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

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
11 May 2017 (11.05.2017)

WIPO | PCT

(10) International Publication Number
WO 2017/076947 A1

(51) International Patent Classification:
C07D 307/68 (2006.01)

(21) International Application Number:
PCT/EP2016/076510

(22) International Filing Date:
3 November 2016 (03.11.2016)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
15193069.0 4 November 2015 (04.11.2015) EP

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(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

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

WO 2017/076947 A1

(54) Title: PROCESS FOR PREPARING FURAN-2,5-DICARBOXYLIC ACID

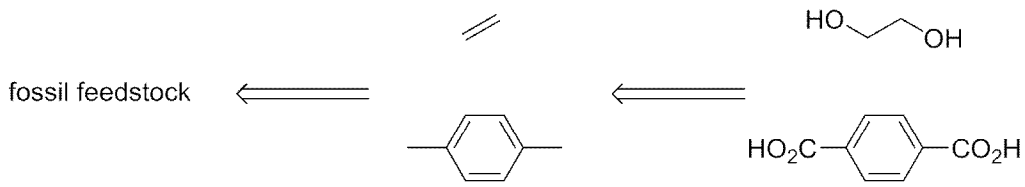
(57) Abstract: The invention relates to a process for preparing furan-2,5-dicarboxylic acid comprising the following steps: (a) preparing or providing a starting material mixture comprising 5-(hydroxymethyl)furfural (HMF) as a first reactant and one or more second reactants selected from the group consisting of esters of 5-(hydroxymethyl)furfural and ethers of 5-(hydroxymethyl)furfural, (b) subjecting said starting material mixture to first oxidation conditions at a temperature in the range TR1 of from 110 to 140 °C so that an amount of said 5-(hydroxymethyl)furfural (HMF) present in the starting material mixture is oxidised to furan-2,5-dicarboxylic acid and a first product mixture results comprising furan-2,5-dicarboxylic acid and an unreacted amount of said one or more second reactants, and (c) subjecting the first product mixture obtained in step (b) or a mixture obtained from the first product mixture obtained in step (b) by additional treatment steps to second oxidation conditions at an increased temperature in the range TR2 of from above 140 to 200 °C so that said at least a fraction of said unreacted amount of said one or more second reactants present in the first product mixture is oxidised and a second product mixture results comprising furan-2,5-dicarboxylic acid.

Process for preparing furan-2,5-dicarboxylic acid

The present invention relates to a process for preparing furan-2,5-dicarboxylic acid. The present invention is defined in the appending claims. Furthermore, preferred configurations and aspect of the present invention are apparent from the detailed description herein below.

5-(Hydroxymethyl)furfural (HMF) and derivatives thereof as well as furan-2,5-dicarboxylic acid (hereinafter FDCA) are important intermediate compounds for production of various products, for example surfactants, polymers and resins.

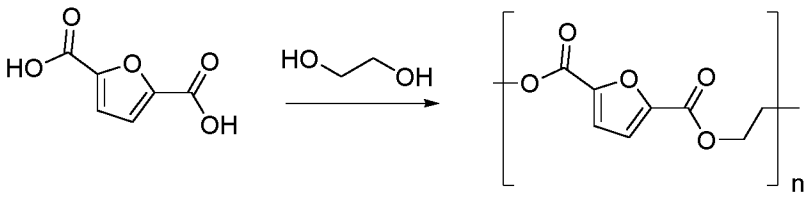
For example, the production of PET relies on ethylene and *p*-xylene which are usually obtained starting from of oil, natural gas or coal, *i.e.* from fossil fuels.



With increasing depletion of fossil feedstocks, starting materials based on renewable resources are needed, e.g. as alternatives to terephthalic acid (a compound used in the production of polyethylene terephthalate, PET). PET is based on ethylene and p-xylene which are usually obtained starting from of oil, natural gas or coal, *i.e.* from fossil fuels. While bio-based routes to ethylene (*e.g.* dehydration of bio-ethanol) are operated on commercial scale a straightforward access to bio-terephthalic acid remains difficult. FDCA is the best bio-based alternative to terephthalic acid (for further information see: Lichtenthaler, F.W., *"Carbohydrates as Organic Raw Materials"* in Ullmann's Encyclopedia of Industrial Chemistry, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, 2010).

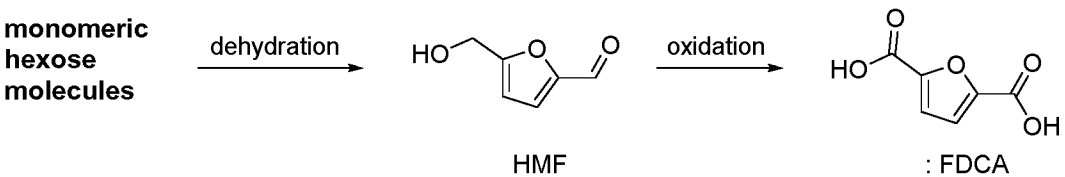
HMF is a versatile platform chemical. Alkoxymethylfurfurals, 2,5-furandicarboxylic acid, 5-hydroxymethylfuroic acid, bishydroxymethylfuran, 2,5-dimethylfuran, and the diether of HMF are furan derivatives with a high potential in fuel and/or polymer applications. Some important non-furanic compounds can also be produced from HMF, namely levulinic acid, adipic acid, 1,6-hexanediol, caprolactam, and caprolactone.

FDCA can be co-polymerized with mono-ethylene glycol to give polyethylene furanoate (PEF), a polyester with properties similar to PET.



FDCA polyethylene furanoate, PEF

FDCA is usually obtained starting from fructose and/or other hexoses via a catalyzed, preferably acid-catalyzed, dehydration to key intermediate 5-(hydroxymethyl)furfural (HMF) followed by oxidation to FDCA. In literature, processes are disclosed where esters of HMF are used as precursors to prepare FDCA (e.g. US 8,242,293 B2).



HMF : FDCA

In the dehydration step by-products are formed, depending on the specific design of the process.

Typical by-products of this process are levulinic acid and formic acid (see scheme below) which are formed upon hydrolysis of HMF.

In processes for preparing a mixture comprising 5-(hydroxymethyl)furfural (HMF) (and one or more by-products) or in processes for preparing FDCA known in the prior art, carbohydrates, preferably a mixture comprising 5-(hydroxymethyl)furfural (HMF) is prepared by subjecting a material mixture, comprising one, two or more compounds selected from the group consisting of hexoses (monomeric hexose molecules, e.g. fructose), oligosaccharides comprising hexose units, and polysaccharides comprising hexose units, to reaction conditions so that a mixture comprising HMF, water and by-products (for example, levulinic acid and formic acid) results. Under the reaction conditions oligo- and/or polysaccharides are usually depolymerised, and subsequently the resulting monosaccharides, e.g. monomeric hexose molecules, are converted into HMF. Hexoses, oligosaccharides and polysaccharides are typically selected from the group consisting of fructose, glucose, and cellulose.

During depolymerisation oligo- or polysaccharides are usually converted into monomeric hexose molecules by hydrolytic cleavage of the ether bonds connecting the different hexose units in an oligo- or polysaccharide molecule (e.g. cellulose). The products of a typical depolymerization process (monomeric hexose molecules) are present in their aldehyde form.

Typically, according to routines at least in part previously undisclosed, depolymerization is conducted by using a catalyst, preferably in a one-pot-procedure. Typically a hydrophilic solvent is used (in particular water), e.g. in order to increase the amount of dissolved cellulose thus increasing the yield per process run. It is typically advantageous to conduct the conversion of cellulose into HMF by means of a heterogeneous catalyst in order to facilitate post-synthetic workup. In a typical depolymerization process, an aqueous solution is used as a solvent, sometimes comprising 50 wt.-% of water or more, based on the total weight of the depolymerization mixture used.

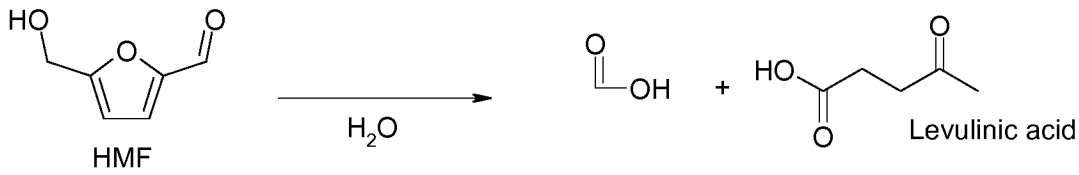
Alternatively, if monosaccharides are used as a starting material for preparing a mixture comprising HMF, water, and by-products, e.g. di-HMF (5,5'(oxy-bis(methylene))bis-2-furfural), no depolymerisation step is needed.

Monosaccharides produced or provided are typically subjected to a dehydration process, wherein the monomeric hexose molecule is typically transferred by isomerisation (via e.g. ketone-enol tautomerization) into its ketone form which is subsequently converted into its ring form. After ring closure, the formed ring-closed hexose molecules are typically dehy-

drated (and optionally further isomerised) resulting in a mixture comprising HMF, by-products (e.g. di-HMF) and water. However, water causes undesirable by-products due to hydrolysis of the formed HMF as described above (for example, humins, levulinic acid and formic acid). In contrast thereto, derivates of HMF as esters of HMF or as ethers of HMF do not to the same extent suffer from such side reactions.

Due to the insolubility of specific monomeric hexose molecules (e.g. fructose) in common organic solvents, a typical dehydration process step in the prior art is performed in an aqueous environment so that an aqueous solution comprising HMF and water is obtained as a (crude) mixture. As mentioned above, the presence of water leads to hydrolysis of HMF into by-products (e.g. levulinic acid and formic acid) and therefore decreases the overall yield of the reaction.

In contrast to the isolation of derivates of HMF, the isolation of HMF from such aqueous mixtures is challenging since HMF often undergoes side-reactions, e.g. hydrolysis (see scheme below).



Hence, the (crude) mixture comprising HMF and water is usually contaminated with by-products to a certain degree and separation of HMF from the by-products is not possible with justifiable effort.

The aforementioned disclosures regarding the depolymerization or dehydration step also apply to a process for preparing furan-2,5-dicarboxylic acid according to the present invention as described in detail hereinbelow. In particular, the successive steps of depolymerization and dehydration can be used to prepare a starting material mixture as employed according to the present invention.

Different teachings regarding the isolation or preparation of FDCA have been reported in the patent literature:

WO 2008/054804 A2 relates to “Hydroxymethyl furfural oxidation methods” (title). It is disclosed that a high solubility of FDCA in an acetic acid/water mixture (volume ratio 40:60) is achieved, compared to the solubility in pure water (cf. paragraph [0058]).

WO 2013/033081 A2 discloses a “process for producing both biobased succinic acid and 2,5-furandicarboxylic acid” (title).

US 2008/103318 discloses “hydroxymethyl furfural oxidation methods” (title) comprising the step of “providing a starting material which includes HMF in a solvent comprising water into reactor”. The starting material is brought into contact “with the catalyst comprising Pt on the support material where the contacting is conducted at a reaction temperature of from about 50°C to about 200°C”.

WO 2011/043661 A1 relates to a “Method for the preparation of 2,5-furandicarboxylic acid and for the preparation of the dialkyl ester of 2,5-furandicarboxylic acid” (title). A method is disclosed “for the preparation of 2,5-furan dicarboxylic acid comprising the step of contacting a feed comprising a compound selected from the group consisting of 5-hydroxymethylfurfural (“HMF”), an ester of 5-hydroxymethylfurfural, 5-methylfurfural, 5-(chloromethyl)furfural, 5-methylfuroic acid, 5-(chloromethyl)furoic acid, 2,5-dimethylfuran and a mixture of two or more of these compounds with an oxidant in the presence of an oxidation catalyst at a temperature higher than 140 °C” (see abstract). The oxidation catalyst comprises cobalt, manganese and/or a source of bromine (see claims 3 and 4).

WO 2009/030512 A2 relates to “hydroxymethylfurfural ethers and esters prepared in ionic liquids” (title). A method is disclosed “for the manufacture of an ether or ester of 5-hydroxymethylfurfural by reacting a hexose-containing starting material or HMF with an alcohol or an organic acid dissolved into an ionic liquid, using a metal chloride as catalyst” (see claim1).

US 2012/0302772 A1 (see also WO 2012/161968 A1) discloses an „oxidation process to produce a crude and/or purified carboxylic acid product” (Title). In one embodiment, a process is disclosed to produce furan-2,5-dicarboxylic acid comprising the following step: “step (a) comprises oxidizing at least one oxidizable compound in an oxidizable raw material stream [...]; wherein the oxidizable raw material stream **30** comprises at least one oxidizable compound selected from the group consisting of 5-(hydroxymethyl)furfural (5-HMF), 5-HMF esters (5-R(CO)OCH_2-furfural where R=alkyl, cycloalkyl and aryl), 5-HMF ethers (5-R'OCHa-furfural, where R'=alkyl, cycloalkyl and aryl), 5-alkyl furfurals (5-Rufurfural, where R"=alkyl, cycloalkyl and aryl), mixed feedstocks of 5-HMF and 5-HMF esters, mixed feedstocks of 5-HMF and 5-HMF ethers, (see [0023]). It is disclosed that with „mixed feedstocks of 5-AMF and 5-HMF or 5-EMF and 5-HMF or 5-MF and 5-HMF or 5-AMF, 5-EMF and 5-HMF, with varying ratios of the components” (see [0040]) similar results can be obtained.

US 2012/0283452 A1 discloses a “method for the preparation of 2,5-furandicarboxylic acid and esters thereof” (Title). The corresponding method comprises “contacting a feed comprising a starting material selected from 5-alkoxymethylfurfural, 2,5-di(alkoxymethyl)furan and a mixture thereof” (see claim 1).

US 2012/0271060 A1 discloses a “method for preparation of 2,5-furandicarboxylic acid and for the preparation of the dialkyl ester of 2,5-furandicarboxylic acid” (Title). The method comprises “contacting a feed comprising a compound selected from the group consisting of 5-hydroxymethylfurfural (“HMF”), an ester of 5-hydroxymethyl-furfural, 5-methylfurfural, 5-(chloromethyl)furfural, 5-methylfuroic acid, 5-(chloromethyl)furoic acid, 2,5-dimethylfuran and a mixture of two or more of these compounds with an oxidant in the presence of an oxidation catalyst at a temperature higher than 140° C. (see claim 1).

WO 2014/014979 relates to a process to produce a carboxylic acid composition. The process comprises oxidizing at least one oxidizable compound in an oxidizable raw material stream in the presence of an oxidizing gas stream, solvent stream, and at least one catalyst system. More particularly, the process comprises oxidizing at least one oxidizable compound selected from the following group: 5-(hydroxymethyl)furfural (5-HMF), 5-HMF esters (5-R(CO)OCH2-furfural where R = alkyl, cycloalkyl and aryl), 5-HMF ethers (5-R’OCH2-furfural, where R’ = alkyl, cycloalkyl and aryl), 5-alkyl furfurals (5-R’’-furfural, where R” = alkyl, cycloalkyl and aryl), mixed feed-stocks of 5-HMF and 5-HMF esters and mixed feed-stocks of 5-HMF and 5-HMF ethers and mixed feed-stocks of 5-HMF and 5-alkyl furfurals in the presence of oxygen, a saturated organic acid solvent having from 2-6 carbon atoms, and a catalyst system at a temperature of about 100°C to about 220°C to produce the carboxylic acid composition comprising furan-2,5-dicarboxylic acid to generate a crude carboxylic acid slurry comprising FDCA, removing impurities from a crude carboxylic acid slurry in a liquid displacement zone to form a low impurity slurry stream.

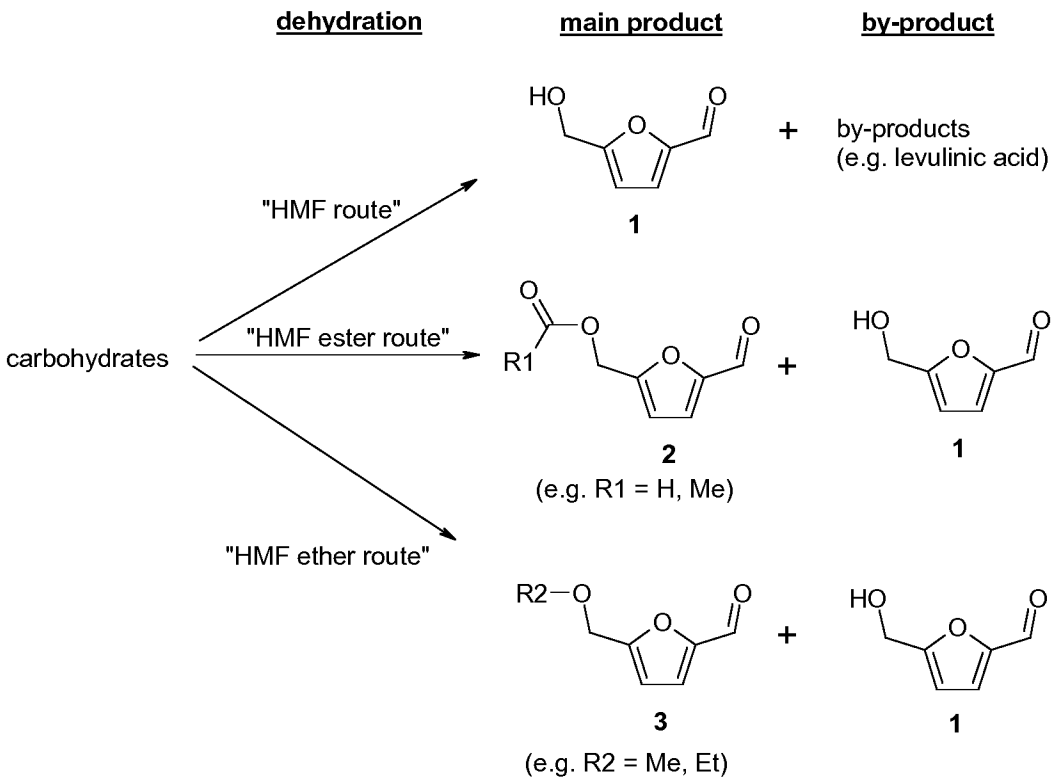
Despite the considerable efforts made by industry, there remains a need for further improvement.

As discussed above, the isolation of HMF from aqueous mixtures is challenging, and furthermore in the synthesis of HMF side reactions occur (resulting in the production of humins, di-HMF, levulinic acid, etc., see “HMF route” in the scheme below). It has to be noted that these side reactions are catalyzed by acids and therefore are catalyzed by the same catalysts that are typically present under the reaction conditions chosen for dehy-

drating carbohydrates, in particular said material mixture, comprising one, two or more compounds selected from the group consisting of hexoses (monomeric hexose molecules, e.g. fructose), oligosaccharides comprising hexose units, and polysaccharides comprising hexose units, to give HMF. Thus, in practice the skilled person typically tends to rather synthesize and produce from said carbohydrates derivatives of HMF (as the major product which may be present in admixture with HMF as a secondary product, see "HMF ester route" and "HMF ether route" below). Typically, derivatives of HMF are not as prone to subsequent side-reactions in the reaction mixture, and typically they can more easily be isolated.

Typical derivatives of HMF, which are produced as an intermediate product in the overall production process finally leading to FDCA and, if appropriate, PEF and other compounds, are esters of 5-(hydroxymethyl)furfural and 5-(alkoxymethyl)furfurals (as well as other ethers of 5-(hydroxymethyl)furfural). Depending on the dehydration conditions used, either or both (esters of 5-(hydroxymethyl)furfural and 5-(alkoxymethyl)furfurals and/or other ethers of 5-(hydroxymethyl)furfural) can be present in an intermediate product mixture .

As stated, these derivatives of HMF are typically produced in admixture with HMF (which is present as a by-product). The derivatives of HMF produced typically are meant to be used as a starting material in a subsequent oxidation step in order to produce FDCA. However, as stated, HMF is present in admixture with said derivatives of HMF, and therefore there is a need in industry for the identification of oxidation conditions in which both, the derivative of HMF and HMF itself, are oxidized to FDCA in a high yield.



In the schematic summary of synthetic routes to valuable intermediate mixtures, the "HMF route" typically involves a dehydration of carbohydrates in water (not preferred according to the present invention, see below), the "HMF ester route" typically involves a dehydration of carbohydrates in the presence of one or more compounds selected from the group consisting of organic acids, anhydrides of organic acids and esters of organic acids, and the "HMF ether route" typically involves a dehydration of carbohydrates in the presence of an aliphatic alcohol.

Thus, according to a first aspect, it was an object of the present invention to provide an improved process for preparing furane-2,5-dicarboxylic acid which avoids or at least alleviates disadvantages of the processes known today (and as stated above) and which can be operated in an economically advantageous manner. Preferred processes to be specified according to further aspects should favourably

- convert a starting material mixture comprising 5-(hydroxymethyl)furfural (HMF), as well as esters of 5-(hydroxymethyl)furfural and/or ethers of 5-(hydroxymethyl)furfural (preferably 5-(alkoxymethyl)furfurals) to FDCA, with a high yield,

and

- be capable of converting said starting material mixture to FDCA at high selectivities compared to processes known in the prior art.

According to the invention with respect to the objective of preparing furane-2,5-dicarboxylic acid, this is achieved by a process for preparing furan-2,5-dicarboxylic acid comprising the following steps:

(a) preparing or providing a starting material mixture comprising

- 5-(hydroxymethyl)furfural (HMF) as a first reactant

and

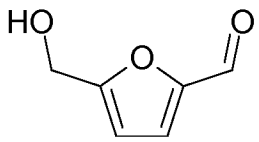
- one or more second reactants selected from the group consisting of esters of 5-(hydroxymethyl)furfural and ethers of 5-(hydroxymethyl)furfural (preferably 5-(alkoxymethyl)furfurals),

(b) subjecting said starting material mixture to first oxidation conditions at a temperature in the range T_{R1} of from 110 to 140 °C, preferably in the range of from 120 to 140 °C, so that an amount of said 5-(hydroxymethyl)furfural (HMF) present in the starting material mixture is oxidised to furan-2,5-dicarboxylic acid and a first product mixture results comprising furan-2,5-dicarboxylic acid and an unreacted amount of said one or more second reactants,

and

(c) subjecting the first product mixture obtained in step (b) or a mixture obtained from the first product mixture obtained in step (b) by additional treatment steps to second oxidation conditions at an increased temperature in the range T_{R2} of from above 140 to 200 °C, preferably in the range of from 140 to 180 °C so that at least a fraction of said unreacted amount of said one or more second reactants present in the first product mixture is oxidised and a second product mixture results comprising furan-2,5-dicarboxylic acid.

5-(hydroxymethyl)furfural (HMF, compound **1**) used as a first reactant in the process of the present invention is represented by the chemical formula:



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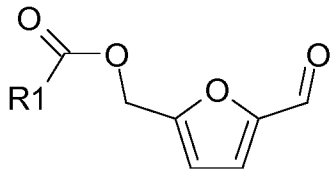
Esters of 5-(hydroxymethyl)furfural (compound **2**) used as a second reactant in the process of the present invention are represented by the following formula:



2

wherein R1 is

- hydrogen
- a branched, cyclic or linear alkyl radical,
- a branched, cyclic or linear alkenyl radical,
- an aryl radical,
- an aralkyl radical,

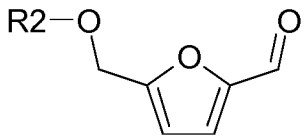
or

- an alkaryl radical,

having

- a total number of carbon atoms in the range of from 1 to 18, preferably 1 to 13, more preferably 1 to 10, even more preferably 1 to 7.

Ethers of 5-(hydroxymethyl)furfural (compound **3**) used as a second reactant in the process of the present invention are represented by the following formula:



3

wherein R2 is

- a branched, cyclic or linear alkyl radical (i.e. compound 3 is a 5-(alkoxymethyl)furfural),
- a branched, cyclic or linear alkenyl radical,
- an aryl radical,
- an aralkyl radical,

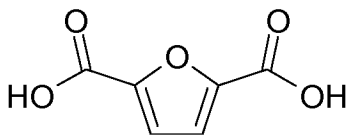
or

- an alkaryl radical,

having

- a total number of carbon atoms in the range of from 1 to 18, preferably 1 to 13, more preferably 1 to 10, eve more preferably 1 to 7.

Furan-2,5-dicarboxylic acid (compound **4**) is represented by the formula:



4

If not indicated otherwise, the „total number“ of carbon atoms in a specified radical is the total number in the radical including any substituents. I.e., when counting the total number of carbon atoms in a branched radical the carbon atoms in the substituent are also counted.

In step (b), the term “first oxidation reactions” indicates conditions causing HMF to react so that furan-2,5-dicarboxylic acid is generated.

Similarly, in step (c), the term "second oxidation conditions" indicates conditions causing the one or more second reactants selected from the group consisting of esters of 5-(hydroxymethyl)furfural and ethers of 5-(hydroxymethyl)furfural (preferably 5-(alkoxymethyl)furfural) to react so that furan-2,5-dicarboxylic acid is generated.

Step (c) comprises subjecting the first product mixture obtained in step (b) or a mixture obtained from the first product mixture obtained in step (b) by additional treatment steps to second oxidation conditions (as specified above or below and in the claims). Preferably, the first product mixture obtained in step (b) is directly used in step (c), i.e. there are no additional treatment steps for making and obtaining a mixture from said first product mixture. However, in some cases said first product mixture is transformed into a mixture for use in step (c) by one or more additional treatment steps which are preferably selected from the group consisting of removing material from the first product mixture and adding material to the first product mixture.

Typically, the steps (b) and (c) are conducted in the same reactor thus decreasing the complexity of the reactor design of the overall process. However, in some industrial cases it is necessary to conduct steps (b) and (c) in two or more separate reactors in series, (in contrast to step-by-step synthesis). In other important industrial cases it is necessary to conduct each reaction step of a process of the invention for preparing furan-2,5-dicarboxylic acid (step (b) or step (c)) each in several separate reactors.

The oxidation agent in steps (b) and/or (c) is preferably an oxygen containing gas, more preferably air or any other gas mixture comprising N_2 and O_2. If not indicated otherwise the term "oxygen" refers to molecular oxygen (O_2) and the term "oxygen gas" refers to a gas substantially consisting of molecular oxygen (O_2).

The invention is inter alia based on the surprising discovery that when oxidising a starting material mixture comprising HMF(first reactant) and one or more compounds selected from the group consisting of esters of HMF and ethers of 5-(hydroxymethyl)furfural (compounds of formula **3**, see above, preferably 5-(alkoxymethyl)furfurals) (second reactants) the maximum yield of FDCA is obtained when the oxidation is started at a (lower) temperature T_{R1} in the range of from 110 to 140 °C and is then increased to a (higher) temperature T_{R2} in the range of from 140 to 200 °C ($T_{R1} < T_{R2}$). Surprisingly, when following such temperature program the FDCA yields are higher in comparison with experimental conditions where the reaction temperature range is exclusively T_{R1} or T_{R2}, and when

following the temperature program as stated the FDCA yields are also higher in comparison with a temperature program where the temperature is decreased from T_{R2} to T_{R1}.

Without wishing to be bound by any theory, it appears that in the lower temperature range T_{R1} the reactant HMF is oxidised at a high reaction rate to give FDCA. At the same time, i.e. in the (lower) temperature range T_R, the second reactant(s) do not react to a significant amount (neither to FDCA nor to any by-products), i.e. their respective reaction rate is low. Preferably, as soon as HMF is almost completely oxidised to FDCA and the conversion rate of HMF decreases the temperature is increased to temperature range T_{R2} and the rate of the oxidation reactions for the second reactant(s) is significantly increased so that they are oxidised to FDCA at an increased rate.

On the other hand, for the sake of comparison, if temperature range T_{R2} is used already at the start of the oxidation reaction HMF quickly reacts, but not selectively to FDCA. I.e. a higher amount of by-products is obtained when HMF and said second reactant(s) are subjected to oxidation conditions where the (higher) temperature range T_{R2} is used as the starting temperature range.

Even further, and again, for the sake of comparison, if the starting material mixture is subjected to oxidation conditions in the (lower) temperature range T_{R1} without a temperature increase to temperature range T_{R2} only HMF is rapidly oxidised to FDCA whereas the one or more second reactants present in the starting material mixture react only slowly and not only to FDCA but also to by-products. Thus, again, the overall yield of FDCA is low when T_{R1} is used as the starting temperature range and when there is no appropriate temperature increase to temperature range T_{R2} at the appropriate time (i.e., preferably as soon as HMF has been almost completely oxidised to FDCA and the conversion rate decreases).

Finally, when starting in the (higher) temperature range T_{R2}, the production of significant amounts of by-products from the oxidation of HMF cannot be avoided. Thus, any decrease of the reaction temperature (starting in the temperature range T_{R2} and then changing to the lower temperature range T_{R1}) does not avoid by-product formation. Again, the overall FDCA yield when using such a comparison temperature program (not according to the invention) is lower in comparison with the temperature program used according to the present invention.

Again, the above statements are not intended to define the mechanisms involved but only to summarize the observations made and the inventor's preliminary understanding of potential reasons for the surprising effects observed.

Preferred is a process as described above or below, wherein

the temperature in step (b) is kept in the range of from 120 to 135 °C, preferably from 125 to 135 °C, for at least 75 % of the duration (e.g. residence time) of step (b)

and/or

the temperature in step (c) is kept in the range of from 145 °C to 190 °C for at least 75 % of the duration (e.g. residence time) of step (c).

Maintaining the reaction temperature for step (b) and step (c) in the temperature ranges as described above for a preferred process results in a more selective conversion of HMF to FDCA in step (b) and in a more selective conversion of the one or more second reactants to FDCA in step (c). Thus, the overall yield to FDCA is increased.

Also preferred is a process as described above or below, wherein step (b)

is at least conducted until 80 %, preferably until 90%, of said 5-(hydroxymethyl)furfural (HMF) present in the starting material mixture has been reacted to furan-2,5-dicarboxylic acid and by-products.

It is advantageous to selectively convert first HMF (as a first reactant) to FDCA as HMF rapidly undergoes undesirable side reactions at higher temperatures.

Also preferred is a process as described above or below, wherein

step (b) is conducted for a residence time in the range of from 10 to 120 minutes, preferably for a residence time in the range of from 30 to 100 minutes

and/or

step (c) is conducted for a residence time in the range of from 10 to 120 minutes, preferably for a residence time in the range of from 30 to 100 minutes.

Depending on the composition of the starting material mixture prepared or provided in step (a), a too short residence time is disadvantageous since no high yields in FDCA can be obtained (for step (b) and/or step (c)).

Again, depending on the composition of the starting material mixture prepared or provided in step (a), a too long residence time is disadvantageous since the overall selectivity towards FDCA is decreased with time due to decomposition of FDCA.

A process of the invention can be conducted in batch, semi-batch or continuous mode. The skilled person would select the most favourable reactor design depending on the exact composition of the starting material mixture prepared or provided in step (a).

Due to the limited thermal stability of the starting material mixture prepared or provided in step (a), back-mixed reactor concepts with low stationary concentrations of first and second reactants and oxidation intermediates are preferred. Examples for suitable reactors include stirred tank reactors operated in semi-batch or continuous mode, or any other type of reactor with at least partial recycling of the effluent to the reaction zone, e.g. tubular reactors with external loop.

In one preferred process according to the invention a stirred tank reactor operated in semi-batch mode with gradually increasing temperature (e.g. by using a temperature ramp) is used.

In another preferred process according to the invention a cascade of two or more continuously stirred tank reactors with gradually increasing temperature (e.g. by using a temperature ramp) is used.

Also preferred is a process as described above or below, wherein for controlling the reaction conditions in the respective mixtures of steps (b) and (c)

(i) in step (b)

the concentrations of one or more compounds selected from the group consisting of

- 5-(hydroxymethyl)furfural (HMF)

- second reactants selected from the group consisting of esters of 5-(hydroxymethyl)furfural and ethers of 5-(hydroxymethyl)furfural (preferably 5-(alkoxymethyl)furfurals),

- furan-2,5-dicarboxylic acid

and/or

- the conversion of the oxidation agent, preferably oxygen,

are monitored

and

(ii) the reaction conditions are changed from the reaction conditions of step (b) to the reaction conditions of step (c) if one or more of said concentrations and/or said conversion of the oxidation agent monitored, preferably oxygen, reach a predetermined value.

In practice, the skilled person will predetermine said value in view of the starting concentrations of HMF (first reactant) and the second reactants and/or on the basis of the oxidation agent chosen (preferably oxygen (O_2) is used as an oxidation agent). E.g., if the skilled person wishes to monitor the concentration of HMF in the mixture present in step (b) the skilled person starts from the starting concentration of HMF and calculates a (lower) concentration of HMF corresponding to a predetermined conversion. Likewise, if, e.g., air or another oxygen containing gas is used as the oxidation agent, the skilled person will typically consider the amount or concentration of oxygen in an outlet gas stream containing oxygen assuming that no conversion takes place (maximum oxygen concentration in the outlet gas stream), and he will consider the amount or concentration of oxygen in the inlet oxidation gas stream.

Furthermore, the skilled person will typically consider how in a given reaction apparatus the outlet stream composition will change when the oxidation agent (e.g. molecular oxygen (O_2)) is not anymore converted in the reaction mixture but remains unreacted. Typically, at the beginning of the oxidation reaction the oxygen concentration in the outlet gas stream is lower in comparison to the situation towards the end of the oxidation of HMF. Thus, towards the end of the oxidation of HMF the concentration of the oxidation agent in the outlet gas stream will increase and enter a concentration range indicating that no

further oxygen conversion takes place in the reaction mixture upon which, for example, the temperature can be increased to temperature range T_{R2}.

Alternatively, instead of monitoring the oxygen concentration, it is also preferred to measure the concentration of small amounts of carbon monoxide or carbon dioxide gas in the outlet gas stream which often corresponds to the selectivity to FDCA and therewith also to the overall yield to FDCA.

In some industrial cases, for example if the oxidation agent cannot conveniently be measured, it is advantageous to measure the concentration of HMF or of the one or more second reactants or of the FDCA produced in the one or more reactors used for the process for preparing furan-2,5-dicarboxylic acid.

Also preferred is a process as described above or below, wherein in step (b) and/or (c) the temperature in the respective mixture is increased stepwise or as a temperature ramp.

Depending on the exact composition of the starting material mixture prepared or provided in step (a), it is advantageous to increase the temperature in step (b) and/or (c) stepwise or as a temperature ramp thus increasing the overall yield of the reaction.

Also preferred is a process as described above or below, wherein in step (a)

(a-est) a starting material mixture comprising 5-(hydroxymethyl)furfural (HMF) as a first reactant and one or more second reactants selected from the group consisting of esters of 5-(hydroxymethyl)furfural is prepared by dehydration of carbohydrates in the presence of one or more compounds selected from the group consisting of organic acids, anhydrides of organic acids and esters of organic acids

or

(a-eth) a starting material mixture comprising 5-(hydroxymethyl)furfural (HMF) as a first reactant and one or more second reactants selected from the group consisting of ethers of 5-(hydroxymethyl)furfural (preferably 5-(alkoxymethyl)furfurals) is prepared by dehydration of carbohydrates in the presence of an aliphatic alcohol as a solvent.

The dehydration of carbohydrates in step (a-est) or in step (a-eth) is preferably an acid-catalyzed dehydration.

Starting material mixtures as described above in step (a-est) or in step (a-eth) are conveniently produced by converting renewably raw materials (e.g. carbohydrates as fructose or glucose) into HMF and are thus a readily available and environmentally friendly source of HMF.

Also preferred is a process as described above or below, wherein in said starting material mixture prepared or provided in step (a)

(r-est) the molar ratio of 5-(hydroxymethyl)furfural (HMF) to esters of 5-(hydroxymethyl)furfural is in the range of from 1:1 to 1:100, preferably in the range of from 1:2 to 1:50,

or

(r-eth) the molar ratio of 5-(hydroxymethyl)furfural (HMF) to ethers of 5-(hydroxymethyl)furfural (preferably 5-(alkoxymethyl)furfurals) is in the range of from 1:1 to 1:100, preferably in the range of from 1:2 to 1:50.

Also preferred is a process as described above or below, wherein in said starting material mixture prepared or provided in step (a) the total amount of 5-(hydroxymethyl)furfural (HMF) is in the range of from 0.3 wt.-% to 30 wt.-%, preferably in the range of from 5 wt.-% to 15 wt, based on the total weight of the reaction mixture.

Also preferred is a process as described above or below, wherein in said starting material mixture prepared or provided in step (a) the total amount of ethers of 5-(hydroxymethyl)furfural (preferably 5-(alkoxymethyl)furfurals) and esters of 5-(hydroxymethyl)furfural is in the range of from 5 wt.-% to 50 wt.-%, preferably in the range of from 10 wt.-% to 30 wt, based on the total weight of the reaction mixture.

If HMF is present in a significant amount in said starting material mixture provided or prepared in step (a), the overall yield to FDCA is increased in a process for preparing FDCA as described herein above or below in comparison to processes known in the prior art.

Also preferred is a process as described above or below, wherein

in step (b) subjecting said starting material mixture to first oxidation conditions comprises contacting the starting material mixture with oxygen in the presence of a catalyst system comprising cobalt, manganese and bromine

and/or

in step (c) subjecting said first product mixture obtained in step (b) or the mixture obtained from the first product mixture obtained in step (b) by additional treatment steps to second oxidation conditions comprises contacting the starting material mixture with oxygen in the presence of a catalyst system comprising cobalt, manganese and bromine.

Preferably, if a catalyst system comprising cobalt, manganese and bromine as described above is used in step (b) and/or step (c) preferably-the total amount of cobalt is in the range of from 0.01 wt.-% to 5 wt.-%, preferably in the range of from 0.1 wt.-% to 1 wt.-%, based on the on the total weight of the starting material mixture prepared or provided in step (a),

and/or

- the total amount of manganese is in the range of from 0.01 wt.-% to 5 wt.-%, preferably in the range of from 0.1 wt.-% to 1 wt.-%, based on the on the total weight of the starting material mixture prepared or provided in step (a),

and/or

- the total amount of bromine is in the range of from 0.01 wt.-% to 5 wt.-%, preferably in the range of from 0.1 wt.-% to 1 wt.-%, based on the on the total weight of the starting material mixture prepared or provided in step (a),

Cobalt, manganese and bromine as described above as well as cerium and/or zirconium accelerate the conversion of HMF, and esters of HMF and/or ethers of 5-(hydroxymethyl)furfural (preferably 5-(alkoxymethyl)furfurals) to FDCA. Further suitable catalysts are disclosed in the literature, see, e.g., "Methodology and scope of metal/bromide autoxidation of hydrocarbons", Catalysis Today 23 (1995) 69-158.

Also preferred is a process as described above or below, preferably according to processes with a catalyst system comprising cobalt, manganese and bromine as described above, wherein the same catalyst system is used in step (b) and step (c).

Using the same catalyst system in step (b) and step (c) reduces the complexity of the reactor design and the corresponding costs.

Also preferred is a process as described above or below, wherein

in step (b) the starting material mixture comprises a saturated organic acid having 2 to 6 carbon atoms (i.e. a total number of carbon atoms in the range of from 2 to 6) as a solvent, preferably acetic acid.

and/or

in step (c) the first product mixture comprises a saturated organic acid having 2 to 6 carbon atoms (i.e. a total number of carbon atoms in the range of from 2 to 6) as a solvent, preferably acetic acid.

Saturated organic acids as specified in the aspect above are preferred solvents for a process for preparing FDCA since they dissolve HMF, esters of 5-(hydroxymethyl)furfural and ethers of 5-(hydroxymethyl)furfural (preferably used are 5-(alkoxymethyl)furfurals) in large quantities.

Also preferred is a process as described above or below, wherein

- in step (a)

(a-est) a starting material mixture comprising 5-(hydroxymethyl)furfural (HMF) as a first reactant and one or more second reactants selected from the group consisting of esters of 5-(hydroxymethyl)furfural is prepared by catalyzed dehydration of carbohydrates

in the presence of one or more compounds selected from the group consisting of organic acids, anhydrides of organic acids and esters of organic acids,

- in said starting material mixture prepared in step (a)

(r-est) the molar ratio of 5-(hydroxymethyl)furfural (HMF) to esters of 5-(hydroxymethyl)furfural is in the range of from 1:1 to 1:100, preferably in the range of from 1:2 to 1:50,

- in step (b) subjecting said starting material mixture to first oxidation conditions comprises contacting the starting material mixture with oxygen in the presence of a catalyst system comprising cobalt, manganese and bromine

and

- in step (c) subjecting said first product mixture obtained in step (b) or the mixture obtained from the first product mixture obtained in step (b) by additional treatment steps to second oxidation conditions comprises contacting the starting material mixture with oxygen in the presence of a catalyst system comprising cobalt, manganese and bromine.

wherein in step (b) and step (c)

- the same catalyst system is used, and

- the starting material mixture comprises a saturated organic acid having 2 to 6 carbon atoms (i.e. a total number of carbon atoms in the range of from 2 to 6) as a solvent, preferably acetic acid.

All advantages of the different specific aspects of the present invention as described herein above also apply to the specific aspect wherein the second reactant is selected from the group consisting of esters of 5-(hydroxymethyl)furfural.

Also preferred is a process as described above or below, wherein

- in step (a)

(a-eth) a starting material mixture comprising 5-(hydroxymethyl)furfural (HMF) as a first reactant and one or more second reactants selected from the group consisting of ethers of 5-(hydroxymethyl)furfural (preferably 5-(alkoxymethyl)furfurals) is prepared by dehydration of carbohydrates in the presence of an aliphatic alcohol as a solvent.

- in said starting material mixture prepared in step (a)

(r-eth) the molar ratio of 5-(hydroxymethyl)furfural (HMF) to ethers of 5-(hydroxymethyl)furfural (preferably 5-(alkoxymethyl)furfurals) is in the range of from 1:1 to 1:100, preferably in the range of from 1:2 to 1:50,

- in step (b) subjecting said starting material mixture to first oxidation conditions comprises contacting the starting material mixture with oxygen in the presence of a catalyst system comprising cobalt, manganese and bromine

and

- in step (c) subjecting said first product mixture obtained in step (b) or the mixture obtained from the first product mixture obtained in step (b) by additional treatment steps to second oxidation conditions comprises contacting the starting material mixture with oxygen in the presence of a catalyst system comprising cobalt, manganese and bromine.

wherein in step (b) and step (c)

- the same catalyst system is used, and

- the starting material mixture comprises a saturated organic acid having 2 to 6 carbon atoms (i.e. a total number of carbon atoms in the range of from 2 to 6) as a solvent, preferably acetic acid.

All advantages of the different specific aspects of the present invention as described hereinabove also apply to the specific aspect wherein the second reactant is selected from the group consisting of esters of 5-(hydroxymethyl)furfural and ethers of 5-(hydroxymethyl)furfural (preferably 5-(alkoxymethyl)furfurals).

Also preferred is a process as described above or below, wherein the first product mixture obtained in step (b) comprises

- 5-(hydroxymethyl)furfural (HMF) in a molar amount below 20 %, preferably below 10 %, even more preferably below 5 % of the molar amount present in said starting material mixture

- furan-2,5-dicarboxylic acid in a molar amount above 75 % of the molar amount of 5-(hydroxymethyl)furfural (HMF) present in said starting material mixture.

The person skilled in the art identifies the corresponding reaction conditions by, e.g., a small series of pre-experiments. For example, in such a series of pre-experiments, he changes the reaction temperature ranges (T_{R1} and/or T_{R2}) and the corresponding residence time and measures the molar amount of HMF and/or the molar amount of FDCA in the first product mixture obtained in step (b).

Also preferred is a process as described above or below,

wherein the first product mixture obtained in step (b) preferably comprises

- 5-(hydroxymethyl)furfural (HMF) in a molar amount below 20 %, preferably below 10 %, even more preferably below 5 % of the molar amount present in said starting material mixture

- furan-2,5-dicarboxylic acid in a molar amount above 75 % of the molar amount of 5-(hydroxymethyl)furfural (HMF) present in said starting material mixture

and

wherein the second product mixture comprises

- furan-2,5-dicarboxylic acid in a molar amount above 80 % of the total molar amount of 5-(hydroxymethyl)furfural (HMF) and said one or more second reactants selected from the group consisting of esters of 5-(hydroxymethyl)furfural and ethers of 5-(hydroxymethyl)furfural (preferably 5-(alkoxymethyl)furfurals) present in said starting material mixture.

The person skilled in the art identifies the corresponding reaction conditions by, e.g., a small series of pre-experiments. For example, in such a series of pre-experiments, he changes the reaction temperature ranges (T_{R1} or T_{R2}) and the corresponding residence

time and measures the molar amount of HMF and/or the molar amount of FDCA in the first product mixture obtained in step (b) and respectively in step (c).

Also preferred is a process as described above or below, wherein one, two or more of said second reactants selected from the group consisting of esters of 5-(hydroxymethyl)furfural and ethers of 5-(hydroxymethyl)furfural (preferably 5-(alkoxymethyl)furfurals) are selected from the group consisting of 5-(acetoxymethyl)furfural (5-AMF), 5-(formyloxymethyl)furfural, 5-(ethoxymethyl)furfural (5-EMF), 5-(methoxymethyl)furfural (5-MMF).

Specific esters of 5-(hydroxymethyl)furfural and ethers of 5-(hydroxymethyl)furfural (preferably 5-(alkoxymethyl)furfurals) as described in the specific aspect above are more conveniently oxidised to FDCA than other esters of 5-(hydroxymethyl)furfural or other ethers of 5-(hydroxymethyl)furfural.

Hereinbelow, the invention is described in more detail by examples.

Examples:

Analytical methods:

Quantitative NMR spectroscopy

Solid products were analyzed using 1H-NMR spectroscopy. The NMR-samples were prepared by dissolving 5-20 mg of the solid product in 1 ml of deuterated DMSO-d6 with 5-20 mg of 1,3,5-trimethoxybenzene as an internal standard.

Quantitative HPLC

Liquid products were analyzed using quantitative HPLC on an Agilent 1100 instrument using a Waters XBridge BEH C18 (5 µm 3x150 mm) column equipped with a UV detector.

Experiments:

Hereinafter, three comparative examples “C1”, “C2” and “C3” are compared with a process according to the invention “E1”.

Comparative example C1 ("temperature: 130 °C"):

A 1.2 L stirred-tank reactor equipped with reflux condenser, baffles and disk stirrer is charged with a catalyst mixture comprising glacial acetic acid (570 mL), $Co(OAc)_2$ (4.4 g), $Mn(OAc)_2$ (300 mg) and hydrobromic acid (4.4 g of a 48 wt.-% solution in water). The autoclave is pressurized to 10 bar with nitrogen, the stirrer is started (1200 rpm) and the catalyst mixture is heated to 130 °C. Once the reaction temperature is reached, the off-gas valve is opened and a constant flow of air (200 NL/h) (as an example of an oxidation agent according to the invention) is passed through the reactor.

A solution of 5-(hydroxymethyl)furfural (5-HMF; 33.6 g, 267 mmol) and 5-(methoxymethyl)furfural (5-MMF; 33.6 g, 240 mmol) in acetic acid (155 g) is prepared as a starting material mixture.

The starting material mixture as prepared is then dosed into the reactor comprising the catalyst mixture over a period of 90 min, wherein the temperature of 130 °C was maintained during dosing. The starting material mixture used mimics a starting material mixture prepared by dehydration of carbohydrates in the presence of an aliphatic alcohol as a solvent, wherein the aliphatic alcohol as a solvent was exchanged by acetic acid after the preparation of the starting material mixture (corresponding to step (a-eth) as described herein above).

After complete addition of the starting material mixture, the resulting reaction mixture is kept at 130 °C for 30 min (= residence time) and subjected to oxidation conditions so that an amount of said 5-HMF present in the starting material mixture is oxidized to furan-2,5-dicarboxylic acid resulting in a product mixture comprising furan-2,5-dicarboxylic acid.

Subsequently, the air-flow is stopped and replaced by a nitrogen flow and the product mixture is cooled to room temperature.

Solid reaction products of the product mixture are isolated by filtration, subsequently washed with acetic acid and water, and dried under vacuum. The thus obtained solid reaction products comprising FDCA and FDCA-monomethylester are analyzed using quantitative NMR (see analysis below, item (i)). Residual quantities of FDCA and the monomethylester of FDCA in the liquid phase of the second product mixture are analyzed using quantitative HPLC-chromatography (see analysis below, item (ii)).

Analysis:

(i) 66.0 g of solid reaction products were analyzed using ^{1}H-NMR spectroscopy: 98.0 wt.-% FDCA.-% and 0.8 wt.-% monomethylester of FDCA.

(ii) 780 g of the acetic-acid layer were analyzed using quantitative HPLC: 0.16 wt.-% FDCA and 0.22 wt.-% monomethylester of FDCA.

Comparative example C2 ("temperature: 160 °C"):

A 1.2 L stirred-tank reactor equipped with reflux condenser, baffles and disk stirrer is charged with a catalyst mixture comprising glacial acetic acid (570 mL), $Co(OAc)_2$ (4.4 g), $Mn(OAc)_2$ (300 mg) and hydrobromic acid (4.4 g of a 48 wt.-% solution in water). The autoclave is pressurized to 10 bar with nitrogen, the stirrer is started (1200 rpm) and the catalyst mixture is heated to 160 °C. Once the reaction temperature is reached, the off-gas valve is opened and a constant flow of air (200 NL/h) (as an example of an oxidation agent according to the invention) is passed through the reactor.

A solution of 5-(hydroxymethyl)furfural (5-HMF; 33.6 g, 267 mmol) and 5-(methoxymethyl)furfural (5-MMF; 33.6 g, 240 mmol) in acetic acid (155 g) is prepared as a starting material mixture.

The starting material mixture as prepared is then dosed into the reactor comprising the catalyst mixture over a period of 90 min, wherein the temperature of 160 °C was maintained during dosing. The starting material mixture used mimics a starting material mixture prepared by dehydration of carbohydrates in the presence of an aliphatic alcohol as a solvent, wherein the aliphatic alcohol as a solvent was exchanged by acetic acid after the preparation of the starting material mixture (corresponding to step (a-eth) as described herein above).

After complete addition of the starting material mixture, the resulting reaction mixture is kept at 160 °C for 30 min (= residence time) and subjected to oxidation conditions so that an amount of said 5-HMF present in the starting material mixture is oxidized to furan-2,5-dicarboxylic acid resulting in a product mixture comprising furan-2,5-dicarboxylic acid.

Subsequently, the air-flow is stopped and replaced by a nitrogen flow and the final reaction mixture is cooled to room temperature.

Solid reaction products of the final reaction mixture are isolated by filtration, subsequently washed with acetic acid and water, and dried under vacuum. The thus obtained solid reaction products comprising FDCA and FDCA-monomethylester are analyzed using quantitative NMR (see analysis below, item (i)). Residual quantities of FDCA and the monomethylester of FDCA in the liquid phase of the second product mixture are analyzed using quantitative LC-chromatography (see analysis below, item (ii)).

Analysis:

(i) 65.3 g of solid reaction products were analyzed using ^{1}H-NMR spectroscopy: 98.2 wt.-% FDCA.-% and 1.0 wt.-% monomethylester of FDCA.

(ii) 782 g of the acetic-acid layer were analyzed using quantitative HPLC: 0.25 wt.-% FDCA and 0.25 wt.-% monomethylester of FDCA.

Comparative example C3 (“temperatures: 150 °C, 170 °C”):

A 1.2 L stirred-tank reactor equipped with reflux condenser, baffles and disk stirrer is charged with a catalyst mixture comprising glacial acetic acid (570 mL), $Co(OAc)_2$ (4.4 g), $Mn(OAc)_2$ (300 mg) and hydrobromic acid (4.4 g of a 48 wt.-% solution in water). The autoclave is pressurized to 10 bar with nitrogen, the stirrer is started (1200 rpm) and the catalyst mixture is heated to 150 °C. Once the reaction temperature is reached, the off-gas valve is opened and a constant flow of air (200 NL/h) (as an example of an oxidation agent according to the invention) is passed through the reactor.

A solution of 5-(hydroxymethyl)furfural (5-HMF; 9.3 g, 73.9 mmol) and 5-(methoxymethyl)furfural (5-MMF; 37.2 g, 266 mmol) in acetic acid (100 g) is prepared as a starting material mixture.

The starting material mixture as prepared is then dosed into the reactor comprising the catalyst mixture over a period of 90 min, wherein a temperature of 150 °C was maintained during dosing. The starting material mixture used mimics a starting material mixture prepared by dehydration of carbohydrates in the presence of an aliphatic alcohol as a solvent, wherein the aliphatic alcohol as a solvent was exchanged by acetic acid after the preparation of the starting material mixture (corresponding to step (a-eth) as described herein above).

After complete addition of the starting material mixture, the resulting reaction mixture is kept at 150 °C for 30 min (= residence time) and subjected to first oxidation conditions so that an amount of said 5-HMF present in the starting material mixture is oxidized to furan-2,5-dicarboxylic acid resulting in a first product mixture comprising furan-2,5-dicarboxylic acid.

Subsequently, the first product mixture obtained is subjected to second oxidation conditions in the range of from above 150 to approximately 170 °C by increasing the temperature of the first product mixture, with a temperature ramp of 2 K/min, so that the temperature of 170 °C is reached after 10 minutes. (Note: In the experiment, the heating process of the reaction mixture from 150 °C to 170 °C is a continuous process which is not interrupted).

Subsequently, the reaction mixture is allowed to further react for 30 min at 170 °C.

During the time when the reaction mixture is in the temperature range of from above 150 to 170 °C (time of step (c)), at least a fraction of said unreacted amount of 5-MMF and oxidation intermediates (DFF, FFCA, HFCA) present in the first product mixture is oxidized resulting in a second product mixture comprising furan-2,5-dicarboxylic acid.

Subsequently, the air-flow is stopped and replaced by a nitrogen flow and the second product mixture is cooled to room temperature.

Solid reaction products of the second product mixture are isolated by filtration, subsequently washed with acetic acid and water, and dried under vacuum. The thus obtained solid reaction products comprising FDCA and FDCA-monomethylester are analyzed using quantitative NMR (see analysis below, item (i)). Residual quantities of FDCA and the monomethylester of FDCA in the liquid phase of the second product mixture are analyzed using quantitative LC-chromatography (see analysis below, item (ii)).

Analysis:

(i) 39.7 g of solid reaction products were obtained and analyzed using ^{1}H-NMR spectroscopy: 96.8 wt.-% of the solid reaction products were FDCA.-% and 1.8 wt.-% of the solid reaction products were monomethylester of FDCA.

(ii) 657 g of the acetic-acid layer were obtained and analyzed using quantitative HPLC: 0.23 wt.-% of the acetic acid layer were FDCA and 0.21 wt.-% of the acetic acid layer were monomethylester of FDCA.

Example E1 (according to the invention; "temperatures 130 °C, 160 °C"):

A 1.2 L stirred-tank reactor equipped with reflux condenser, baffles and disk stirrer is charged with a catalyst mixture comprising glacial acetic acid (570 mL), $Co(OAc)_2$ (4.4 g), $Mn(OAc)_2$ (300 mg) and hydrobromic acid (4.4 g of a 48 wt.-% solution in water). The autoclave is pressurized to 10 bar with nitrogen, the stirrer is started (1200 rpm) and the catalyst mixture is heated to 130 °C. Once the reaction temperature is reached, the off-gas valve is opened and a constant flow of air (200 NL/h) (as an example of an oxidation agent according to the invention) is passed through the reactor.

A solution of 5-(hydroxymethyl)furfural (5-HMF; 33.6 g, 267 mmol) and 5-(methoxymethyl)furfural (5-MMF; 33.6 g, 240 mmol) in acetic acid (155 g) is prepared as a starting material mixture.

The starting material mixture as prepared is then dosed into the reactor comprising the catalyst mixture over a period of 90 min, wherein the temperature of 130 °C was maintained during dosing. The starting material mixture used mimics a starting material mixture prepared by dehydration of carbohydrates in the presence of an aliphatic alcohol as a solvent, wherein the aliphatic alcohol as a solvent was exchanged by acetic acid after the preparation of the starting material mixture (corresponding to step (a-eth) as described herein above).

After complete addition of the starting material mixture, the resulting reaction mixture is kept at 130 °C for 30 min (= residence time) and subjected to first oxidation conditions so that an amount of said 5-HMF present in the starting material mixture is oxidized to furan-2,5-dicarboxylic acid resulting in a first product mixture comprising furan-2,5-dicarboxylic acid (step (b)).

Subsequently, the first product mixture obtained is subjected to second oxidation conditions in the range of from above 140 to approximately 160 °C by increasing the temperature of the first product mixture obtained in step (b), with a temperature ramp of 2 K/min, so that the temperature of 160 °C is reached after 15 minutes. (Note: In the experiment,

the heating process of the reaction mixture from 130 °C to 160 °C is a continuous process which is not interrupted.)

Subsequently, the reaction mixture is allowed to further react for 30 min at 160 °C.

During the time when the reaction mixture is in the temperature range of from above 140 to 160 °C (time of step (c)), at least a fraction of said unreacted amount of 5-MMF and oxidation intermediates (DFF, FFCA, HFCA) present in the first product mixture is oxidized resulting in a second product mixture comprising furan-2,5-dicarboxylic acid.

Subsequently, the air-flow is stopped and replaced by a nitrogen flow and the second product mixture is cooled to room temperature.

Solid reaction products of the second product mixture are isolated by filtration, subsequently washed with acetic acid and water, and dried under vacuum. The thus obtained solid reaction products comprising FDCA and FDCA-monomethylester are analyzed using quantitative NMR (see analysis below, item (i)). Residual quantities of FDCA and the monomethylester of FDCA in the liquid phase of the second product mixture are analyzed using quantitative LC-chromatography (see analysis below, item (ii)).

Analysis:

(i) 69.0 g of solid reaction products were obtained and analyzed using ^{1}H-NMR spectroscopy: 96.8 wt.-% of the solid reaction products were FDCA.-% and 1.8 wt.-% of the solid reaction products were monomethylester of FDCA.

(ii) 770 g of the acetic-acid layer were obtained and analyzed using quantitative HPLC: 0.24 wt.-% of the acetic acid layer were FDCA and 0.38 wt.-% of the acetic acid layer were monomethylester of FDCA.

Results:

From the analytical data obtained the yield of the products (1) (FDCA) and (2) (FDCA-monomethylester) can be calculated according to formula (I) and (II), respectively.

The yield of FDCA can be calculated by formula (I)

$$yield(1) = \frac{n_{1(solid)} + n_{1(liquid)}}{n_{HMF} + n_{MMF}} \quad \text{(I)},$$

wherein n_{HMF} and n_{MMF} are the molar amounts of the starting materials used. $n_{1(solid)}$ and $n_{1(liquid)}$ are calculated using the fraction of product (1) in the solid reaction product or in the acetic acid layer, respectively (wt.%(1)) as well as the molar mass of FDCA (M_1) according to:

$$n_{1(solid)} = mass\ of\ solid\ reaction\ products \cdot wt.\%(1) / M_1$$

and

$$n_{1(liquid)} = mass\ of\ liquid\ reaction\ layer \cdot wt.\%(1) / M_1.$$

Correspondingly, the yield of FDCA-monomethylester can be calculated by formula (II)

$$yield(2) = \frac{n_{2(solid)} + n_{2(liquid)}}{n_{HMF} + n_{MMF}} \quad \text{(II)},$$

wherein n_{HMF} and n_{MMF} are the molar amounts of the starting materials used. $n_{2(solid)}$ and $n_{2(liquid)}$ are calculated using the fraction of product (2) in the solid reaction product or in the acetic acid layer, respectively (wt.%(2)) as well as the molar mass of FDCA-monomethylester (M_2) according to:

$$n_{2(solid)} = mass\ of\ solid\ reaction\ products \cdot wt.\%(2) / M_2$$

and

$$n_{2(liquid)} = mass\ of\ liquid\ reaction\ layer \cdot wt.\%(2) / M_2.$$

The calculated yields for example E1 and comparative examples C1, C2 and C3 are summarized in table 1.

Table 1: Yields of experiments C1, C2, C3 and E1

experiment	yield(1) FDCA / %	yield(2) FDCA-monomethylester / %	sum of yield(1) and yield(2) / %
C1	84	3	87
C2	81	3	84
C3	73	2	75
E1	87	4	91

The results summarized in table 1 show that, in a process according to the invention (E1), the yield of FDCA (yield(1) in table 1) as well as the yield of FDCA-monomethylester (yield(2) in table 1) is increased in comparison with the corresponding yields of comparative examples C1, C2 and C3. Consequently, in the process according to the invention the overall yield of FDCA and FDCA-monomethylester (see last column of table 1) is increased compared to C1, C2 and C3. Therefore, it can be shown that with a process according to the invention more FDCA and FDCA-monomethylester and fewer waste products are obtained.

Claims:

1. Process for preparing furan-2,5-dicarboxylic acid comprising the following steps:

(a) preparing or providing a starting material mixture comprising

- 5-(hydroxymethyl)furfural (HMF) as a first reactant

and

- one or more second reactants selected from the group consisting of esters of 5-(hydroxymethyl)furfural and ethers of 5-(hydroxymethyl)furfural,

(b) subjecting said starting material mixture to first oxidation conditions at a temperature in the range T_{R1} of from 110 to 140 °C so that an amount of said 5-(hydroxymethyl)furfural (HMF) present in the starting material mixture is oxidised to furan-2,5-dicarboxylic acid and a first product mixture results comprising furan-2,5-dicarboxylic acid and an unreacted amount of said one or more second reactants,

and

(c) subjecting the first product mixture obtained in step (b) or a mixture obtained from the first product mixture obtained in step (b) by additional treatment steps to second oxidation conditions at an increased temperature in the range T_{R2} of from above 140 to 200 °C so that at least a fraction of said unreacted amount of said one or more second reactants present in the first product mixture is oxidised and a second product mixture results comprising furan-2,5-dicarboxylic acid.

2. Process according to claim 1, wherein

the temperature in step (b) is kept in the range of from 120 to 135 °C, preferably from 125 to 135 °C, for at least 75 % of the duration of step (b)

and/or

the temperature in step (c) is kept in the range of from 145 °C to 190 °C for at least 75 % of the duration of step (c).

3. Process according to claim 1, wherein step (b)

is at least conducted until 80 %, preferably until 90%, of said 5-(hydroxymethyl)furfural (HMF) present in the starting material mixture has been reacted to furan-2,5-dicarboxylic acid and by-products.

4. Process according to any preceding claim, wherein

step (b) is conducted for a residence time in the range of from 10 to 120 minutes, preferably for a residence time in the range of from 30 to 100 minutes

and/or

step (c) is conducted for a residence time in the range of from 10 to 120 minutes, preferably for a residence time in the range of from 30 to 100 minutes.

5. Process according to any preceding claim, wherein for controlling the reaction conditions in the respective mixtures of steps (b) and (c)

(i) in step (b)

the concentrations of one or more compounds selected from the group consisting of

- 5-(hydroxymethyl)furfural (HMF)

- second reactants selected from the group consisting of esters of 5-(hydroxymethyl)furfural and ethers of 5-(hydroxymethyl)furfural,

- furan-2,5-dicarboxylic acid

and/or

- the conversion of the oxidation agent, preferably oxygen,

are monitored

and

(ii) the reaction conditions are changed from the reaction conditions of step (b) to the reaction conditions of step (c) if one or more of said concentrations and/or said conversion of the oxidation agent monitored, preferably oxygen, reach a predetermined value.

6. Process according to any preceding claim, wherein in step (b) and/or (c) the temperature in the respective mixture is increased stepwise or as a temperature ramp.

7. Process according to any preceding claim, wherein in step (a)

(a-est) a starting material mixture comprising 5-(hydroxymethyl)furfural (HMF) as a first reactant and one or more second reactants selected from the group consisting of esters of 5-(hydroxymethyl)furfural is prepared by dehydration of carbohydrates in the presence of one or more compounds selected from the group consisting of organic acids, anhydrides of organic acids and esters of organic acids

or

(a-eth) a starting material mixture comprising 5-(hydroxymethyl)furfural (HMF) as a first reactant and one or more second reactants selected from the group consisting of ethers of 5-(hydroxymethyl)furfural is prepared by dehydration of carbohydrates in the presence of an aliphatic alcohol as a solvent.

8. Process according to any preceding claim, wherein in said starting material mixture prepared or provided in step (a)

(r-est) the molar ratio of 5-(hydroxymethyl)furfural (HMF) to esters of 5-(hydroxymethyl)furfural is in the range of from 1:1 to 1:100, preferably in the range of from 1:2 to 1:50,

or

(r-eth) the molar ratio of 5-(hydroxymethyl)furfural (HMF) to ethers of 5-(hydroxymethyl)furfural is in the range of from 1:1 to 1:100, preferably in the range of from 1:2 to 1:50.

9. Process according to any preceding claim, wherein

in step (b) subjecting said starting material mixture to first oxidation conditions comprises contacting the starting material mixture with oxygen in the presence of a catalyst system comprising cobalt, manganese and bromine

and/or

in step (c) subjecting said first product mixture obtained in step (b) or the mixture obtained from the first product mixture obtained in step (b) by additional treatment steps to second oxidation conditions comprises contacting the starting material mixture with oxygen in the presence of a catalyst system comprising cobalt, manganese and bromine.

10. Process according to any preceding claim, preferably according to claim 9, wherein the same catalyst system is used in step (b) and step (c).

11. Process according to any preceding claim, wherein

in step (b) the starting material mixture comprises a saturated organic acid having 2 to 6 carbon atoms as a solvent, preferably acetic acid.

and/or

in step (c) the first product mixture comprises a saturated organic acid having 2 to 6 carbon atoms as a solvent, preferably acetic acid.

12. Process according to any preceding claim, wherein

- in step (a)

(a-est) a starting material mixture comprising 5-(hydroxymethyl)furfural (HMF) as a first reactant and one or more second reactants selected from the group consisting of esters of 5-(hydroxymethyl)furfural is prepared by catalyzed dehydration of carbohydrates in the presence of one or more compounds selected from the group consisting of organic acids, anhydrides of organic acids and esters of organic acids,

- in said starting material mixture prepared in step (a)

(r-est) the molar ratio of 5-(hydroxymethyl)furfural (HMF) to esters of 5-(hydroxymethyl)furfural is in the range of from 1:1 to 1:100

- in step (b) subjecting said starting material mixture to first oxidation conditions comprises contacting the starting material mixture with oxygen in the presence of a catalyst system comprising cobalt, manganese and bromine

and

- in step (c) subjecting said first product mixture obtained in step (b) or the mixture obtained from the first product mixture obtained in step (b) by additional treatment steps to second oxidation conditions comprises contacting the starting material mixture with oxygen in the presence of a catalyst system comprising cobalt, manganese and bromine.

wherein in step (b) and step (c)

- the same catalyst system is used, and

- the starting material mixture comprises a saturated organic acid having 2 to 6 carbon atoms as a solvent, preferably acetic acid.

13. Process according to any preceding claim, wherein

- in step (a)

(a-eth) a starting material mixture comprising 5-(hydroxymethyl)furfural (HMF) as a first reactant and one or more second reactants selected from the group consisting of 5-(alkoxymethyl)furfurals is prepared by dehydration of carbohydrates in the presence of an aliphatic alcohol as a solvent.

- in said starting material mixture prepared in step (a)

(r-eth) the molar ratio of 5-(hydroxymethyl)furfural (HMF) to ethers of 5-(hydroxymethyl)furfural is in the range of from 1:1 to 1:100

- in step (b) subjecting said starting material mixture to first oxidation conditions comprises contacting the starting material mixture with oxygen in the presence of a catalyst system comprising cobalt, manganese and bromine

and

- in step (c) subjecting said first product mixture obtained in step (b) or the mixture obtained from the first product mixture obtained in step (b) by additional treatment steps to second oxidation conditions comprises contacting the starting material mixture with oxygen in the presence of a catalyst system comprising cobalt, manganese and bromine.

wherein in step (b) and step (c)

- the same catalyst system is used, and

- the starting material mixture comprises a saturated organic acid having 2 to 6 carbon atoms as a solvent, preferably acetic acid.

14. Process according to any preceding claim,

wherein the first product mixture obtained in step (b) comprises

- 5-(hydroxymethyl)furfural (HMF) in a molar amount below 20 % of the molar amount present in said starting material mixture, and

- furan-2,5-dicarboxylic acid in a molar amount above 75 % of the molar amount of 5-(hydroxymethyl)furfural (HMF) present in said starting material mixture,

and/or

wherein the second product mixture comprises

- furan-2,5-dicarboxylic acid in a molar amount above 80 % of the total molar amount of 5-(hydroxymethyl)furfural (HMF) and said one or more second reactants selected from the group consisting of esters of 5-(hydroxymethyl)furfural and ethers of 5-(hydroxymethyl)furfural present in said starting material mixture.

15. Process according to any preceding claim, wherein one, two or more of said second reactants selected from the group consisting of esters of 5-(hydroxymethyl)furfural and ethers of 5-(hydroxymethyl)furfural are selected from the group consisting of 5-(acetoxymethyl)furfural (5-AMF), 5-(formyloxymethyl)furfural, 5-(ethoxymethyl)furfural (5-EMF), 5-(methoxymethyl)furfural (5-MMF).

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2016/076510

A. CLASSIFICATION OF SUBJECT MATTER
INV. C07D307/68
ADD.

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)
C07D

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)
EPO-Internal, CHEM ABS Data, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 2014/014979 A1 (EASTMAN CHEM CO [US]) 23 January 2014 (2014-01-23) the whole document; in particular, claims 1, 7, 13, and the examples	1-15
Y	WO 2012/161968 A1 (EASTMAN CHEM CO [US]) 29 November 2012 (2012-11-29) cited in the application the whole document; in particular, "example sets" 1 and 5, and page 18, line 14- page 19, line 5	1-15
A	WO 2011/043661 A1 (FURANIX TECHNOLOGIES BV [NL]; MUNOZ DE DIEGO CESAR [NL]; DAM MATHEUS A) 14 April 2011 (2011-04-14) cited in the application the whole document; in particular, the example 1, table 1, and claim 15	1-15

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

☒ See patent family annex.

* Special categories of cited documents :

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
23 November 2016	05/12/2016

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2016/076510

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