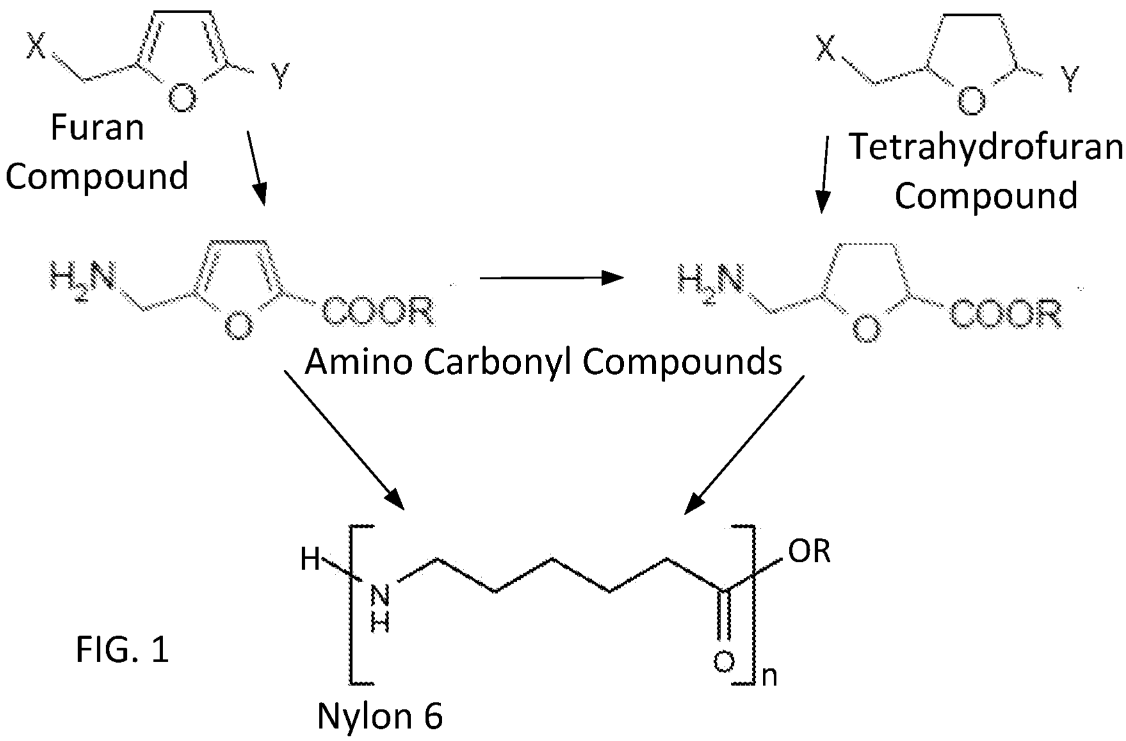

X
Y
Furan
Compound
Tetrahydrofuran
Compound
H2N
COOR
Amino Carbonyl Compounds
H
N
H
OR
O
n
Nylon 6

FIG. 1

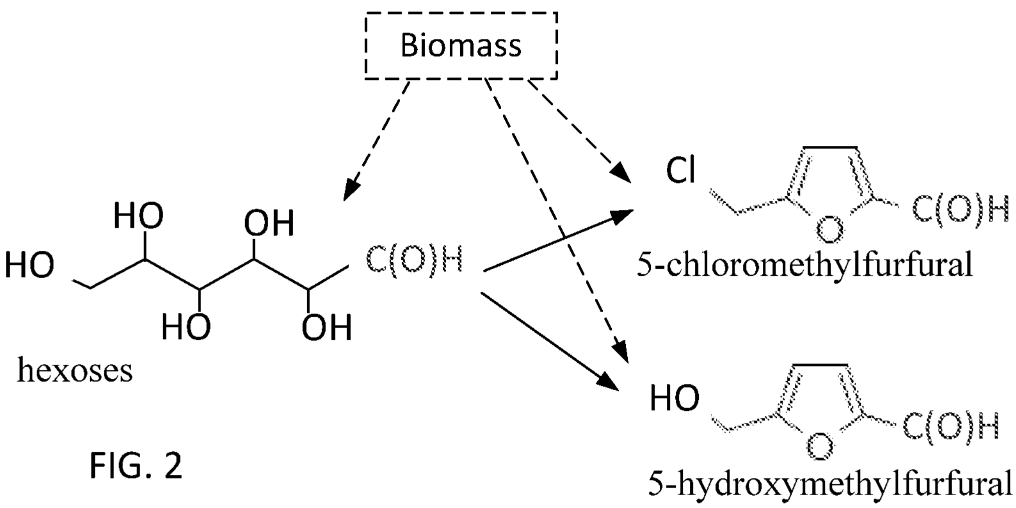

Biomass
HO
HO
OH
HO
OH
C(O)H
hexoses
Cl
C(O)H
5-chloromethylfurfural
HO
C(O)H
5-hydroxymethylfurfural

FIG. 2

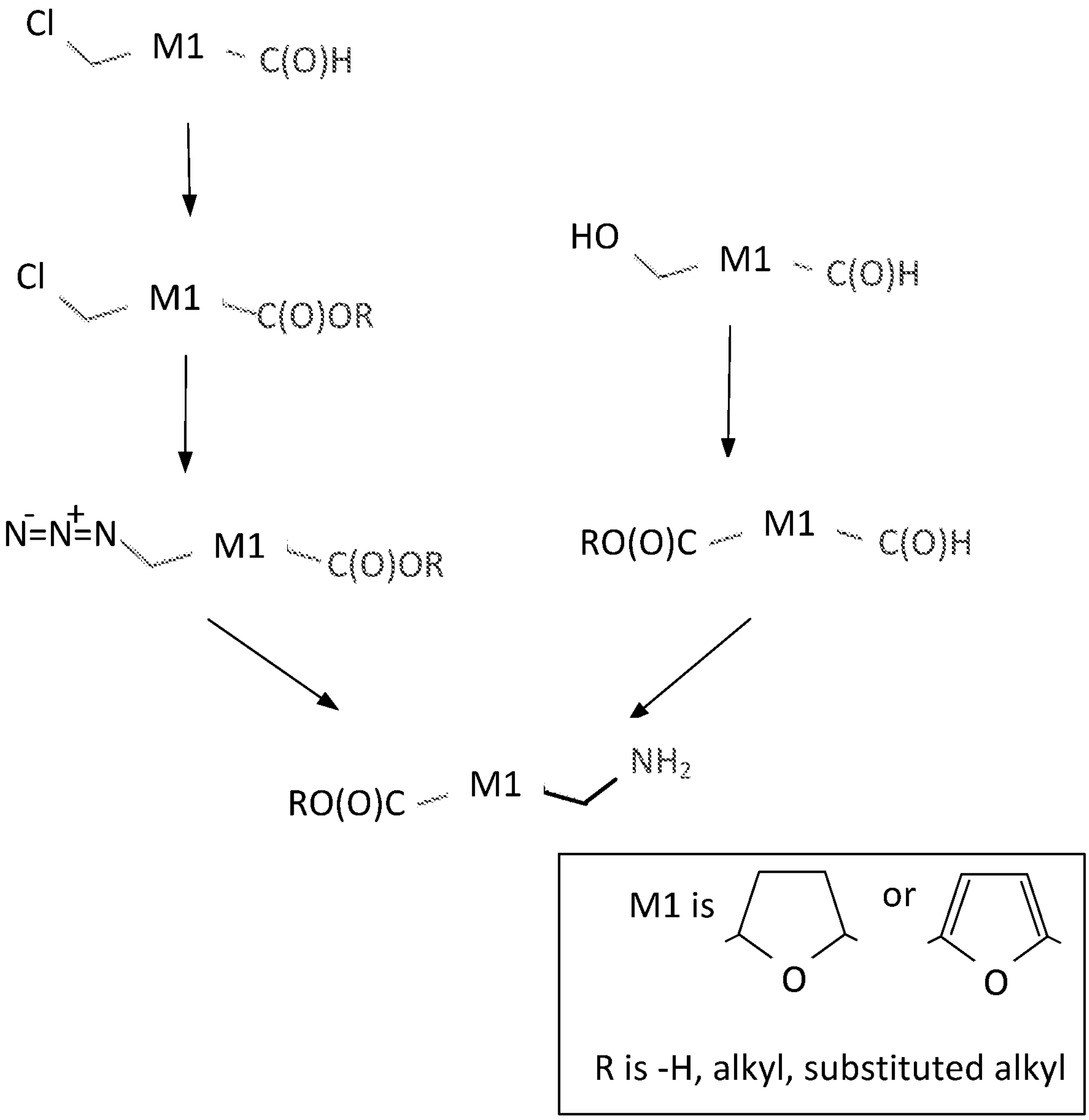

Cl
M1
C(O)H
Cl
M1
C(O)OR
HO
M1
C(O)H
N=N=N
M1
C(O)OR
RO(O)C
M1
C(O)H
RO(O)C
M1
NH2
M1 is
or
O
O
R is -H, alkyl, substituted alkyl

FIG. 3A

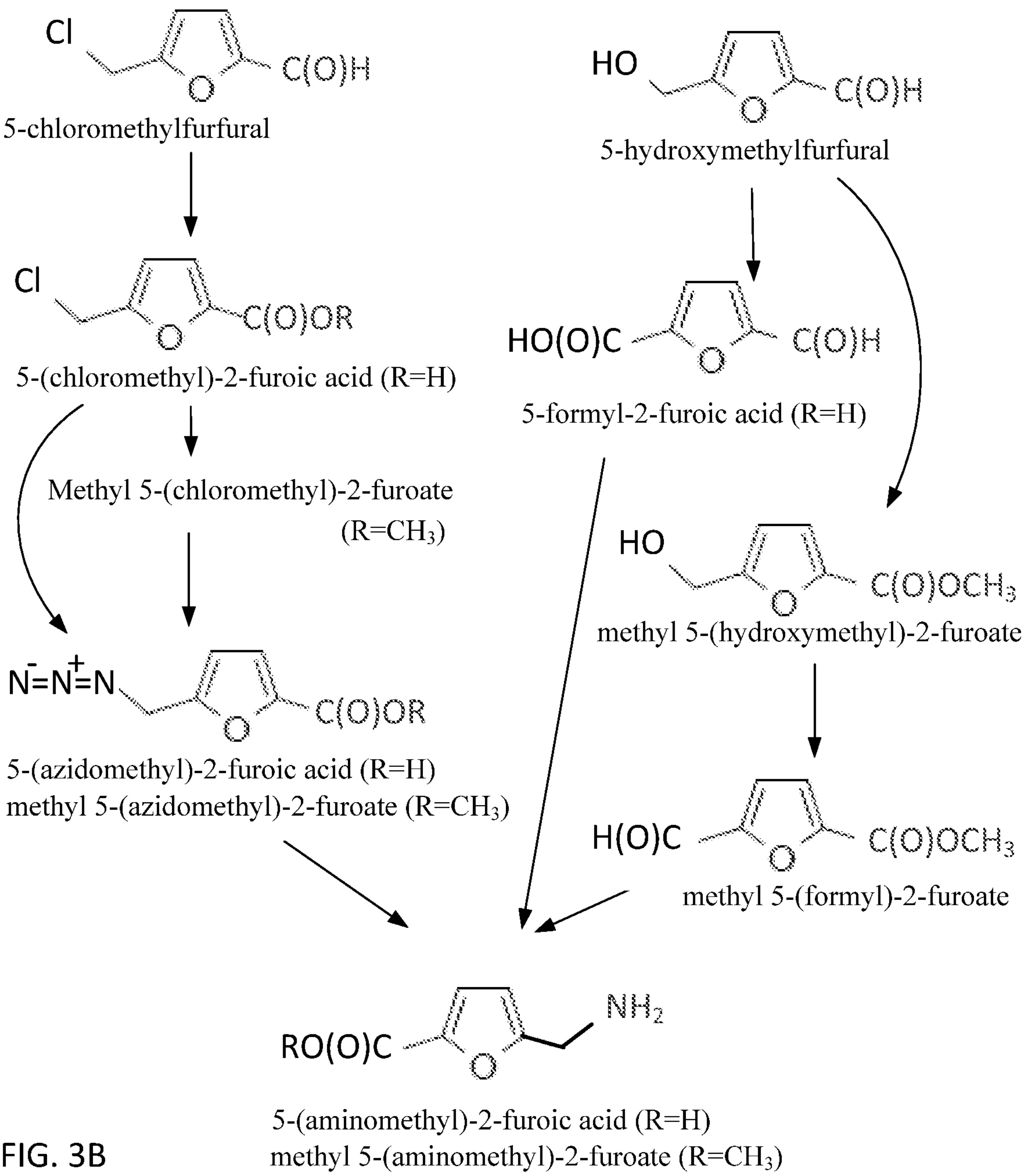
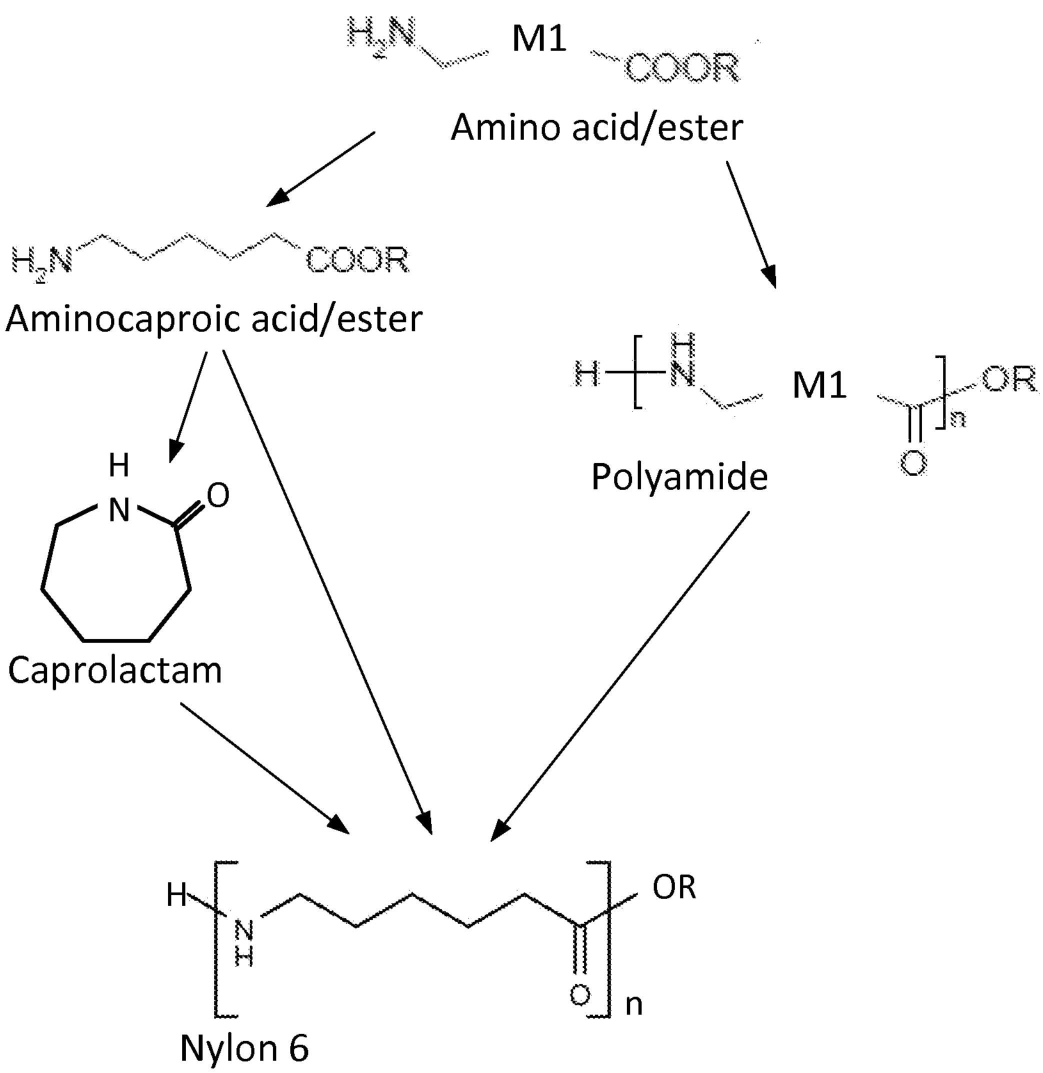

Cl
C(O)H
5-chloromethylfurfural
HO
C(O)H
5-hydroxymethylfurfural
Cl
C(O)OR
5-(chloromethyl)-2-furoic acid (R=H)
HO(O)C
C(O)H
5-formyl-2-furoic acid (R=H)
Methyl 5-(chloromethyl)-2-furoate
(R=CH3)
HO
C(O)OCH3
methyl 5-(hydroxymethyl)-2-furoate
N=N=N
C(O)OR
5-(azidomethyl)-2-furoic acid (R=H)
methyl 5-(azidomethyl)-2-furoate (R=CH3)
H(O)C
C(O)OCH3
methyl 5-(formyl)-2-furoate
NH2
RO(O)C
5-(aminomethyl)-2-furoic acid (R=H)
methyl 5-(aminomethyl)-2-furoate (R=CH3)

FIG. 3B


H2N M1 COOR
Amino acid/ester
H2N COOR
Aminocaproic acid/ester
H N M1 O n OR
Polyamide
H N O
Caprolactam
H N H O n OR
Nylon 6

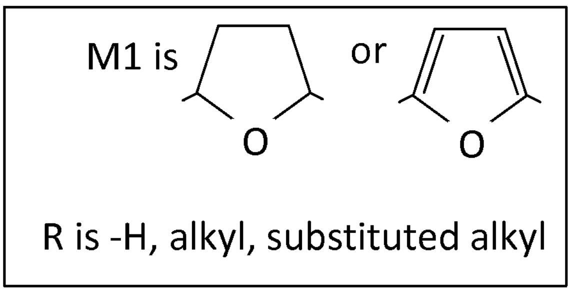

M1 is
or
O
O
R is -H, alkyl, substituted alkyl

FIG. 4

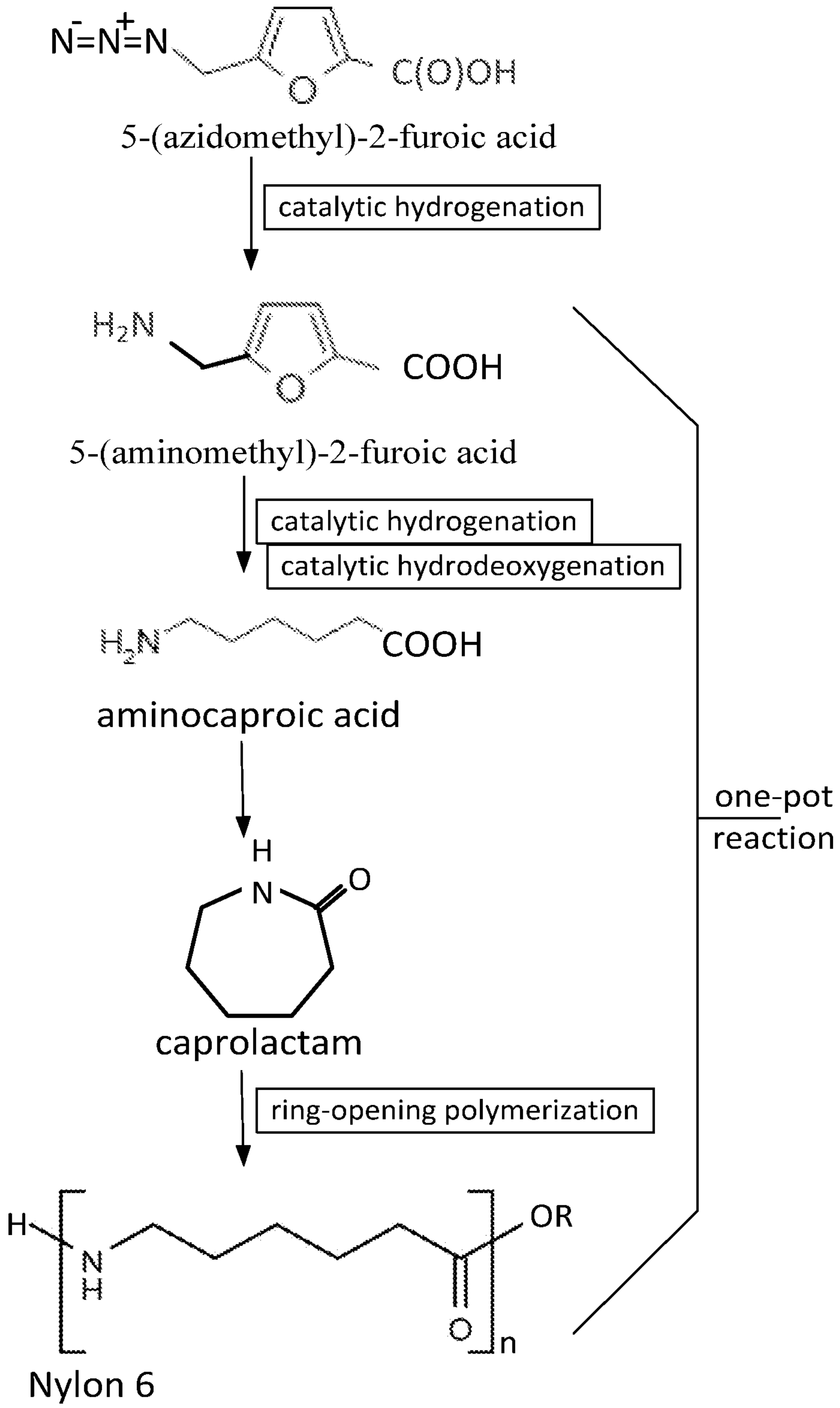

N=N=N
C(O)OH
5-(azidomethyl)-2-furoic acid
catalytic hydrogenation
H2N
COOH
5-(aminomethyl)-2-furoic acid
catalytic hydrogenation
catalytic hydrodeoxygenation
H2N
COOH
aminocaproic acid
H
N
O
caprolactam
ring-opening polymerization
H
N
H
OR
O
n
Nylon 6
one-pot
reaction

FIG. 5

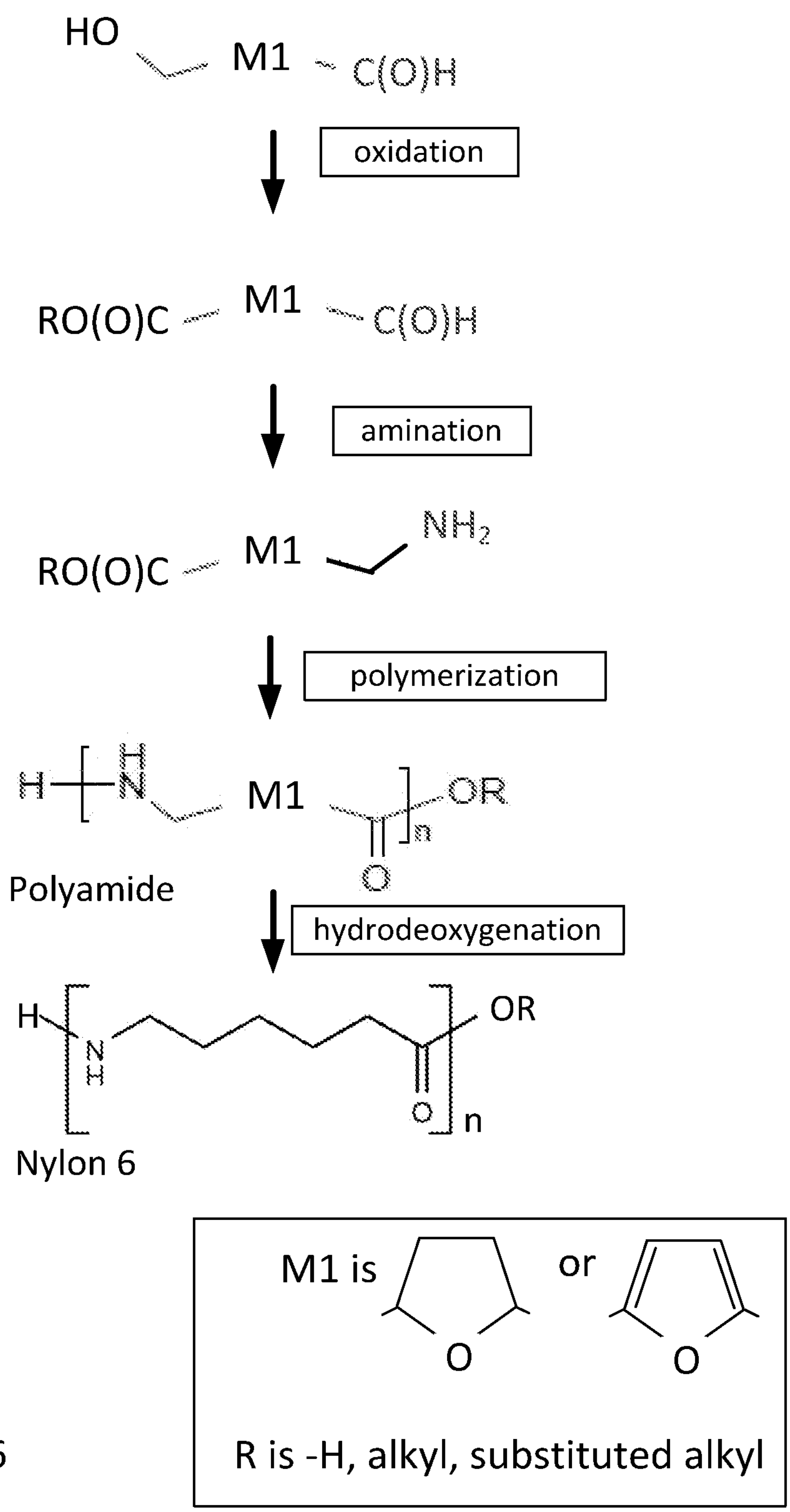

HO
M1
C(O)H
oxidation
RO(O)C
M1
C(O)H
amination
RO(O)C
M1
NH2
polymerization
H
N
H
M1
OR
n
O
Polyamide
hydrodeoxygenation
H
N
H
OR
O
n
Nylon 6
M1 is
or
O
O
R is -H, alkyl, substituted alkyl

FIG. 6

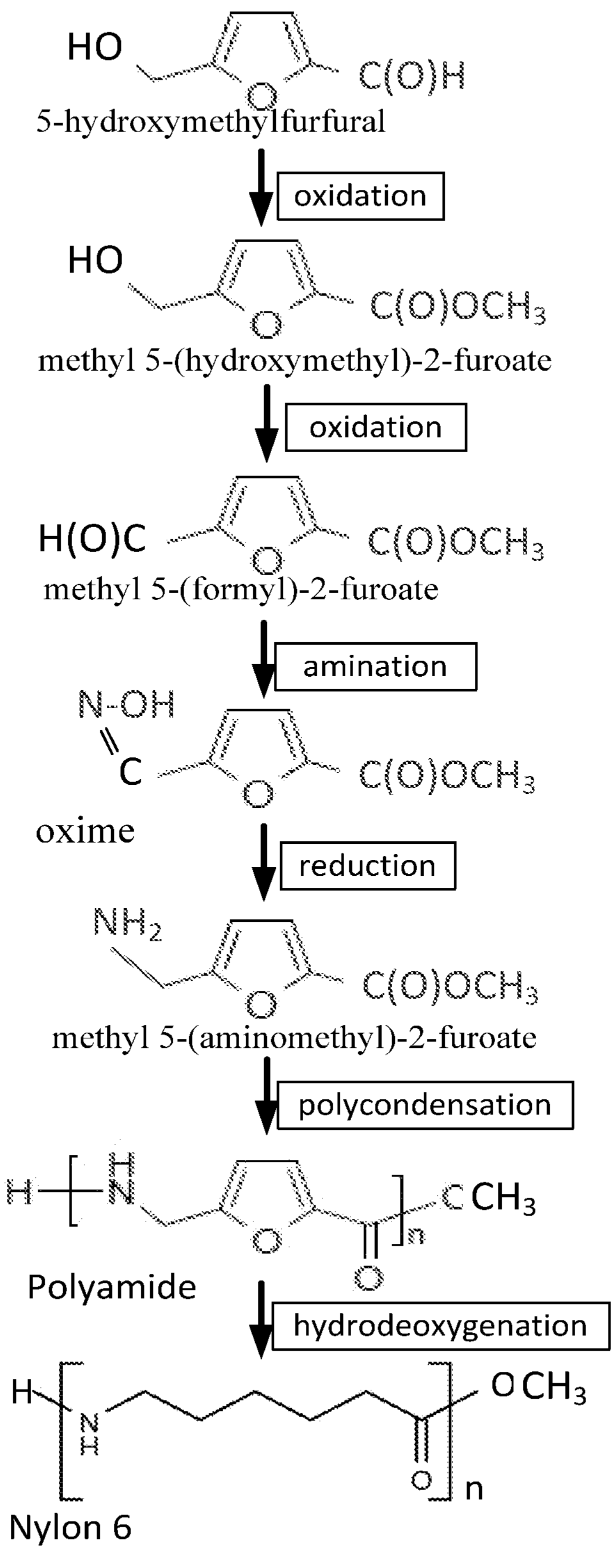

HO
C(O)H
5-hydroxymethylfurfural
oxidation
HO
C(O)OCH3
methyl 5-(hydroxymethyl)-2-furoate
oxidation
H(O)C
C(O)OCH3
methyl 5-(formyl)-2-furoate
amination
N-OH
C
C(O)OCH3
oxime
reduction
NH2
C(O)OCH3
methyl 5-(aminomethyl)-2-furoate
polycondensation
H
N
H
n
CH3
O
Polyamide
hydrodeoxygenation
H
N
H
OCH3
O
n
Nylon 6

FIG. 7A

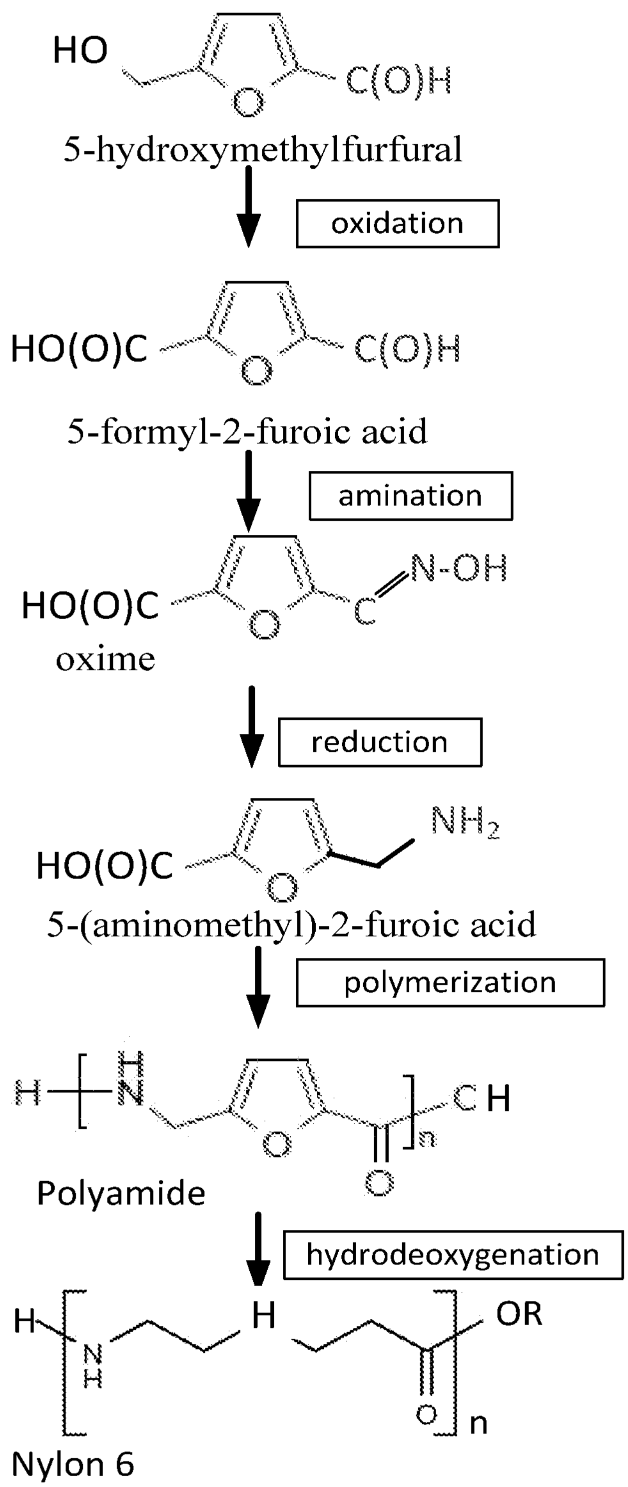
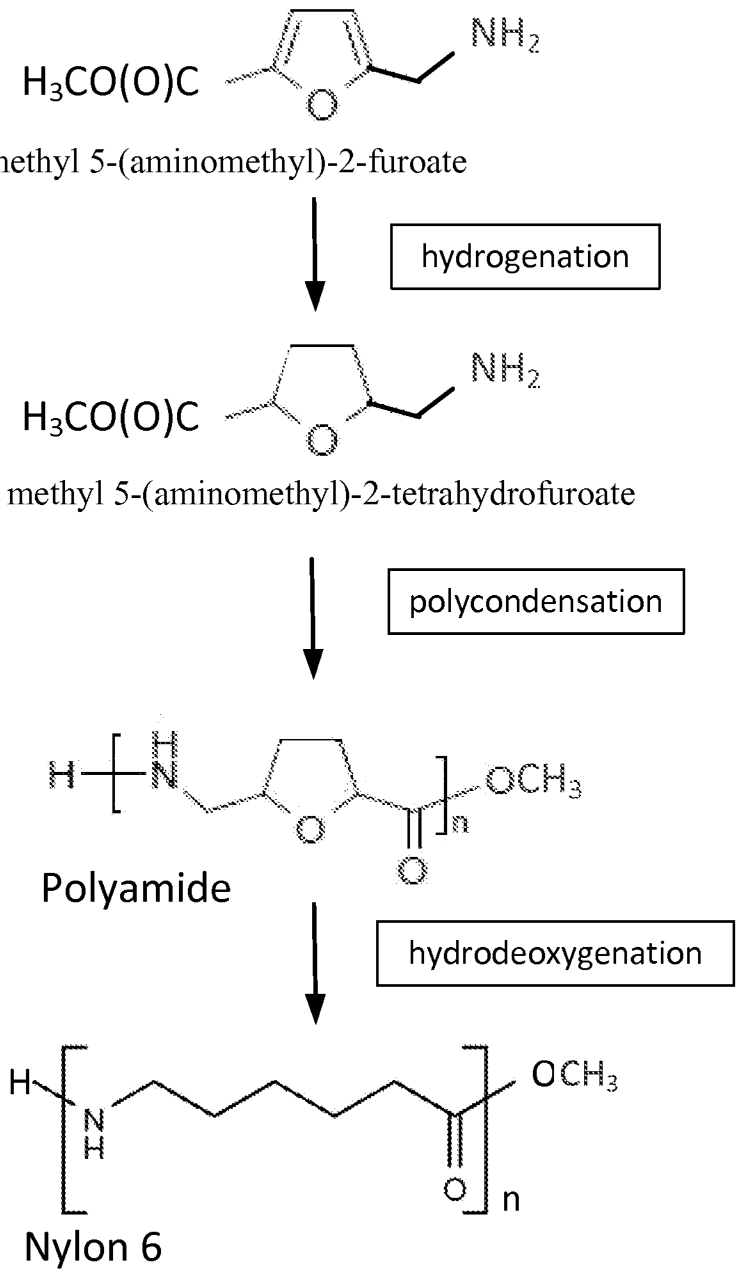

HO
C(O)H
5-hydroxymethylfurfural
oxidation
HO(O)C
C(O)H
5-formyl-2-furoic acid
amination
N-OH
HO(O)C
C
oxime
reduction
$NH_2$
HO(O)C
5-(aminomethyl)-2-furoic acid
polymerization
H
N
H
CH
n
Polyamide
hydrodeoxygenation
H
N
H
H
OR
n
Nylon 6

FIG. 7B



H3CO(O)C
NH2
methyl 5-(aminomethyl)-2-furoate
hydrogenation
H3CO(O)C
NH2
methyl 5-(aminomethyl)-2-tetrahydrofuroate
polycondensation
H
N
OCH3
O
n
Polyamide
hydrodeoxygenation
H
N
H
OCH3
O
n
Nylon 6


FIG. 8

# INTERNATIONAL SEARCH REPORT

International application No.
PCT/US13/66171

A. CLASSIFICATION OF SUBJECT MATTER
IPC(8) - C08G 69/08, 69/14, 73/10 (2014.01)
USPC - 528/310, 313, 319, 320
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): C08G 69/08, 69/14, 73/10; C07D 201/02 (2014.01)
USPC: 528/310, 313, 319, 320, 323; 540/539

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: nylon 6, furanic, furan, tetrahydrofuran, amino carbonyl, two-pot, catalyst, halide, halogen, precursor, diazomethane, caprolactam

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| A | US 7,977,450 B2 (FROST, JW) 12 July 2011; claim 1, column 4, lines 46-60, reaction 1 | 1-103 |
| A | WO 2011/149339 A1 (DE VRIES, JG et al.) 01 December 2011; claim 1, page 5, lines 15-20, page 24 | 1-103 |
| A | US 2010/0317822 A1 (BOUSSIE, TR et al.) 16 December 2010; paragraphs [0012] and [0016] | 1-103 |
| A | US 5,264,541 A (YUO, WB et al.) 23 November 1993; entire document | 1-103 |
| A | US 5,346,984 A (HASEGAWA, N et al.) 13 September 1994; entire document | 1-103 |
| A | US 6,331,624 B1 (KOCH, TA et al.) 18 December 2001; entire document | 1-103 |
| A | US 6,362,307 B1 (MOHRSCHLADT, R et al.) 26 March 2002; entire document | 1-103 |
| A | US 6,437,089 B1 (COHEN, JD et al.) 20 August 2002; entire document | 1-103 |
| A | US 6,699,960 B1 (OHLBACH, F et al.) 02 March 2004; entire document | 1-103 |
| A | US 2013/0095272 A1 (CARMAN JR., HS et al.) 18 April 2013; entire document | 1-103 |
| A | US 2002/0183478 A1 (FERGUSSON, SB et al.) 05 December 2002; entire document | 1-103 |
| A | US 2003/0130478 A1 (WAY, TF et al.) 10 July 2003; entire document | 1-103 |
| A | US 2004/0214982 A1 (ALSOP, AW et al.) 28 October 2004; entire document | 1-103 |

☒ 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 |
|---|---|
| 04 February 2014 (04.02.2014) | 21 FEB 2014 |

| Name and mailing address of the ISA/US | Authorized officer: |
|---|---|
| Mail Stop PCT, Attn: ISA/US, Commissioner for Patents<br>P.O. Box 1450, Alexandria, Virginia 22313-1450<br>Facsimile No. 571-273-3201 | Shane Thomas<br>PCT Helpdesk: 571-272-4300<br>PCT OSP: 571-272-7774 |

**INTERNATIONAL SEARCH REPORT**

International application No.
PCT/US13/66171

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| A | US 5,260,246 A (YUO, WB et al.) 09 November 1993; entire document | 1-103 |