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(54) **SPRAY OXIDATION PROCESS FOR PRODUCING 2,5-FURANDICARBOXYLIC ACID FROM HYDROXYMETHYLFURFURAL**

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(57) **ABSTRACT**

A process is provided for carrying out an oxidation on a sprayable feed including a furanic substrate to be oxidized and a catalytically effective combination of cobalt, manganese, and bromide components for catalyzing the oxidation of the furanic substrate, which process comprises spraying the feed into a reactor vessel as a mist, supplying an oxidant, reacting the furanic substrate and the oxidant, and managing the exothermic temperature rise due to the reaction through a selection and control of the operating pressure within the reactor vessel. A crude dehydration product from the dehydration of fructose, glucose or both, including 5-hydroxymethylfurfural, can be directly oxidized by the process to produce 2,5-furandicarboxylic acid in surprisingly increased yields.

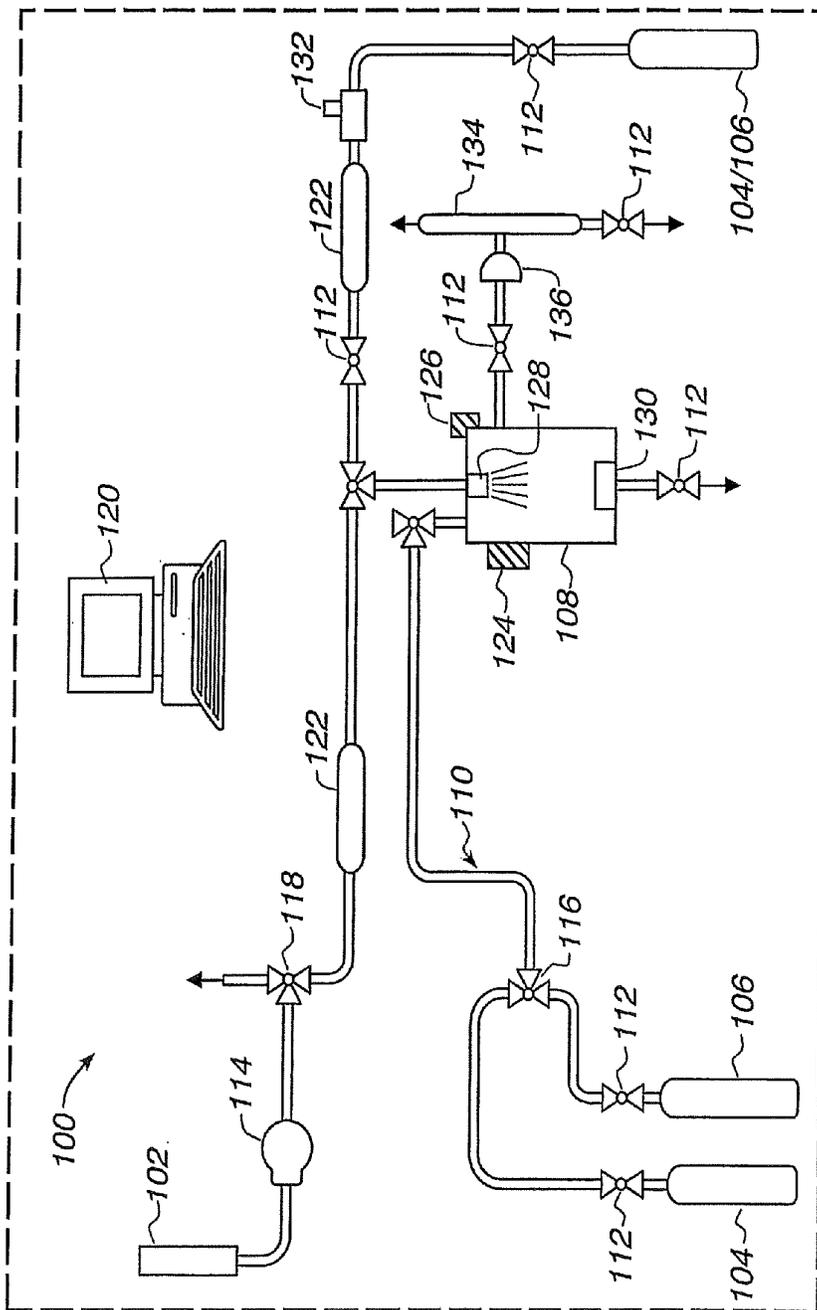


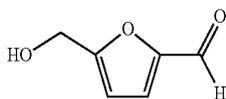
Fig. 1

**SPRAY OXIDATION PROCESS FOR
PRODUCING 2,5-FURANDICARBOXYLIC
ACID FROM HYDROXYMETHYLFURFURAL**

BACKGROUND

[0001] The use of natural products as starting materials for the manufacture of various large-scale chemical and fuel products which are presently made from petroleum- or fossil fuel-based starting materials, or for the manufacture of bio-based equivalents or analogs thereto, has been an area of increasing importance. For example, a great deal of research has been conducted into the conversion of natural products into fuels, as a cleaner and, certainly, as a more sustainable alternative to fossil-fuel based energy sources.

[0002] Agricultural raw materials such as starch, cellulose, sucrose or inulin are inexpensive and renewable starting materials for the manufacture of hexoses, such as glucose and fructose. It has long been appreciated in turn that glucose and other hexoses, in particular fructose, may be converted into other useful materials, such as 2-hydroxymethyl-5-furfuraldehyde, also known as 5-hydroxymethylfurfural or simply hydroxymethylfurfural (HMF):



Hydroxymethylfurfural

The sheer abundance of biomass carbohydrates available provides a strong renewable resource base for the development of commodity chemical and fuel products based on HMF. For example, U.S. Pat. No. 7,385,081, issued in June 2008 to Gong, estimates, for example, that of the approximately 200 billion tons of biomass produced annually, 95% was in the form of carbohydrates, and only 3 to 4% of the total carbohydrates were then used for food and other purposes.

[0003] In view of this fact, and due to HMF's various functionalities, it has been proposed that the HMF thus obtainable from hexoses such as fructose and glucose, could be utilized to produce a wide range of products derived from renewable resources, such as polymers, solvents, surfactants, pharmaceuticals, and plant protection agents. HMF has in this regard been proposed, as either a starting material or intermediate, in the synthesis of a wide variety of compounds, such as furfuryl dialcohols, dialdehydes, esters, ethers, halides and carboxylic acids.

[0004] A number of the products discussed in the literature derive from the oxidation of HMF. Included are hydroxymethylfuran carboxylic acid (HmFCA), formylfuran carboxylic acid (FFCA), 2,5-furandicarboxylic acid (FDCA, also known as dehydromucic acid), and diformylfuran (DFF). Of these, FDCA has been discussed as a bio-based, renewable substitute in the production of such multi-megaton polyester polymers as poly(ethylene terephthalate) or poly(butylene terephthalate). Derivatives such as FDCA can be made from 2,5-dihydroxymethylfuran and 2,5-bis(hydroxymethyl)tetrahydrofuran and used to make polyester polymers. FDCA esters have also recently been evaluated as replacements for phthalate

2011/023590A1, both assigned to Evonik Oxeno GmbH, as well as R.D. Sanderson et al., *Journal of Appl. Pol. Sci.* 1994, vol. 53, pp. 1785-1793.

[0005] While FDCA and its derivatives have attracted a great deal of recent commercial interest, with FDCA being identified, for instance, by the United States Department of Energy in a 2004 study as one of 12 priority chemicals for establishing the "green" chemical industry of the future, the potential of FDCA (due to its structural similarity to terephthalic acid) to be used in making polyesters has been recognized at least as early as 1946, see GB 621,971 to Drewitt et al., "Improvements in Polymer".

[0006] Unfortunately, while HMF and its oxidation-based derivatives such as FDCA have thus long been considered as promising bio-based starting materials, intermediates and final products for a variety of applications, viable commercial-scale processes have proven elusive. Acid-based dehydration methods have long been known for making HMF, being used at least as of 1895 to prepare HMF from levulose (Dull, *Chem. Ztg.*, 19, 216) and from sucrose (Kiermayer, *Chem. Ztg.*, 19, 1003). However, these initial syntheses were not practical methods for producing HMF due to low conversion of the starting material to product. Inexpensive inorganic acids such as H₂SO₄, H₃PO₄, and HCl have been used, but these are used in solution and are difficult to recycle. In order to avoid the regeneration and disposal problems, solid sulfonic acid catalysts have also been used. The solid acid resins have not proven entirely successful as alternatives, however, because of the formation of deactivating humin polymers on the surface of the resins. Still other acid-catalyzed methods for forming HMF from hexose carbohydrates are described in Zhao et al., *Science*, Jun. 15, 2007, No. 316, pp. 1597-1600 and in Bicker et al., *Green Chemistry*, 2003, no. 5, pp. 280-284. In Zhao et al., hexoses are treated with a metal salt such as chromium (II) chloride in the presence of an ionic liquid, at 100 degrees Celsius for three hours to result in a 70% yield of HMF, whereas in Bicker et al., sugars are dehydrocyclicized to HMF at nearly 70% reported selectivity by the action of sub-or super-critical acetone and a sulfuric acid catalyst.

[0007] In the acid-based dehydration methods, additional complications arise from the rehydration of HMF, which yields by-products such as levulinic and formic acids. Another unwanted side reaction includes the polymerization of HMF and/or fructose resulting in humin polymers, which are solid waste products and act as catalyst poisons where solid acid resin catalysts are employed, as just mentioned. Further complications may arise as a result of solvent selection. Water is easy to dispose of and dissolves fructose, but unfortunately, low selectivity and the formation of polymers and humin increases under aqueous conditions.

[0008] In consideration of these difficulties and in further consideration of previous efforts toward a commercially viable process for making HMF, Sanborn et al. in US Published Patent Application 2009/0156841A1 (Sanborn et al) describe a method for producing "substantially pure" HMF by heating a carbohydrate starting material (preferably fructose) in a solvent in a column, continuously flowing the heated carbohydrate and solvent through a solid phase catalyst (preferably an acidic ion exchange resin) and using differences in the elution rates of HMF and the other constituents of the product mixture to recover a "substantially pure" HMF product, where "substantially pure" is described as meaning a purity of about 70% or greater, optionally about 80% or

producing HMF esters performs the conversion in the presence of an organic acid, which can also serve as the solvent. Acetic acid is mentioned in particular as a solvent for fructose. The resulting acetylated HMF product is reported to be "more stable" than HMF, because upon heating HMF is described as decomposing and producing byproducts "that are not easily isolated or removed," page 4, paragraph 0048.

[0009] Further, the acetylated HMF is said to be more easily recovered by distillation or by extraction, though filtration, evaporation and combinations of methods for isolating the HMF esters are also described (page 2, para. 0017). The product, HMF ester which may include some residual HMF, can then be mixed in one embodiment with organic acid, cobalt acetate, manganese acetate and sodium bromide and oxidized to FDCA in the presence of oxygen and at elevated temperatures and pressures. In the examples, a Parr reactor is used for performing the oxidation.

[0010] Those familiar with the manufacture of terephthalic acid will appreciate the fact that the same Co/Mn/Br catalyst system conventionally used in the Mid-Century Process, for liquid-phase oxidation of para-xylene to terephthalic acid, was thus shown to be useful in the oxidation of HMF esters and residual HMF to TPA's biobased analog FDCA. The capacity to source and use, for converting biobased materials, the same catalyst as used predominantly in the processing of petroleum-derived materials is a valuable and desirable feature.

[0011] Very recently published WO 2011/043661 (hereinafter, "WO'661") describes continuing efforts to produce FDCA commercially from carbohydrates such as fructose and glucose through HMF and HMF derivatives as intermediates. After summarizing their view or interpretation of previously published methods for the oxidation of HMF to FDCA in an aqueous medium using a Pt-group catalyst or involving the oxidation of HMF over a gold-based catalyst, the inventors in WO'661 contend that Sanborn et al. failed in fact to produce FDCA from the 5-(acetoxymethyl)furfural (AMF) ester formed through the reaction of HMF with the acetic acid solvent. "Surprisingly" the inventors in WO'661 find that when using an oxidation catalyst based on cobalt and manganese and containing a bromide, various furan-based materials inclusive of 5-(acetoxymethyl)furfural and other like ester derivatives of HMF can provide FDCA in "high yields" provided reaction temperatures higher than 140 degrees Celsius are employed.

[0012] The HMF ester starting materials common to both Sanborn et al. and WO'661 are indicated in WO'661 as proceeding from known methods, wherein a carbohydrate source is converted in the presence of an alkyl carboxylic acid into products comprising an HMF ester and optionally HMF. Then an HMF ester and optional HMF feed is isolated from the products for subsequent oxidation at the greater than 140 degree Fahrenheit, alleged critical temperatures. While batch, semi-continuous and continuous processes are contemplated generally, "operation in the batch mode with increasing temperature at specific times, increasing pressure at specific times, variation of the catalyst concentration at the beginning of the reaction, and variation of the catalyst composition during the reaction" is indicated as preferred (pg 4, lines 28-32). And, while the pressure in the oxidation process of WO'661 is expressly observed to be dependent on the solvent pressure, page 4, last line to page 5, line 1, the preference is that the pressure should be such that the solvent is "mainly in

SUMMARY OF THE INVENTION

[0013] In contrast, the present invention, in one aspect, relates to a process for carrying out an oxidation of a sprayable feed comprising a catalytically effective combination of cobalt, manganese and bromide components with a furanic substrate to be oxidized, wherein the feed is sprayed into a reactor, combined and reacted with an oxidant therein. Further, the exothermic temperature rise within the reactor is limited at least in part by selection and control of the pressure within the reactor.

[0014] Preferably, the pressure within the reactor is selected and controlled so that the boiling point of a liquid present in the reactor as the highly exothermic oxidation proceeds (which boiling point will of course vary based on the pressure acting on the liquid) is only from 10 to 30 degrees Celsius greater than the temperature at the start of the oxidation. By selecting and controlling the pressure so that the boiling point of a liquid does not significantly exceed the temperature at the start of the oxidation, a portion of the heat generated from the oxidation process is accounted for in vaporizing the liquid and so the exothermic temperature rise within the reactor can be limited. It will be appreciated that in limiting the exothermic temperature rise, yield losses due to higher temperature byproducts and degradation products, as well as to due to solvent burning, can correspondingly be reduced.

[0015] In the HMF to FDCA process, conveniently, the same acetic acid solvent/carrier used for the HMF and the Co/Mn/Br catalyst in the WO'661 reference, in Sanborn et al., and in the Partenheimer (Adv. Synth. Catal. 2001, vol. 343, pp. 102-111) and Grushin (WO 01/72732) references described in WO'661's background can serve as the liquid, having a boiling point at modest pressures that corresponds closely to the typically desired oxidation temperatures. The vaporization of acetic acid in this case offers a further benefit, as well. While the various components of the feed and while intermediates in the conversion of HMF to its oxidized derivative FDCA remain soluble in the acetic acid, FDCA is minimally soluble in acetic acid and thus can precipitate out (either in the reactor itself and/or upon cooling the reaction mixture exiting the reactor) and be recovered as a substantially pure solid product.

[0016] In a second aspect, the present invention provides a fundamental improvement in the oxidation of a biobased furanic substrate to produce FDCA as variously addressed in the past by Sanborn et al., by WO'661, by the Partenheimer and Grushin references, as well as WO 2010/132740 to Sanborn. As discussed above, the tendency of HMF to self-polymerize and degrade in acidic environments and at elevated temperatures has led to efforts in recent years to derivatize HMF to a more stable intermediate that can still be oxidized to produce FDCA. In this second aspect, a process is provided for making FDCA from fructose, glucose or a combination thereof, based upon the discovery that in the context of the inventive spray oxidation process using a Co/Mn/Br Mid-Century Process-type oxidation catalyst, the crude dehydration product mixture resulting from a conventional acid dehydration of the carbohydrate can be directly solubilized in the solvent, sprayed into the reactor and oxidized with subsequent recovery of the FDCA product in an unexpectedly high yield. No isolation or purification of the HMF is required, and no derivatization of the HMF is needed (though the present invention extends to such HMF derivatives as furanic sub-

Examples below, use of a crude dehydration product (crude HMF) can provide greater than 100 percent yield of FDCA based on the HMF content of the feed coming into the oxidation process.

DESCRIPTION OF THE FIGURE

[0017] FIG. 1 is a schematic diagram of an illustrative embodiment of an oxidation reaction system.

DETAILED DESCRIPTION OF CERTAIN EMBODIMENTS

[0018] The present invention may be more completely understood by describing certain embodiments in greater detail. These embodiments are not to be taken as limiting the scope and breadth of the current invention as more particularly defined in the claims that follow, but are illustrative of the principles behind the invention and demonstrate various ways and options for how those principles can be applied in carrying out the invention.

[0019] One embodiment of a process for carrying out an oxidation of a sprayable feed which comprises a catalytically effective combination of cobalt, manganese and bromide components with a furanic substrate to be oxidized, involves spraying the feed into a reactor and combining and reacting the furanic substrate in the feed with an oxidant (such as an oxidizing gas), while managing and limiting the exothermic temperature rise within the reactor by selection and control of the pressure within the reactor.

[0020] While a variety of furanic substrates can be contemplated for oxidation according to the inventive process, preferably the furanic substrates are those derived in whole or in significant part from renewable sources and that can be considered as “biobased” or “bioderived”. These terms may be used herein identically to refer to materials whose carbon content is shown by ASTM D6866, in whole or in significant part (for example, at least about 20 percent or more), to be derived from or based upon biological products or renewable agricultural materials (including but not limited to plant, animal and marine materials) or forestry materials. In this respect ASTM Method D6866, similar to radiocarbon dating, compares how much of a decaying carbon isotope remains in a sample to how much would be in the same sample if it were made of entirely recently grown materials. The percentage is called the biobased content of the product. Samples are combusted in a quartz sample tube and the gaseous combustion products are transferred to a borosilicate break seal tube. In one method, liquid scintillation is used to count the relative amounts of carbon isotopes in the carbon dioxide in the gaseous combustion products. In a second method, $^{13}\text{C}/^{12}\text{C}$ and $^{14}\text{C}/^{12}\text{C}$ isotope ratios are counted (^{14}C) and measured ($^{13}\text{C}/^{12}\text{C}$) using accelerator mass spectrometry. Zero percent ^{14}C indicates the entire lack of ^{14}C atoms in a material, thus indicating a fossil (for example, petroleum based) carbon source. One hundred percent ^{14}C , after correction for the post-1950 bomb injection of ^{14}C into the atmosphere, indicates a modern carbon source. ASTM D6866 effectively distinguishes between biobased materials and petroleum derived materials in part because isotopic fractionation due to physiological processes, such as, for example, carbon dioxide transport within plants during photosynthesis, leads to specific isotopic ratios in natural or biobased compounds. By contrast, the $^{13}\text{C}/^{12}\text{C}$ carbon isotopic ratio of petroleum and

ratios in natural or bioderived compounds due to different chemical processes and isotopic fractionation during the generation of petroleum. In addition, radioactive decay of the unstable ^{14}C carbon radioisotope leads to different isotope ratios in biobased products compared to petroleum products.

[0021] More particularly, preferred furanic substrates are those which can be derived from readily available carbohydrates from agricultural raw materials such as starch, cellulose, sucrose or inulin, especially fructose, glucose or a combination of fructose and glucose, though any such carbohydrate source can be used generally. Examples of suitable carbohydrate sources that can be used to provide the furanic substrates of interest include, but are not limited to, hexose, fructose syrup, crystalline fructose, and process streams from the crystallization of fructose. Suitable mixed carbohydrate sources may comprise any industrially convenient carbohydrate source, such as corn syrup. Other mixed carbohydrate sources include, but are not limited to, hexoses, fructose syrup, crystalline fructose, high fructose corn syrup, crude fructose, purified fructose, high fructose corn syrup refinery intermediates and by-products, process streams from crystallizing fructose or glucose or xylose, and molasses, such as soy molasses resulting from production of soy protein concentrate, or a mixture thereof.

[0022] Especially of interest are the furanic substrates of this natural carbohydrate-derived character, which can be spray oxidized in the presence of a homogeneous oxidation catalyst contained in a sprayable feed including the furanic substrate, to provide products of commercial interest such as 2,5-furandicarboxylic acid (FDCA). In WO'661, for example, a variety of furanic substrates are identified which can be oxidized in the presence of mixed metal bromide catalysts, such as Co/Mn/Br catalysts, to provide FDCA 5-hydroxymethylfurfural (HMF), esters of HMF, 5-methylfurfural, 5-(chloromethyl)furfural, 5-methylfuroic acid, 5-(chloromethyl)furoic acid and 2,5-dimethylfuran (as well as mixtures of any of these) being named.

[0023] Most preferably, however, the furanic substrates which are fed to the process are simply those which are formed by an acid-catalyzed dehydration reaction from fructose, glucose or a combination of these according to the various well-known methods of this character, principally comprising HMF and the esters of HMF formed with an organic acid or organic acid salt.

[0024] As has been indicated previously, one such organic acid, acetic acid, has been found especially useful as a solvent for the subsequent Co/Mn/Br-catalyzed oxidation of HMF and HMF esters, such as the 5-(acetoxymethyl)furfural (AcHMF) ester of HMF and acetic acid. Acetic acid as noted in the WO'661 reference is helpfully regenerated from AcHMF through the oxidation step, and is a good solvent for the HMF and its derivatives but is not a good solvent for FDCA—substantially simplifying separation and recovery of a substantially pure FDCA solid product. Further, as noted by Sanborn et al., AcHMF and HMF can be oxidized together to yield the single FDCA product in reasonable yields. In the context of the present invention, acetic acid has the still added beneficial attribute of having a boiling point at reasonable pressures that is within the desired range of 10 degrees to 30 degrees Celsius above the preferred temperature range for carrying out the Co/Mn/Br-catalyzed oxidation of the HMF and HMF esters to FDCA, so that by selecting an operating pressure and also controlling the system pressure to maintain

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