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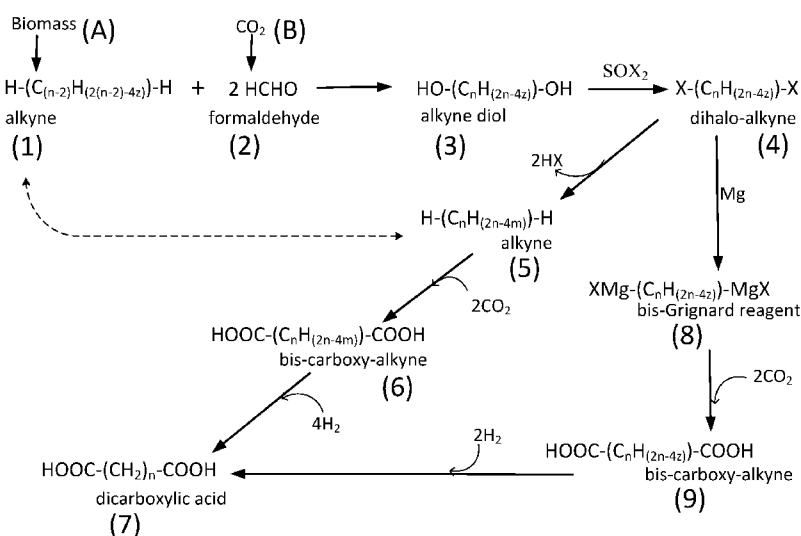
(54) **Title:** METHODS OF PRODUCING DICARBONYL COMPOUNDS

FIG. 1

(57) **Abstract:** Dicarboxylic acids, such as adipic acid, and diesters, such as adipates, may be produced by hydrogenating alkynes that may be produced from raw materials salvaged from waste stream processes. The carbons of the dicarboxylic acids are provided by alkynes generated from biomass waste and carbon dioxide recovered from waste streams such as exhaust gases.

METHODS OF PRODUCING DICARBONYL COMPOUNDS

BACKGROUND

[0001] Dicarbonyl compounds may include dicarboxylic acids, organic compounds that contain two carboxylic acid (-COOH) functional groups, and diesters, organic compounds that contain two ester functionalities (-COOR, where R may be an alkyl group or other organic moiety). Dicarbonyl compounds may be straight chain, branched chain, or aromatic, and are suitable substrates for preparing organic constituents for the pharmaceutical and food industries. For example, dicarboxylic acids are useful materials for preparing fragrances, polyamides, adhesives, lubricants, polyesters, and other commercially valuable products.

[0002] Adipic acid, as an example dicarboxylic acid, is a commodity chemical with global production on the order of 2.5 million metric tons, annually, and the primary commercial use of adipic acid is as a monomer in the manufacture of Nylon 6,6. Nylon 6,6 is a polyamide of the diamine hexamethylenediamine (IUPAC name: hexane-1,6-diamine) and the dicarboxylic acid adipic acid (IUPAC name: hexanedioic acid) and may be produced by the polycondensation of the diamine and the dicarboxylic acid. Types of nylons, such as Nylon 6,6, are distinguished by a numerical suffix that specifies the numbers of carbons donated by the monomers, with the number of carbons from the diamine monomer listed first, followed by the number of carbons from the dicarboxylic acid monomer. Other nylons that may be formed from dicarboxylic acids may include Nylon 6,9, Nylon 6,12, and Nylon 4,6.

[0003] Adipic acid and esters thereof (adipates), as well as other dicarboxylic acids and diesters, are often produced from the petrochemically derived raw materials benzene or butadiene. Efforts to replace these petrochemically derived raw materials are ongoing, and there remains a need to provide alternative scalable and cost effective

approaches for commercially producing diesters and dicarboxylic acids using alternative carbon sources.

SUMMARY

[0004] Trapping of carbon dioxide from waste emissions and incorporation of the carbon dioxide into commodity chemicals that may be useable in producing diesters, dicarboxylic acids, or other materials, provides an alternative method for producing diesters and dicarboxylic acids while reducing waste carbon dioxide emissions into the atmosphere. In some embodiments, the methods disclosed herein use waste carbon dioxide streams.

[0005] In an embodiment, a method for producing dicarbonyl compounds of formula I: $\text{ROOC}-(\text{CH}_2)_n-\text{COOR}$, wherein R is -H, alkyl, or substituted alkyl, and $n \geq 2$, includes hydrogenating a bis-carbonyl alkyne of formula II: $\text{ROOC}-(\text{C}_n\text{H}_{2n-4m})-\text{COOR}$, wherein m is a number of $(-\text{C}\equiv\text{C}-)$ and $n/2 \geq m \geq 1$.

[0006] In an embodiment, a method for producing adipates with waste stream products includes obtaining carbon dioxide from a waste stream of another process, obtaining biomass from a waste stream of another process, pyrolyzing the biomass to produce acetylene, and using the acetylene and the carbon dioxide as reactants for producing adipates.

BRIEF DESCRIPTION OF THE FIGURES

[0007] FIG. 1 depicts a general reaction scheme for producing dicarboxylic acids from alkynes according to some embodiments.

[0008] FIG. 2 depicts reaction steps for producing adipic acid from waste stream products according to embodiments.

[0009] FIG. 3 depicts reaction steps for producing a dialkyl ester from waste stream products according to embodiments.

[0010] FIG. 4 depicts reaction steps for producing a dialkyl adipate from waste stream products according to embodiments.

DETAILED DESCRIPTION

[0011] Elementary saturated dicarboxylic acids and corresponding diesters, may generally be represented by the formula - ROOC-(CH₂)_n-COOR, where R is -H for the diacids, and R is any alkyl or aryl group for diesters. For diesters, each R may be a same or different alkyl or aryl group. Methods disclosed herein may be used to produce dicarboxylic acids and diesters having (*n*) intermediate carbon atoms disposed between the two carbons provided by the terminal carbonyl groups, for a total of (*n*+2) carbons. Some examples of dicarboxylic acids and corresponding diesters are represented in Table 1.

Table 1

	ROOC-(CH ₂) _n -COOR		
	Diacids R=H		Diesters R= alkyl
<i>n</i> =	<i>Common Name</i>	<i>IUPAC Name</i>	<i>Common Name</i>
0	oxalic acid	ethanedioic acid	dialkyl oxalate
1	malonic acid	propanedioic acid	dialkyl malonate
2	succinic acid	butanedioic acid	dialkyl succinate
3	glutaric acid	pentanedioic acid	dialkyl glutarate
4	adipic acid	hexanedioic acid	dialkyl adipate
5	pimelic acid	heptanedioic acid	dialkyl pimelate
6	suberic acid	octanedioic acid	dialkyl suberate
7	azeleic acid	nonanedioic acid	dialkyl azelate
8	sebacic acid	decanedioic acid	dialkyl sebacate
18		icosanedioic acid	

[0012] The methods disclosed herein are particularly well suited for production of dicarbonyl compounds such as dicarboxylic acids and diesters where $n \geq 2$. Dicarbonyl compounds (dicarboxylic acids and diesters) of formula $\text{ROOC}-(\text{CH}_2)_n-\text{COOR}$, where $n \geq 2$, R is -H for the diacids, and R is any alkyl or aryl group for diesters, may be produced from alkynes, which are unsaturated hydrocarbons having at least one triple bond between two adjacent carbon atoms ($-\text{C}\equiv\text{C}-$). The simplest alkyne with $n=2$ is acetylene $\text{H}-\text{C}\equiv\text{C}-\text{H}$.

[0013] Dicarbonyl compounds of formula $\text{ROOC}-(\text{CH}_2)_n-\text{COOR}$, where $n \geq 2$ may be produced by hydrogenating bis-carbonyl alkynes of formula $\text{ROOC}-(\text{C}_n\text{H}_{(2n-4m)})-\text{COOR}$, where m is a number of ($-\text{C}\equiv\text{C}-$) and $n/2 \geq m \geq 1$. In an embodiment, n may be less than or equal to about 20. As examples, n may be 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19 or 20. In an embodiment, the hydrogenating may include catalytic hydrogenation.

[0014] In an embodiment for producing diacids as shown in FIG. 1, dicarboxylic acids **7** may be produced by hydrogenating bis-carboxy-alkynes **6** or **9**. More specifically, in an embodiment as shown in FIG. 2, adipic acid **17** may be produced by hydrogenating dicarboxydiacetylene **16** or bis-carboxy-butyne **19**. (For nomenclature purposes, in chemistry, the prefix bis- may sometimes be used instead of the prefix di-. For example, bis-carboxy alkyne refers to an alkyne with 2 carboxy groups.) Some examples of bis-carbonyl alkynes and dicarboxylic acids that may be produced therefrom are represented in Table 2.

Table 2

$n=$	$m=$	$2n-4m=$	<i>bis-carbonyl alkyne</i> $\text{ROOC}-(\text{C}_n\text{H}_{(2n-4m)})-\text{COOR}$	<i>diester R=alkyl, aryl</i> <i>dicarboxylic acid R=H</i> $\text{ROOC}-(\text{CH}_2)_n-\text{COOR}$
2	1	0	$\text{ROOC}-\text{C}\equiv\text{C}-\text{COOR}$	$\text{ROOC}-(\text{CH}_2)_2-\text{COOR}$
3	1	2	$\text{ROOC}-\text{C}\equiv\text{C}-\text{CH}_2-\text{COOR}$	$\text{ROOC}-(\text{CH}_2)_3-\text{COOR}$

4	1	4	$\text{ROOC-C}\equiv\text{C-CH}_2\text{-CH}_2\text{-COOR}$	$\text{ROOC-(CH}_2)_4\text{-COOR}$
4	2	0	$\text{ROOC-C}\equiv\text{C-C}\equiv\text{C-COOR}$	$\text{ROOC-(CH}_2)_4\text{-COOR}$
5	1	6	$\text{ROOC-C}\equiv\text{C-CH}_2\text{-CH}_2\text{-CH}_2\text{-COOR}$	$\text{ROOC-(CH}_2)_5\text{-COOR}$
5	2	2	$\text{ROOC-C}\equiv\text{C-CH}_2\text{-C}\equiv\text{C-COOR}$	$\text{ROOC-(CH}_2)_5\text{-COOR}$
6	3	0	$\text{ROOC-C}\equiv\text{C-C}\equiv\text{C-C}\equiv\text{C-COOR}$	$\text{ROOC-(CH}_2)_6\text{-COOR}$

[0015] Referring to FIG. 1, the alkynes **6, 9** may be catalytically hydrogenated by contacting the alkynes with hydrogen in the presence of a hydrogenation catalyst to produce the dicarboxylic acids **7**. The reaction may be conducted at temperatures of about ambient temperature to about 100 °C, and at pressures of about 1 bar to about 100 bar. In an embodiment, the reaction may be done at ambient temperature and pressure. The hydrogenation catalyst may include platinum, palladium, rhodium, ruthenium, nickel, cobalt, iron, molybdenum, iridium, rhenium, gold, or any combination thereof.

[0016] While the starting raw materials for producing dicarboxylic acids or diesters may be obtained from petrochemical or other conventional sources, the dicarboxylic acids produced in accordance with methods described herein may be composites of carbon atoms produced from waste stream materials. Referring to FIG. 1, one starting material may include alkynes **1** that may be derived from biomass waste products **A**, and another starting material may include formaldehyde (HCHO) **2** that may be produced from carbon dioxide (CO₂) **B** collected from waste exhaust streams.

[0017] To reduce reliance on petrochemicals for the producing dicarboxylic acids and diesters, raw material alkynes may be produced from biomass **A** in FIG. 1, which may be waste stream biomass, instead of the typical starting materials of methane or hydrocarbons. Some examples of waste biomass may include industrial waste, such as saw-dust and wood scraps from lumber mills, or pulp waste from production of paper products, and municipal

waste, such as garbage, and tree and yard trimmings. In an embodiment, for example, acetylene **11**, in FIGS. 2 and 4, may be produced from lignocellulosic biomass by rapid pyrolysis of the biomass. Rapid pyrolysis of dry lignin produces a gas that is about 14% acetylene by volume.

[0018] Carbon dioxide **B** in FIGS. 1 to 4, and as used in the embodiments described herein, may be obtained from a waste stream of another process, such as, for example, flue gas from combusting fossil fuels to generate electricity, or from incinerating waste. As such, carbon dioxide may be removed or recovered from waste streams so that excessive carbon dioxide does not enter the atmosphere where it may cause environmental concerns. A system for collecting carbon dioxide, such as the LCDesign™ CO₂ Capture Systems from HTC Pureenergy, Saskatchewan, Canada, may be used to capture carbon dioxide from exhaust gases produced by combusting hydrocarbons for generating electricity.

[0019] In some embodiments, the carbon dioxide **B** may be catalytically reduced to produce formaldehyde **2**, **12** in FIGS 1 and 2, and the formaldehyde as used in the embodiments described herein. The catalytic reduction can be photocatalytic reduction. For example, a glass tube containing a suspension of titanium dioxide photocatalyst in water may be illuminated with a xenon or mercury arc lamp and carbon dioxide may be bubbled into the tube for several hours to yield an aqueous mixture of formaldehyde **2**, **12** and methanol. The formaldehyde **2**, **12** may then be separated from the methanol.

[0020] In some embodiments, for example as shown in FIG. 1, a dicarboxylic acid **7** of formula $\text{HOOC}-(\text{CH}_2)_n-\text{COOH}$, where $n \geq 2$, may be produced from alkynes **1** of formula $\text{H}-(\text{C}_{(n-2)}\text{H}_{(2(n-2)-4z)})-\text{H}$, where z is the number of original triple bonds ($-\text{C}\equiv\text{C}-$). By reacting the alkynes **1** with two equivalents of formaldehyde (HCHO) **2** in the presence of a second metal catalyst, alkyne diols **3** of formula $\text{HO}-(\text{C}_n\text{H}_{(2n-4z)})-\text{OH}$ may be produced. By using waste biomass to make the alkynes and waste carbon dioxide to make the

formaldehyde, all of the carbons of the alkyne diol **3** may be provided, in some embodiments, by waste materials. In an embodiment, the second metal catalyst may be copper, silver, bismuth, or a combination thereof. In an embodiment, as depicted in FIG. 2 for example, butynediol **13** may be produced by a Reppe process that involves treatment of an aqueous mixture of formaldehyde **12** and a copper-bismuth catalyst with acetylene **11** to yield butynediol **13**.

[0021] In some embodiments, for example as shown in FIG. 1, the alkyne diols **3** of formula $\text{HO}-(\text{C}_n\text{H}_{(2n-4z)})-\text{OH}$ may be treated with thionyl halides (SOX_2) to produce dihalo-alkynes **4** of formula $\text{X}-(\text{C}_n\text{H}_{(2n-4z)})-\text{X}$, where X may be any halogen, F, Cl, Br, I, or At. In an embodiment, the treating with thionyl halides may be performed in the presence of a reaction catalyst. Alternative halogenating reagents may include phosphorous trihalides (PX_3) or phosphorus pentahalides (PX_5). The reaction catalyst may be pyridine, dimethylformamide, or both. In an embodiment, the diols may be cooled with pyridine in an ice bath, and the halogenating reagent may be slowly added. The alkynes may be isolated by solvent extraction from the reaction mixture.

[0022] As shown in FIG. 1, dihalo-alkynes **4** may be converted to dicarboxylic acids **7** by at least two different reaction sequences. In a first sequence, the dihalo-alkynes **4** of formula $\text{X}-(\text{C}_n\text{H}_{(2n-4z)})-\text{X}$ may be converted to alkynes **5** of formula $\text{H}-(\text{C}_n\text{H}_{(2n-4m)})-\text{H}$, where m is the number of triple bonds ($-\text{C}\equiv\text{C}-$) and $m = z+1$. This conversion may be carried out by a base promoted elimination of hydrogen halide from the dihalo-alkynes **4**. In an embodiment, the dihalo-alkynes may be added slowly to a mixture of aqueous potassium hydroxide and dimethyl sulfoxide while bubbling an inert gas through the solution. The produced gases may be conducted into a solvent, such as tetrahydrofuran to capture the alkynes.

[0023] At this juncture, as represented by the dashed line in FIG. 1, if longer alkynes are desired, the above reaction sequence may be repeated with a substitution of the alkynes **5** into the sequence for alkynes **1**. Alternatively, bis-carboxy alkynes **6** of formula $\text{HOOC}-(\text{C}_n\text{H}_{(2n-4m)})-\text{COOH}$ may be produced by carboxylation of the alkynes **5** of formula $\text{H}-(\text{C}_n\text{H}_{(2n-4m)})-\text{H}$ with two equivalents of carbon dioxide. The carboxylation may be performed with or without the presence of a first metal catalyst. The first metal catalyst may be copper, silver, bismuth, or any combination thereof. In an embodiment, the carboxylation may be conducted by bubbling carbon dioxide gas through ice cold mixture of a dianion of the alkyne with lithium or magnesium as a counter ion. The carbon dioxide, as mentioned above, may be obtained from a waste stream of another process, thereby adding two additional waste stream carbons to the alkynes. As discussed previously, the bis-carboxy alkynes **6** may be catalytically hydrogenated by contacting the alkynes with hydrogen in the presence of a hydrogenation catalyst to produce the dicarboxylic acids **7**.

[0024] In another embodiment, a second sequence in FIG. 1 for converting the dihalo-alkynes **4** to the dicarboxylic acids **7** may be through an intermediate organometallic compound, such as a Grignard reagent **8**. The dihalo-alkynes **4** of formula $\text{X}-(\text{C}_n\text{H}_{(2n-4z)})-\text{X}$ may be converted to a corresponding bis-Grignard reagent **8** of formula $\text{XMg}-(\text{C}_n\text{H}_{(2n-4z)})-\text{MgX}$ by treating the dihalo-alkynes with magnesium metal, wherein each X may be the same or different one of F, Cl, Br, I and At. The bis-Grignard reagent may subsequently be treated with excess carbon dioxide to yield bis-carboxy-alkynes **9** of formula $\text{HOOC}-(\text{C}_n\text{H}_{(2n-4z)})-\text{COOH}$. The CO_2 for this reaction may also be obtained from a waste stream of another process, thereby adding two additional waste stream carbons to the alkyne. As discussed previously, the bis-carboxy alkynes **9** may be catalytically hydrogenated by contacting the alkynes with hydrogen in the presence of a hydrogenation catalyst to produce the dicarboxylic acids **7**.

[0025] The reaction sequence as described above may be followed as described for producing dicarboxylic acids **7** from biomass **A** and carbon dioxide **B**, or if other materials mentioned are available as raw materials, or produced to be raw materials via other processes, the sequence described may be picked up at the appropriate point in the sequence. For example, if alkynes **5** of an appropriate carbon length are available, the alkynes **5** could be the starting material, and would be carboxylated to produce bis-carboxy-alkynes **6**, that subsequently would be hydrogenated to produce the desired dicarboxylic acid **7**. Thus, the methods may be practiced with waste streams as source of reactants, or with commercially available reactants, or a combination thereof.

[0026] In the embodiments as shown in FIG. 2, adipic acid **17** may be produced from acetylene **11** and formaldehyde **12**, which may be produced respectively from biomass **A** and carbon dioxide **B**. Thus, adipic acid may be produced from the waste stream carbon dioxide and waste biomass, where four of the six carbon atoms of adipic acid may be provided from carbon dioxide and the other two carbon atoms from biomass derived acetylene. In general, a process for producing adipic acid **17** may therefore include obtaining biomass **A** from a waste stream, obtaining carbon dioxide **B** from a waste stream, pyrolyzing the biomass to produce acetylene **11**, and using the acetylene and the carbon dioxide as reactants for producing adipic acid.

[0027] In some embodiments, for example as shown in FIG. 2, the carbon dioxide **B** may be reduced to formaldehyde **12** so that each formaldehyde carbon may be provided by a carbon of waste carbon dioxide. In a subsequent reaction step, 2-butyne-1,4-diol **13** may be produced by contacting acetylene **11** and formaldehyde **12** in the presence of a second metal catalyst as described herein. As such, the 2-butyne-1,4-diol **13** may have all four carbons provided by waste material, two from the acetylene, and one from each of two molecules of formaldehyde.

[0028] The 2-butyne-1,4-diol may be treated with a thionyl halide such as thionyl chloride (SOCl_2) to produce dichlorobutyne **14** (1,4-dichloro-2-butyne), retaining the four waste material carbons. The dichlorobutyne **14** may then subsequently be converted to adipic acid **17** by either hydrogen elimination route or the Grignard reagent route described above.

[0029] By following the first sequence, diacetylene **15** may be produced by base promoted elimination of HCl from the dichlorobutyne **14**. The diacetylene **15** may then be carboxylated in the presence of a first metal catalyst to produce dicarboxydiacetylene **16**, adding two additional carbons and increasing the number of carbons to six. The first metal catalyst may include copper, silver, bismuth, or combinations thereof. If the carboxylation is done with waste stream carbon dioxide the additional two carbons may also be waste stream carbons, so that four of the six carbons are from waste carbon dioxide and the other two carbons from waste biomass. The dicarboxydiacetylene **16** may then be hydrogenated to produce adipic acid **17**, retaining the six waste stream carbons.

[0030] Alternatively, by following the second sequence, a dihalo-alkyne such as dichlorobutyne **14** may be converted to the corresponding bis-Grignard reagent **18** of formula $\text{XMg}-(\text{C}_n\text{H}_{(2n-4z)})-\text{MgX}$ by treating the dihalo-alkyne (dichlorobutyne **14** in FIG. 2) with magnesium metal, , wherein each X may be the same or different one of F, Cl, Br, I and At. The Grignard reagent **18** may then be carboxylated to yield bis-carboxy-butyne **19**, which may then be hydrogenated to produce adipic acid **17**. As above, the carboxylation may be performed with waste stream carbon dioxide so that all of the carbons in the adipic acid may be waste stream carbons.

[0031] In an embodiment for producing diesters, as generally represented in FIG. 3, diesters of formula $\text{ROOC}-(\text{CH}_2)_n-\text{COOR}$ may be produced by hydrogenating diester-alkynes of formula $\text{ROOC}-(\text{C}_n\text{H}_{(2n-4m)})-\text{COOR}$. The diester-alkynes may be produced from carbon dioxide and alkynes that, as discussed above, may be from waste stream processes.

Carboxylation of an alkyne with carbon dioxide may produce mono-carboxyl-alkynes having only one terminal carboxyl group leaving the other terminal end available for dimerization. Mono-ester alkynes may be prepared from the mono-carboxyl-alkynes by esterification of the carboxyl groups. Mono-ester alkynes may be dimerized to produce the diester alkynes. The dimerization can, for example, be Glaser-Hay dimerization.

[0032] More specifically, in an embodiment as shown in FIG. 4, the diester, dialkyl adipate **27**, may be produced by hydrogenating dialkyl diacetylene dicarboxylate **26**. In an embodiment, each R may be the same or a different one of any alkyl or aryl group. In embodiments, R may be C1-C5 alkyl, or substituted alkyl. In embodiments, R may be methyl, ethyl, propyl, butyl, or pentyl. In the representation of FIG. 4, R may also be -H and the adipate product would then be the diacid adipic acid.

[0033] As discussed above, waste biomass **A** may be converted to acetylene **11**. Mono anions of acetylene **11** may be reacted with carbon dioxide **B** that may be from a waste stream of another process, to produce propiolic acid **20**. Similarly, alkynes of various other carbon-chain lengths may be carboxylated to produce mono-carboxy-alkynes of the corresponding carbon-chain length. The carboxylic acid **20** may be converted to an ester, which as depicted in the embodiment of FIG. 4 may be methyl propiolate **22**, by an esterification process with an alkanol (alkyl alcohol), wherein methyl alcohol may provide methyl propiolate, for example. A catalyzed dimerization of the esterified terminal alkynes **22** may be used to produce diester-alkynes **26**, which as depicted in the embodiment of FIG. 4 may be dialkyl diacetylene dicarboxylate. Hydrogenation of the diester-alkynes **26** may then produce diesters **27**, which as depicted in the embodiment of FIG. 4 may be dialkyl adipate.

EXAMPLES**EXAMPLE 1: A Method for Producing Adipic Acid**

[0034] Adipic acid ($\text{HOOC}-(\text{CH}_2)_4-\text{COOH}$) **17** is produced by hydrogenating dicarboxydiacetylene ($\text{HOOC}-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-\text{COOH}$) **16** in the presence of platinum as a catalyst. A mixture of the di-lithium salt of dicarboxydiacetylene (1 equivalent), 10% platinum on activated carbon (0.05 equivalent platinum), and 1 M phosphate buffer (pH 7.4) in an autoclave is treated with hydrogen gas (about 35 atmospheres) for about 3 hours. The catalyst is removed by filtration and the filtrate is acidified by addition of concentrated hydrochloric acid. After cooling in an ice bath the solid is filtered and dried under reduced pressure to yield adipic acid.

EXAMPLE 2: Production of 1,4-dichloro-2-butyne

[0035] Adipic acid **17** is produced from acetylene **A**, derived from waste stream biomass materials, and waste stream carbon dioxide **B**. A system for collecting carbon dioxide **B**, such as the LCDesign™ CO₂ Capture Systems from HTC Purenergy, Saskatchewan, Canada, is used to capture CO₂ from exhaust gases produced by combusting hydrocarbons for generating electricity. The carbon dioxide **B** is photocatalytically reduced to formaldehyde **12** by providing a glass tube containing a suspension of titanium dioxide photocatalyst in water and illuminated with a xenon or mercury arc lamp, and bubbling carbon dioxide into the tube for several hours to yield an aqueous mixture of formaldehyde and methanol, and separating the formaldehyde from the methanol.

[0036] 2-Butyne-1,4-diol is synthesized from acetylene **11** and formaldehyde **12** in the presence of a catalyst. Into a mixture of 45% aqueous formaldehyde (1 equivalent) and malachite crystal-based copper-acetylide complex catalyst (0.0017 equivalent) is bubbled acetylene at a pressure of about 5 psig while heating at about 90 °C and maintaining the pH at about 6 with saturated sodium bicarbonate solution for about 2 hours. After removal of the

catalyst by filtration, fractional distillation under reduced pressure yields 2-butyne-1,4-diol **13**.

[0037] The 2-butyne-1,4-diol **13** is then halogenated. A mixture of butynediol (1 equivalent) and pyridine (0.1 equivalent) is cooled in an ice-salt bath, and ice cold thionyl chloride (2 equivalents) is slowly added. After about 1 hour the ice-salt bath is replaced with an ice-water bath, and the mixture is stirred for about 20 hours, after which ice-water is added and the mixture is extracted with diethyl ether. The extract is dried over magnesium sulfate and concentrated under reduced pressure. The residue is purified by reduced pressure distillation to yield 1,4-dichloro-2-butyne **14**.

EXAMPLE 3: Production of Adipic Acid via Diacetylene

[0038] The 1,4-dichloro-2-butyne **14** of Example 2 is de-halogenated by base promoted elimination of HCl to produce diacetylene **15**. A mixture of 4 M aqueous potassium hydroxide (3 equivalents) and dimethyl sulfoxide (1 mL per 16 mmol potassium hydroxide) is heated to about 70-75 °C. 1,4-dichloro-2-butyne (1 equivalent) is added slowly to the mixture while bubbling argon through the solution. The volatile product is directed through a series of two gas washing bottles containing dilute aqueous potassium hydroxide followed by two calcium chloride drying tubes and into a vessel containing anhydrous tetrahydrofuran cooled in an ice-calcium chloride bath to yield a tetrahydrofuran solution of diacetylene **15**.

[0039] The solution of diacetylene (1 equivalent) in tetrahydrofuran is cooled in an ice-calcium chloride bath, and a 1.6 M solution of n-butyl lithium (2 equivalents) in hexane is slowly added. Into this mixture is bubbled dry carbon dioxide. The cooling bath is replaced with an ice-water bath and bubbling with carbon dioxide is continued for about 1 hour. The reaction is quenched by treatment with a minimum volume of water. Removal of solvents under reduced pressure yields the di-lithium salt of diacetylene dicarboxylic acid.

[0040] Adipic acid **17** is then produced from the dicarboxydiacetylene **16** by hydrogenating the dicarboxydiacetylene in the presence of palladium as a catalyst according to the method described in Example 1.

EXAMPLE 4: Production of Dimethyl Adipate

[0041] Dimethyl adipate **27** may be derived from waste stream biomass materials **A**, and waste stream carbon dioxide **B**. Biomass material **A** is converted to acetylene **11**, and the acetylene is reacted with CO₂ **B** to produce propiolic acid **20**. Via an esterification of the propiolic acid **20** with methanol, the propiolic acid is converted to methyl propiolate (in FIG. 4, structure **22** with R= CH₃).

[0042] A Glaser-Hay dimerization involving copper catalyzed dimerization of terminal alkynes is used to convert the methyl propiolate **22** to dimethyl diacetylene dicarboxylate (in FIG. 4, structure **26** with R= CH₃). A mixture of copper (II) chloride (0.1 equivalent), tetramethylethylenediamine (0.03 equivalent) and acetone as solvent is stirred for 40 minutes. To this mixture is added a solution of methyl propiolate (1 equivalent) in acetone. After bubbling oxygen through the mixture for 2 hours, the solvent is removed under reduced pressure, and the residue is treated with diethyl ether. The organic phase is washed with 5% hydrochloric acid, dried over magnesium sulfate, and concentrated under reduced pressure to yield dimethyl diacetylene dicarboxylate **26**.

[0043] For hydrogenation of the alkyne, a mixture of dimethyl diacetylene dicarboxylate (1 equivalent), 10% palladium on carbon (0.02 equivalent palladium) and ethyl acetate as solvent is treated with hydrogen gas (3 atmospheres). After about 5 hours, the catalyst is removed by filtration, and the filtrate is concentrated under reduced pressure to yield dimethyl adipate.

[0044] Therefore, the examples demonstrate that dicarboxylic acids, such as adipic acid, and diesters, such as adipates, can be produced from waste materials derived

from biomass and/or collected from waste stream processes that generate waste carbon dioxide, thereby reducing the need for petrochemically derived raw materials.

[0045] 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.

[0046] 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.

[0047] 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.

[0048] 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.”

[0049] 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.

[0050] 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.

[0051] It will be understood by those within the art that, in general, terms used herein, and especially in the appended claims (*e.g.*, bodies of the appended claims) are generally intended as “open” terms (*e.g.*, the term “including” should be interpreted as “including but not limited to,” the term “having” should be interpreted as “having at least,” the term “includes” should be interpreted as “includes but is not limited to,” etc.). It will be further understood by those within the art that if a specific number of an introduced claim

recitation is intended, such an intent will be explicitly recited in the claim, and in the absence of such recitation no such intent is present. For example, as an aid to understanding, the following appended claims may contain usage of the introductory phrases "at least one" and "one or more" to introduce claim recitations. However, the use of such phrases should not be construed to imply that the introduction of a claim recitation by the indefinite articles "a" or "an" limits any particular claim containing such introduced claim recitation to embodiments containing only one such recitation, even when the same claim includes the introductory phrases "one or more" or "at least one" and indefinite articles such as "a" or "an" (*e.g.*, "a" and/or "an" should be interpreted to mean "at least one" or "one or more"); the same holds true for the use of definite articles used to introduce claim recitations. In addition, even if a specific number of an introduced claim recitation is explicitly recited, those skilled in the art will recognize that such recitation should be interpreted to mean at least the recited number (*e.g.*, the bare recitation of "two recitations," without other modifiers, means at least two recitations, or two or more recitations). Furthermore, in those instances where a convention analogous to "at least one of A, B, and C, etc." is used, in general such a construction is intended in the sense one having skill in the art would understand the convention (*e.g.*, "a system having at least one of A, B, and C" would include but not be limited to systems that have A alone, B alone, C alone, A and B together, A and C together, B and C together, and/or A, B, and C together, etc.). In those instances where a convention analogous to "at least one of A, B, or C, etc." is used, in general such a construction is intended in the sense one having skill in the art would understand the convention (*e.g.*, "a system having at least one of A, B, or C" would include but not be limited to systems that have A alone, B alone, C alone, A and B together, A and C together, B and C together, and/or A, B, and C together, etc.). It will be further understood by those within the art that virtually any disjunctive word and/or phrase presenting two or more alternative terms, whether in the description, claims, or drawings,

should be understood to contemplate the possibilities of including one of the terms, either of the terms, or both terms. For example, the phrase “A or B” will be understood to include the possibilities of “A” or “B” or “A and B.”

[0052] 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.

[0053] 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.

[0054] 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.

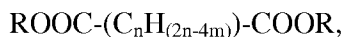
CLAIMS

What Is Claimed Is:

1. A method for producing dicarbonyl compounds of formula I:

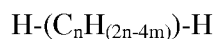


wherein R is -H, aryl, alkyl or substituted alkyl, and $n \geq 2$, the method comprising hydrogenating a bis-carbonyl alkyne of formula II:



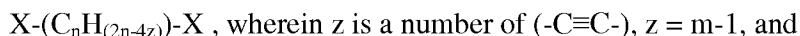
wherein m is a number of $(-\text{C}\equiv\text{C}-)$ with $n/2 \geq m \geq 1$.

2. The method of claim 1, wherein n is less than or equal to about 20.
3. The method of claim 1, wherein the hydrogenating comprises a catalytic hydrogenation.
4. The method of claim 1, wherein R=H, the compound of formula I is a dicarboxylic acid, and the bis-carbonyl alkyne of formula II is produced by carboxylating an alkyne of formula III:



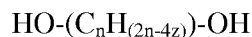
with two equivalents of CO_2 in the presence of a first metal catalyst.

5. The method of claim 4, wherein the first metal catalyst comprises copper, silver, bismuth, or combinations thereof.
6. The method of claim 4, wherein the CO_2 is obtained from a waste stream from another process.
7. The method of claim 4, wherein the alkyne of formula III is prepared by base promoted elimination of hydrogen halide from a dihalo-alkyne of formula IV:



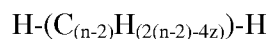
each X comprises a same or different one of F, Cl, Br, I, and At.

8. The method of claim 7, wherein the dihalo alkyne of formula IV is prepared by treating an alkyne diol of formula V:



with thionyl halides of formula SOX_2 .

9. The method of claim 8, wherein the alkyne diol of formula V is prepared by reacting an alkyne of formula VI:



with 2 equivalents of formaldehyde in the presence of a second metal catalyst.

10. The method of claim 9, wherein the second metal catalyst comprises copper, silver, bismuth, or combinations thereof.

11. The method of claim 9, wherein the formaldehyde is prepared by catalytically reducing CO_2 .

12. The method of claim 11, wherein catalytically reducing comprises photocatalytically reducing.

13. The method of claim 11, wherein the CO_2 is obtained from a waste stream of another process.

14. The method of claim 1, wherein $\text{R}=\text{H}$, $n=4$, $m=2$, the compound of formula I is a dicarboxylic acid, and the bis-carbonyl alkyne is a bis-carboxy alkyne of a formula $\text{HOOC}-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-\text{COOH}$.

15. The method of claim 14, further comprising producing the bis-carboxy alkyne of formula $\text{HOOC-C}\equiv\text{C-C}\equiv\text{C-COOH}$ by carboxylating diacetylene with CO_2 in the presence of a first metal catalyst.

16. The method of claim 15, wherein the first metal catalyst comprises copper, silver, bismuth, or combinations thereof.

17. The method of claim 15, further comprising producing the diacetylene by base promoted elimination of HCl from 1,4-dihalo-2-butyne.

18. The method of claim 17, further comprising producing the 1,4-dihalo-2-butyne by treating 2-butyne-1,4-diol with thionyl halide.

19. The method of claim 18, wherein the thionyl halide is thionyl chloride and the 1,4-dihalo-2-butyne is 1,4-dichloro-2-butyne.

20. The method of claim 18, further comprising producing the 2-butyne-1,4-diol by contacting acetylene and formaldehyde in the presence of a second metal catalyst.

21. The method of claim 20, wherein the second metal catalyst comprises copper, silver, bismuth, or combinations thereof.

22. The method of claim 20, further comprising producing the formaldehyde by catalytically reducing CO_2 .

23. The method of claim 20, further comprising producing the acetylene by pyrolysis of lignocellulosic biomass.

24. The method of claim 1, wherein $n=4$, $m=1$, the compound of formula I is a dicarboxylic acid, and the bis-carbonyl alkyne is a bis-carboxy alkyne is of formula $\text{HOOC-CH}_2\text{-C}\equiv\text{C-CH}_2\text{-COOH}$.

25. The method of claim 24, further comprising producing the bis-carboxy alkyne of formula $\text{HOOC-CH}_2\text{-C}\equiv\text{C-CH}_2\text{-COOH}$ by treating a bis-Grignard reagent of formula $\text{XMg-CH}_2\text{-C}\equiv\text{C-CH}_2\text{-MgX}$ with CO_2 , wherein each X is a same or different one of F, Cl, Br, I, and At.

26. The method of claim 25, further comprising producing the bis-Grignard reagent by treating 1,4-dihalo-2-butyne with magnesium metal.

27. The method of claim 26, further comprising producing the 1,4-dihalo-2-butyne by treating 2-butyne-1,4-diol with thionyl halide.

28. The method of claim 27, wherein the thionyl halide is thionyl chloride and the 1,4-dihalo-2-butyne is 1,4-dichloro-2-butyne.

29. The method of claim 27, further comprising producing the 2-butyne-1,4-diol by contacting acetylene and formaldehyde in the presence of a metal catalyst.

30. The method of claim 29, wherein the metal catalyst comprises copper, silver, bismuth, or combinations thereof.

31. The method of claim 29, further comprising producing the formaldehyde by catalytically reducing CO_2 .

32. The method of claim 29, further comprising producing the acetylene by pyrolysis of lignocellulosic biomass.

33. The method of claim 1, wherein R is alkyl, the compound of formula I is a diester, and the bis-carbonyl alkyne of formula II is a diester alkyne.

34. The method of claim 33, wherein R is C1 to C5 alkyl.

35. The method of claim 33, wherein the diester alkyne is produced by dimerization of mono-ester alkynes.

36. The method of claim 35, wherein the dimerization is a Glaser-Hay dimerization.

37. The method of claim 35, wherein the mono-ester alkyne is prepared by esterification of a carboxy alkyne.

38. The method of claim 35, wherein the CO₂ is obtained from a waste stream from another process.

39. The method of claim 35, wherein the alkyne is acetylene, the carboxy alkyne is propiolic acid, the mono-ester alkyne is an alkyl propiolate, the diester alkyne is a dialkyl diacetylene dicarboxylate, and the diester is a dialkyl dicarboxylate.

40. The method of claim 39, further comprises producing the acetylene by pyrolysis of lignocellulosic biomass.

41. A method for producing adipates with waste stream products, the waste stream products comprising CO₂ and biomass, and the method comprising:

obtaining CO₂ from a waste stream of another process;

obtaining biomass from a waste stream of another process;

pyrolyzing the biomass to produce acetylene; and

using the acetylene and the CO₂ as reactants for producing adipates.

42. The method of claim 41, wherein the biomass is lignocellulosic biomass.

43. The method of claim 41, further comprising reducing at least a portion of the CO₂ to produce formaldehyde.

44. The method of claim 43, wherein the reducing comprises reducing CO₂ by photocatalytic reduction.

45. The method of claim 43, further comprising:

contacting the formaldehyde with the acetylene to produce 2-butyne-1,4-diol;
halogenating the 2-butyne-1,4-diol to produce 1,4-dihalo-2-butyne;
carboxylating the 1,4-dihalo-2-butyne with another portion of the CO₂ to form
a bis-carboxy-alkyne; and
hydrogenating the bis-carboxy-alkyne to form adipic acid.

46. The method of claim 45, wherein contacting the formaldehyde with the acetylene is conducted in the presence of a second metal catalyst.

47. The method of claim 45, wherein the second metal catalyst comprises copper, silver, bismuth, or combinations thereof.

48. The method of claim 45, wherein halogenating the 2-butyne-1,4-diol comprises halogenating with thionyl halide.

49. The method of claim 45, wherein halogenating the 2-butyne-1,4-diol comprises chlorinating with thionyl chloride.

50. The method of claim 45, wherein hydrogenating the bis-carboxy-alkyne comprises hydrogenating in the presence of a hydrogenation catalyst.

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

52. The method of claim 45, wherein the carboxylating comprises:

converting 1,4-dihalo-2-butyne to diacetylene; and
carboxylating the diacetylene with the another portion of the CO₂ in the presence of a first metal catalyst.

53. The method of claim 52, wherein the first metal catalyst comprises copper, silver, bismuth, or combinations thereof.

54. The method of claim 45, wherein the carboxylating comprises:
treating 1,4-dihalo-2-butyne with magnesium metal to produce bis-Grignard reagent; and
treating the bis-Grignard reagent with the additional portion of the CO₂.
55. The method of claim 43, further comprising:
contacting the acetylene with the CO₂ to produce propiolic acid;
esterifying the propiolic acid with alkanol to produce alkyl propiolate;
dimerizing the alkyl propiolate to produce dialkyl diacetylene dicarboxylate;
and
hydrogenating the dialkyl diacetylene dicarboxylate to form dialkyl adipate.
56. The method of claim 56, wherein the alkanol is a C1 to C5 alkyl alcohol.
57. The method of claim 56, wherein the alkanol is methanol or ethanol and the dialkyl adipate is dimethyl adipate or diethyl adipate.
58. The method of claim 55, wherein hydrogenating the dialkyl diacetylene dicarboxylate comprises hydrogenating in the presence of a hydrogenation catalyst.
59. The method of claim 58, wherein the hydrogenation catalyst comprises palladium, platinum, rhodium, ruthenium, or any combination thereof.
60. The method of claim 55, wherein the dimerization comprises a Glaser-Hay dimerization in the presence of a copper catalyst.

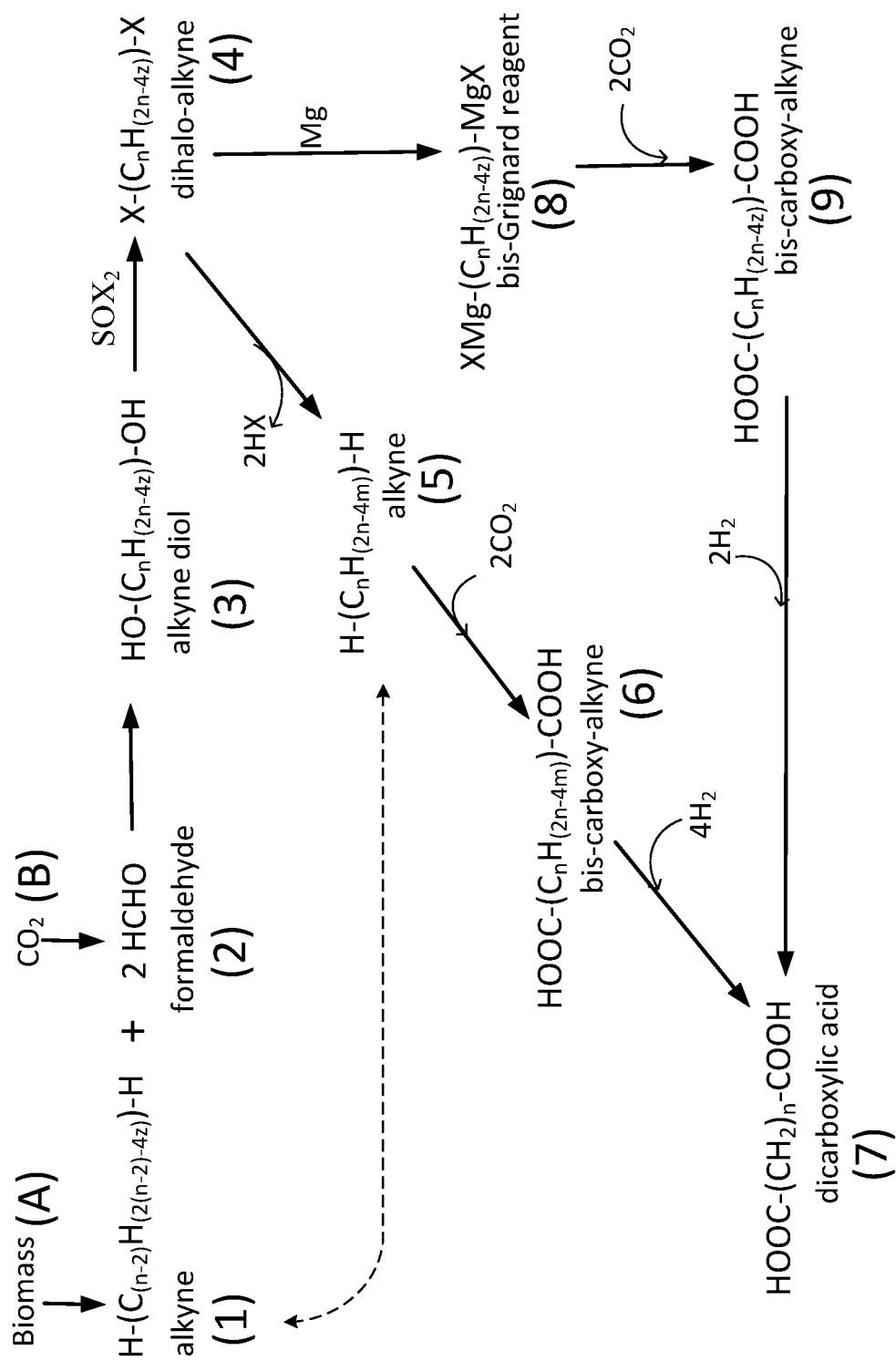


FIG. 1

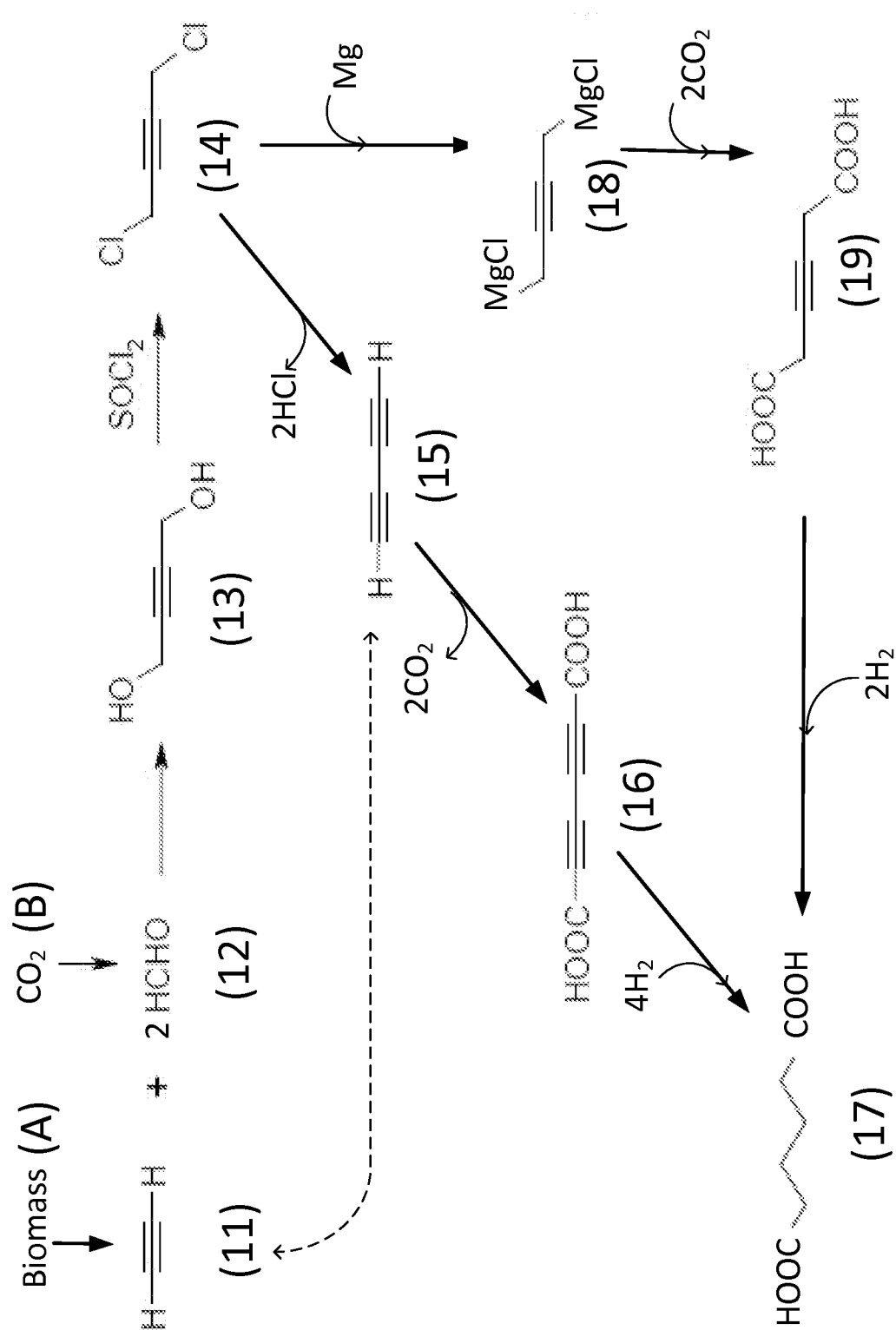


FIG. 2

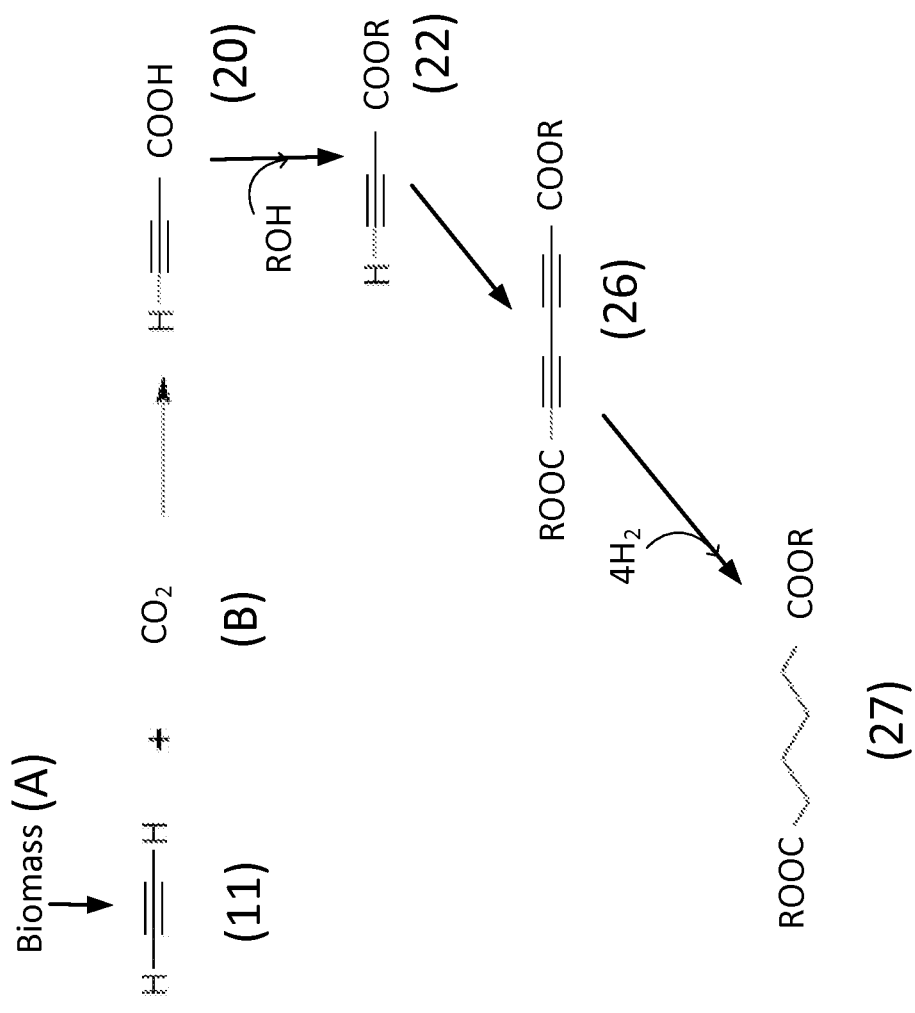


FIG. 4

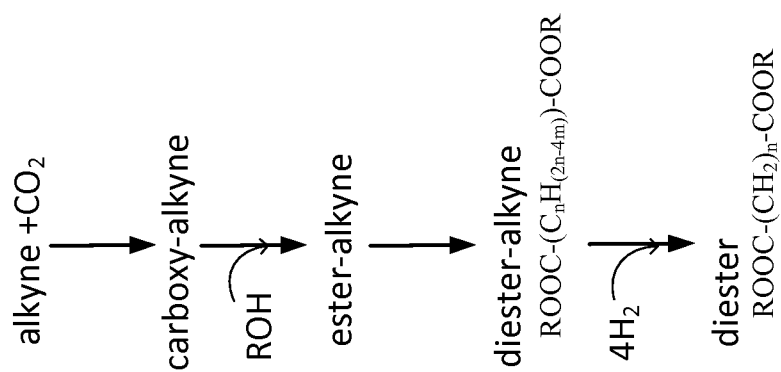


FIG. 3

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 13/66827

A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - C07C 69/76; C07C 69/52 (2013.01)

USPC - 560/76, 223, 78

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 C07C 69/76; C07C 69/52 (2013.01)

USPC 560/76, 223,78

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

USPC 560/76, 223,78 (Keyword limited, terms below)

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

PatBase, Google Patents, Google Scholar (NPL); Keywords: ADIPATE, DICARBONYL, DICARBOXYLATE, ACETYLENE biomass lignocellulose, alkyne adipic acid co2

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4681707 A1 (Alper et al.) 21 July 1987 (21.07.1987) col 1, ln 58-64; col 2, ln 41-51; col 5, ln 45-62)	1-60
A	US 2010/0152481 A1 (Staffel et al.) 17 June 2010 (17.06.2010) para [0001]	1-60
A	US 3,853,961 A (Birkenstock et al.) 10 December 1974 (10.12.1974) abstract	1-40
A	WO 2009/066975 A1 (Abdul Rahman et al.) 28 May 2009 (28.05.2009) pg 2, ln 10-15	1-60
A	US 2012/0077252 A1 (Picataggio et al.) 29 March 2012 (29.03.2012) para [0034]	41-60
A	US 2012/0199298 A1 (Dyer) 09 August 2012 (09.08.2012) para [0094]	41-60



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

10 February 2014 (10.02.2014)

Date of mailing of the international search report

03 MAR 2014

Name and mailing address of the ISA/US

Mail Stop PCT, Attn: ISA/US, Commissioner for Patents
P.O. Box 1450, Alexandria, Virginia 22313-1450

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