

European patent application No. 10768600.8

**APPEAL**  
for immediate attention

## I. Findings

1.  Appeal in which **more than one party** is involved (opposition procedure, except when all oppositions have been withdrawn). **Refer the case to the Board of Appeal without delay using EPO Form 2703.**
2.  Appeal in which **only one party** is involved (examination procedure and opposition procedure if all oppositions have been withdrawn).

### 2.1 Requirements of Article 108 EPC

The **notice of appeal** has been filed within the time limit.      yes       no   
 The **appeal fee** has been paid within the time limit.            yes       no   
 The **statement of grounds** has been filed within the time limit.    yes       no

If **one** of the answers set out above is 'no' and if no request for re-establishment of rights under Article 122 EPC has been filed (see I.2.2), **refer the case to the Board of Appeal without delay using EPO Form 2703.** The Board of Appeal decides on the admissibility of the appeal.

If **all** the answers set out above are "yes", continue under II/III.2.

- 2.2  A request for re-establishment of rights into the appeal period has been filed. Refer the case to the SCAPE of the SIS Unit without delay.
- 2.3 Special cases which have to be referred to the Board of Appeal without delay using EPO Form 2703
- Withdrawal of appeal
  - Request for correction of appeal (R. 139 EPC)
  - Expiry of three-month time limit for interlocutory revision (Art. 109(2) EPC)

17-07-2015  
.....  
Date

Pfitzner, Gabriele    Clarke, Kati  
.....  
Formalities Officer

.....  
Director/SCAPE (for information)

## II. Appeal against the decision of the Formalities Officer

1.  Re-establishment of rights (Guidelines E-VII, 2.2.7)
- The conditions for granting re-establishment of rights are fulfilled. The request can be granted if this can be done within the three-month time limit of Article 109(2) EPC and if the conditions for granting interlocutory revision are fulfilled. Continue under II.2.
  - The request for re-establishment of rights cannot be granted. **Refer the case to the Board of Appeal without delay using EPO Form 2703.**
2.  The appeal is allowable and well-founded. The decision under appeal is rectified (Art. 109(1) EPC). EPO Form 2710 is to be dispatched.
- The decision under appeal is not rectified. **Refer the case to the Board of Appeal without delay using EPO Form 2703 (Art. 109(2) EPC).**

3. Reimbursement of appeal fee

- No request for reimbursement of the appeal fee has been filed.
  - The Formalities Officer orders reimbursement of the appeal fee of his own motion (R. 103 EPC, Guidelines E-X, 7.3).
- A request for reimbursement of the appeal fee has been filed.
  - Reimbursement of the appeal fee is ordered (R. 103 EPC).
  - The request for reimbursement of the appeal fee cannot be allowed. **Refer the case to the Board of Appeal without delay using EPO Form 2703 (R. 103(2) EPC).**

.....  
 Date    Formalities Officer    SCAPE (for information)

**III. Appeal against the decision of the Examining/Opposition Division**

- 1.  Re-establishment of rights (Guidelines E-VII, 2.2.7)
  - The conditions for granting re-establishment of rights are fulfilled. The request can be granted if this can be done within the three-month time limit of Article 109(2) EPC and if the conditions for granting interlocutory revision are fulfilled. Continue under III.2.
  - The request for re-establishment of rights cannot be granted. **Refer the case to the Board of Appeal without delay using EPO Form 2703.**
- 2.  **To the Examining Division**     **To the Opposition Division**

.....  
 Date    Formalities Officer

**To the Formalities Officer**

- 3.  The appeal is allowable and well-founded. The decision under appeal is rectified (Art. 109(1) EPC). EPO Form 2710 is to be dispatched.
  - The decision under appeal is not rectified. **Refer the case to the Board of Appeal without delay using EPO Form 2703 (Art. 109(2) EPC).**
- 4. Reimbursement of appeal fee
  - No request for reimbursement of the appeal fee has been filed.
    - The Division orders reimbursement of the appeal fee of its own motion (R. 103 EPC, Guidelines E-X, 7.3).
  - A request for reimbursement of the appeal fee has been filed.
    - Reimbursement of the appeal fee is ordered (R. 103 EPC).
    - The request for reimbursement of the appeal fee cannot be allowed. **Refer the case to the Board of Appeal without delay using EPO Form 2703 (R. 103(2) EPC).**

.....  
 Date     Examining Division     Opposition Division

.....  
 Chairman    2nd Examiner    Primary Examiner    Legal Member

## Acknowledgement of receipt

We hereby acknowledge receipt of the following subsequently filed document(s):

Submission number	3633630	
Application number	EP10768600.8	
Date of receipt	15 July 2015	
Receiving Office	European Patent Office, The Hague	
Your reference	P30061EP00	
Applicant	All applicants as on file	
Documents submitted	package-data.xml  epf1038.pdf (1 p.)  DG3-CLMS.pdf\P30061EP00 - FUR 19b EP Sec Aux Req claims.pdf (2 p.)	ep-sfd-request.xml  APPEAL-GRDS-1.pdf\P30061EP00 letter to EPO.pdf (13 p.)  APPEAL-CDOC.pdf\Ribeiro 2003 Cooperative effect of cobalt acetylacetonate.pdf (4 p.)
Submitted by	CN=Robbert-Jan de Lang 27152	
Method of submission	Online	
Date and time receipt generated	15 July 2015, 14:36 (CEST)	
Message Digest	B9:2E:21:69:18:A9:00:33:9E:40:1F:A0:1F:6F:B0:5D:C3:08:B9:3B	

### Correction by the EPO of errors in debit instructions filed by eOLF

Errors in debit instructions filed by eOLF that are caused by the editing of Form 1038E entries or the continued use of outdated software (all forms) may be corrected automatically by the EPO, leaving the payment date unchanged (see decision T 152/82, OJ EPO 1984, 301 and point 6.3 ff ADA, Supplement to OJ EPO 10/2007).

P30061EP00

## Second Auxiliary Request

## CLAIMS

1. Method for the preparation of 2,5-furan dicarboxylic acid comprising the step of  
5 contacting in a reactor a feed comprising a compound selected from the group consisting of  
esters of 5-hydroxymethylfurfural ("HMF") and a mixture of esters of HMF and HMF, with an  
oxygen-containing gas being continuously fed and removed to and from the reactor in the  
presence of an oxidation catalyst comprising at least one metal selected from Co and Mn, at  
a temperature between 140 and 200 °C at an oxygen partial pressure of 1 to 10 bar, wherein  
10 a solvent or solvent mixture comprising acetic acid or acetic acid and water mixtures is  
present.
2. Method according to claim 1, wherein the oxidation catalyst comprises a source of  
bromine.  
15
3. Method according to claim 2, wherein the oxidation catalyst contains both Co and  
Mn.
4. Method according to claim 3, wherein the oxidation catalyst comprises at least one  
20 additional metal.
5. Method according to claim 4, wherein the additional metal is Zr and/or Ce.
6. Method according to claims 1-5, wherein the oxygen-containing gas is selected  
25 from oxygen, air or other oxygen-containing gases.
7. Method according to any of the previous claims wherein the temperature is  
between 160 and 190 °C.
8. Method according to any of the previous claims, wherein the feed comprises an  
30 ester of HMF containing an ester moiety of an alkyl carboxylic acid wherein the alkyl group  
contains up to 6 carbon atoms, preferably from 1 to 5 carbon atoms.
9. Process for the preparation of a dialkyl ester of 2,5-furan dicarboxylic acid,  
35 comprising the step of contacting in a reactor a feed comprising a compound selected from  
the group consisting of esters of 5-hydroxymethylfurfural ("HMF") and a mixture of esters of  
HMF and HMF, with an oxygen-containing gas being continuously fed and removed to and

from the reactor, in the presence of an oxidation catalyst comprising at least one metal selected from Co and Mn, at a temperature between 140 and 200 °C at an oxygen partial pressure of 1 to 10 bar wherein a solvent or solvent mixture comprising acetic acid or acetic acid and water mixtures, is present, and esterifying the thus obtained product.

5

10. Process according to claim 9, wherein the product is esterified with a C<sub>1</sub>-C<sub>5</sub> alkyl alcohol.

10

11. Process according to claim 10, wherein the C<sub>1</sub>-C<sub>5</sub> alkyl alcohol is methanol and the dialkyl ester is the dimethylester of 2,5-furan dicarboxylic acid.



## Letter accompanying subsequently filed items

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The document(s) listed below is (are) subsequently filed documents pertaining to the following application:

Application number

10768600.8

Applicant's or representative's reference

P30061EP00

	Description of document	Original file name	Assigned file name
1	Statement of grounds of appeal	P30061EP00 letter to EPO.pdf	APPEAL-GRDS-1.pdf
2	Claims (appeal procedure)	P30061EP00 - FUR 19b EP Sec Aux Req claims.pdf	DG3-CLMS.pdf
3	Cited document during appeal procedure	Ribeiro 2003 Cooperative effect of cobalt acetylacetonate.pdf	APPEAL-CDOC.pdf

### Signatures

Place:

Date:

**15 July 2015**

Signed by:

**Robbert-Jan de Lang 27152**

Association:

**EP&C**

Representative name:

**lang**

Capacity:

**(Representative)**



# Cooperative effect of cobalt acetylacetonate and silica in the catalytic cyclization and oxidation of fructose to 2,5-furandicarboxylic acid

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## Abstract

Cobalt acetylacetonate encapsulated in sol–gel silica is shown to be a very efficient bifunctional acidic and redox catalyst, giving 2,5-furandicarboxylic acid with 99% selectivity directly from fructose at a conversion of 72%. A cooperative effect of the functions of the catalyst is operative, as the same reaction performed in two consecutive steps gives much lower conversions.

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*Keywords:* Fructose; 5-Hydroxymethylfurfural; 2,5-Furandicarboxylic acid; Cooperative effect; Cobalt acetylacetonate; Sol–gel silica

## 1. Introduction

The search for new environmentally friendly technologies in combination with starting materials from renewable resources is a continuously growing field. Substances extracted from natural sources might generate new compounds that, through new methodologies of chemical transformation, are able to supply products of commercial interest with high added value [1]. Under this context, the production of 2,5-furandicarboxylic acid (FDA, **3**) using fructose (**1**), an abundant substance in vege-

tables, as starting material, is an interesting alternative. The FDA can be a potential substitute for terephthalic acid, obtained from fossil resources, in the synthesis of poly(ethylene terephthalate) (PET), widely used in the manufacture of different materials [2,3]. The intermediate in the synthesis of FDA is 5-hydroxymethylfurfural (HMF, **2**), which further reacts to levulinic and formic acid, as shown in Fig. 1.

The first step (from **1** to **2**) is catalyzed by acids, ion-exchange resins, zeolites or other silica matrixes, with or without metals in their framework [4–7]. The second step (from **2** to **3**) is catalyzed by Pd, Pt, Bi, Co or other metal compounds encapsulated in a variety of matrixes [3,8–10]. The one-pot synthesis directly from **1** to **3** would need a special catalyst, which combines the acid and

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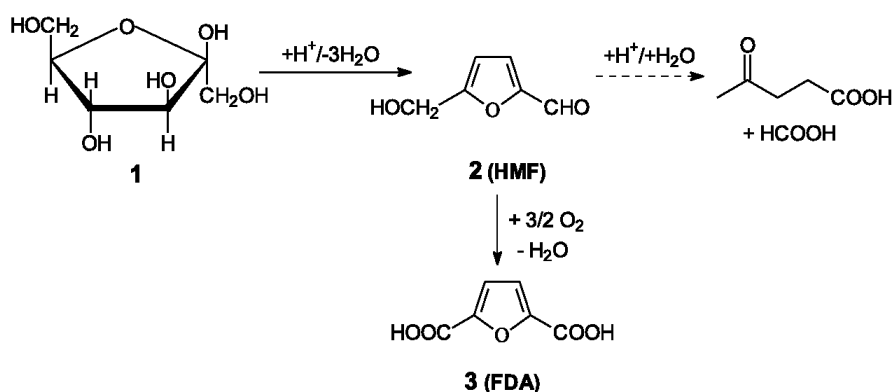


Fig. 1. Synthetic route from fructose to FDA via HMF.

metallic properties. This system would allow to minimize the losses of the intermediate **2**, which in this case would be promptly oxidized to **3**.

Herein we report the use of  $\text{Co}(\text{acac})_3$  encapsulated in a sol-gel silica matrix for the direct catalytic conversion of **1**–**3**. A cooperative effect is observed by the combination of the solid acid and the metal species, encapsulated in the matrix. Some tests have been carried out with the two steps separately [8], which allowed for the understanding of each reaction and to improve the one-pot synthesis.

## 2. Experimental

### 2.1. Catalyst preparation

*SiO<sub>2</sub>-gel*: 2.70 ml of tetraethyl orthosilicate (Merck), 2.10 ml of ethanol (99.5%, Merck) and 0.4 ml of deionized water were mixed in a 25 ml beaker, which was kept under rapid stirring during 30 min. After that, a mixture of 0.5 ml of deionized water and 5  $\mu\text{l}$  of 1 M HCl was slowly added and the stirring continued for 5 min. The mixture was kept in a fume hood during one week. The transparent solid formed was ground and kept in a desiccator over silica gel.

*Co(acac)<sub>3</sub>* (Aldrich) was used without further purification.

*Co-gel*: The same procedure described for the *SiO<sub>2</sub>-gel* was used, however the 1 M HCl was substituted by 100 mg of  $\text{Co}(\text{acac})_3$  (Aldrich). The Co-content of the Co-gel was 2.3%.

### 2.2. Catalytic experiments

Synthesis of 5-hydroxymethylfurfural (HMF, **2**): 50 ml of methyl isobutyl ketone (MIBK), 7 g of fructose (Synth) dissolved in 6 ml of deionized water and 0.1 g of the catalyst were added to a round-bottomed flask, coupled to a condenser. The system was kept under stirring at 88 °C for 8 h. The mixture was then filtered, the aqueous and the organic phases were separated, and both were kept in a refrigerator for posterior analysis.

2,5-Furandicarboxylic acid (FDA, **3**) synthesis starting from HMF (**2**): to 9.4 ml of MIBK in a 50 ml round bottom flask, 0.6 ml of deionized water and 0.1 g of the catalyst were added. The system was kept under a flow of synthetic air during 30 min at 80 °C under magnetic stirring. Then 40  $\mu\text{l}$  of the HMF (Fluka) were added, and the reaction was carried out for 4 h.

FDA synthesis starting from fructose (**1**): 6 ml of deionized water, 0.1 g of fructose, and 0.0025–0.5 g of catalyst were added to a 25 ml autoclave. The reactions were carried out under 20 bar of synthetic air at 160 °C during 65 min, using magnetic stirring. The reaction mixture was cooled, filtered and stored for posterior analysis.

The analyses were made using a Waters 510 HPLC pump and a Bio-Rad Aminex HPX 87-H column, coupled to a Waters 410 refraction index detector. The mobile phase was 0.01 M trifluoroacetic acid (TFA, Riedel-de-Haën). Analysis conditions: flow rate 0.7 ml/min, column temperature 50 °C, detector temperature 50 °C. Authentic samples of the substrate and the products (Fluka)



were used as standards and calibration curves were used for quantification.

### 3. Results and discussion

The results obtained for the synthesis of 5-hydroxymethylfurfural (HMF, **2**) from fructose are shown in Table 1.

The SiO<sub>2</sub>-gel catalyst is four times more active in the dehydration of fructose to **2** than Co(acac)<sub>3</sub>, which does not show any additional effect when combined with the silica matrix (Co-gel), giving the same yields as silica alone. The selectivity for **2** was 100% and no levulinic or formic acid were formed. This suggests that either another transition state selectivity or different proton transfer rates are operating at the active sites of the heterogeneous catalyst, favouring the formation of **2**.

However under the given conditions, none of the catalysts is appropriate for the conversion of **2** to 2,5-furandicarboxylic acid (**3**) (Table 1). Silica totally suppresses the conversion of **2** and the activity of the Co-catalysts is rather small.

In the one-pot reactions, which were carried out in an autoclave at 160 °C, we used only water as under these conditions all compounds were soluble and could easily interact with the Co-gel. The results are shown in Table 2.

In the absence of a catalyst **3** is not formed directly from fructose and the yields of **2** are very small. When the reaction is carried out in the presence of Si-gel, conversions of fructose are 50% and **2**

Table 1  
Yields of 5-hydroxymethyl-2-furfural (**2**) and of 2,5-furandicarboxylic acid (**3**)

Catalyst	Reactant	Yield of <b>2</b> (%) <sup>a</sup>	Yield of <b>3</b> (%) <sup>b</sup>
Blank	<b>1</b>	4	–
SiO <sub>2</sub> -gel	<b>1</b>	47	–
Co(acac) <sub>3</sub>	<b>1</b>	12	–
Co-gel	<b>1</b>	46	–
Blank	<b>2</b>	–	14
SiO <sub>2</sub> -gel	<b>2</b>	–	0
Co(acac) <sub>3</sub>	<b>2</b>	–	19
Co-gel	<b>2</b>	–	16

<sup>a</sup> 50 ml of MIBK, 7 g of fructose dissolved in 6 ml deionized water with, 0.1 g of catalyst, 88 °C, 8 h.

<sup>b</sup> 9.4 ml of MIBK, 0.6 ml deionized water, 0.1 g of catalyst, 40 µl of **2**, 80 °C, 4 h.

Table 2

Conversions and selectivities in the one-pot synthesis of 2,5-furandicarboxylic acid (**3**)<sup>a</sup>

Catalyst	Conversion (%)		
	<b>1</b>	<b>2</b>	<b>3</b>
Blank	6	100	0
SiO <sub>2</sub> -gel (0.0500 g)	50	100	0
SiO <sub>2</sub> -gel (0.5000 g)	52	100	0
Co(acac) <sub>3</sub> (0.0025 g)	46	17	83
Co-gel (0.0100 g)	10	19	81
Co-gel (0.0500 g)	72	<1	99

<sup>a</sup> 6 ml deionized water, 0.1 g of fructose, autoclave, 20 bar of synthetic air, 160 °C, 65 min.

is formed with very high selectivity. In the presence of Co(acac)<sub>3</sub>, **3** can be obtained with 46% conversion of **1** and 83% selectivity. However, we observed a surprisingly strong cooperative effect in the conversion of **1–3** when 0.05 g Co-gel is used as catalyst, allowing a yield of **3** of more than 70% in a one-pot reaction. The low conversion observed with 0.01 g of Co-gel indicates that there were not enough acid sites available to accomplish the conversion of **1–2**.

The first step of the reaction probably occurs at the surface of the silica matrix, where fructose is dehydrated at the acid sites. Once formed, **2** enters the matrix pore channels to be oxidized by the metal occluded therein. Higher temperatures and pressure are required for the proper diffusion of **2**. The high selectivity of the catalytic system is confirmed by the absence of any by-products, suggesting that the conversion of the intermediate **2–3** occurs rapidly, thus preventing its degradation to levulinic and formic acids.

### 4. Conclusion

The evaluation of the two reaction steps in the synthesis of **3** in separate, i.e. the dehydration of fructose and the oxidation of **2**, allows the understanding of the catalyst action in both systems. The SiO<sub>2</sub>-gel is suitable for the dehydration of fructose, avoiding the formation of by-products, while the activity of free Co(acac)<sub>3</sub> depends on the reaction conditions, as it is strongly increased by higher temperatures and pressures. The easily prepared Co(acac)<sub>3</sub>-gel catalyst shows to be very

suitable for the one-pot conversion of fructose to **3**. The cooperative effect of the acidic matrix and the metal complex occluded therein works properly under the more drastic reaction conditions used and **3** is obtained with high selectivity, without the formation of any by-products.

### Acknowledgements

Fellowships from CNPq and FAPESP are gratefully acknowledged.

### References

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Rijswijk, July 14, 2015

Your ref. :  
Our ref. : P30061EP00/RLA/JRO  
Contact : Tel. 31-30-2737510/ email: Pasteur@epc.nl

Application no. : 10768600.8~  
Patent no. :  
Country : Europe  
In the name of : Furanix Technologies B.V.  
Title : Method for the preparation of 2,5-furandicarboxylic acid from 5-hydroxymethylfurfural and/or derivatives thereof, and th

Dear Madam or Sir,

Following our letter dated May 18, 2015, by which we filed a notice of appeal concerning the decision by the Examining Division of March 18, 2015, to refuse the above –mentioned application, we herewith submit the statement of the grounds of the appeal.

In the Decision the Examining Division refused the Main Request because the Main Request allegedly did not involve an inventive step. The Auxiliary Request was refused in view of alleged breach of Rule 43(4) EPC and Article 56 EPC. The Examining Division's objections will be discussed hereinafter.

### Main Request

1. In its decision the Examining Division has concluded that the Main Request fulfils the requirements of Article 123 EPC, Article 83 EPC and Article 54 EPC. The only outstanding item is the question whether the method according to the claims involves an inventive step.
2. The present invention concerns a method for the production of 2,5-furandicarboxylic acid ("FDCA") from a feed comprising at least one certain specific furfural compound by oxidizing the feed with an oxygen-containing gas in the presence of a catalyst that comprises at least one of cobalt and manganese, and in the presence of a solvent comprising acetic acid or acetic acid/water mixtures. The reaction conditions include a

temperature of between 140 and 200 °C and an oxygen partial pressure of 1 to 10 bar. In addition, the feed is contained in a reactor, with the oxygen-containing gas being continuously fed to and removed from the reactor. The specific furfural compounds are selected from the group consisting of 5-hydroxymethylfurfural ("HMF"), an ester of HMF, 5-methylfurfural, 5-(chloromethyl)furfural, 5-methylfuroic acid, 2,5-dimethylfuran and a mixture of two or more of these compounds.

3. The application indicates that the objective of the inventors was the provision of FDCA in high yields and originally it was found that this objective could be achieved by applying a reaction temperature of at least 140 °C.
4. In the search report and written opinion prior art was discussed which prior art was considered prejudicial as to the novelty of the claims as originally filed. The prior art and objections required a reformulation of the technical problem and the solution thereto. This will be elaborated below.
5. When assessing the involvement of an inventive step it is recommended to follow the problem-solution approach. It is submitted that the Examining Division did not follow this approach correctly. A correct conduct of the problem-solution approach comprises:
  - (i) determining the "closest prior art",
  - (ii) establishing the "objective technical problem" to be solved, and
  - (iii) considering whether or not the claimed invention, starting from the closest prior art and the objective technical problem, would have been obvious to the skilled person.
6. The closest prior art is constituted by WO 01/72732 (D8). As already indicated in our letter of November 27, 2014, D8 is directed to five different processes.
7. The first process concerns the preparation of a dialdehyde from a compound with an alcohol and aldehyde function ("alcohol/aldehyde compound") by oxidation thereof with an oxidant in the presence of a metal bromide catalyst and optionally isolating the dialdehyde. In particular this relates to the preparation of diformylfuran ("DFF") from HMF.
8. The second process relates to the production of a diacid from a compound with an alcohol/aldehyde compound in a number of steps wherein the alcohol/aldehyde compound is first oxidized to an alcohol/carboxylic acid compound; wherein subsequently the alcohol/carboxylic acid compound is oxidized to an acid/aldehyde compound; and wherein the acid/aldehyde compound is oxidized to a diacid compound. After each step the respective product is optionally isolated.  
In translation to the reaction presently considered, the second process in D8 describes the consecutive conversions of HMF to 5-hydroxymethylfuroic acid, of 5-hydroxymethylfuroic acid to 5-formyl furoic acid and of 5-formyl furoic acid to FDCA, wherein after each conversion the product is optionally isolated.
9. The third process in D8 claims the preparation of a diacid from an alcohol/aldehyde compound in a number of process steps, wherein the alcohol/aldehyde compound is oxidized to a dialdehyde compound; wherein the dialdehyde is oxidized to form an acid/aldehyde compound; and wherein the acid/aldehyde compound is oxidized to a diacid compound. After each step

the respective product is optionally isolated.

In relation to the present application this means that HMF is first oxidized to DFF, the DFF is then oxidized to 5-formyl furoic acid, and 5-formyl furoic acid is oxidized to FDCA, wherein after each conversion the product is optionally isolated.

10. D8 further describes a fourth process, wherein a hydroxymethylarene is oxidized to an aldehyde product, and a fifth process wherein a polyester polymer is formed. These processes are of no relevance vis-à-vis the present invention.
11. In the first three processes of D8 the oxidation steps may all be conducted with an oxygen-containing gas, in the presence of a Co and/or Mn-containing catalyst and in the presence of a solvent comprising acetic acid. In all three processes the starting material is the same. Also the reactants, viz. oxidant and the catalyst, are the same. In one occasion a dialdehyde is formed; in another occasion a diacid is formed via the formation of an alcohol/carboxylic acid compound; and in a third occasion a diacid is formed via a dialdehyde compound. When considering D8, the skilled person will wonder what conditions would lead to which of the processes. D8 provides confusing teachings in response to this question.
12. D8 teaches: *“For the preparation of the dialdehyde, the preferred temperatures are about 20 to 200 °C, most preferably about 40 to 130 °C. The corresponding pressure is such to keep the solvent mostly in the liquid phase. The preferred time of the reaction is determined by the temperature, pressure, and catalyst concentration such that maximum yield of dialdehyde is obtained. For preparation of diacid, the preferred temperatures are about 50 to 250 °C, most preferentially about 50 to 160 °C. The corresponding pressure is such to keep the solvent mostly in the liquid phase. The preferred time of the reaction is determined by the temperature, pressure and catalyst concentration such that a maximum yield of diacid is obtained.”*(cf. D8, page 6, line 36 – page 7, line 7.)
13. It is evident that the skilled person is taught a series of overlapping temperature ranges and is given the same teaching as to the pressure to be applied. In order to arrive at the maximum yield of the desired product the advice provided boils down to a recommendation to vary temperature, pressure, catalyst concentration and reaction duration. As to the distinction between the second process and the third process no teaching is provided whatsoever. Prima facie it would seem an undue burden for the skilled person to come up with the correct reaction conditions. He may operate the conversion process within the ranges that are disclosed in order to arrive at the production of the dialdehyde, but produce diacid and vice versa.
14. The only guidance that is given to the skilled person is provided in relation to a batch process for the preparation of FDCA, wherein the skilled person is advised to increase the temperature and pressure at specific times, to vary the catalyst concentration at the beginning of the reaction and to vary the catalyst composition during the reaction (cf. D8, page 8, line 27-30). Nowhere in D8 has the skilled person been given a clear teaching on how to conduct the oxidation to arrive at the desired product.
15. For any further teaching the skilled person will look at the examples in D8. In a first series of examples DFF is the desired product. The temperature was 75 °C or was increased in stages from 50 to 75 or 95 °C, the pressure was ambient (1 bar), the catalyst

concentration was varied, the catalyst composition was varied, and the reaction duration was varied. In all experiments the maximum selectivity to DFF was in the range of 41 – 57%. The specification is silent about by-products, but a loss of HMF is acknowledged through oxidation to carbon oxides. It is also disclosed that 3-5% acetoxyethyl furfural is formed. It is observed that the lowest yield was obtained in an experiment wherein a staged temperature of 50 and 95 °C was applied, wherein the higher temperature was applied for the longer period (cf. Example 2). If any teaching can be derived from this series of experiments, it would seem the only feature taught is that at higher catalyst concentrations, the reaction proceeds faster.

16. In a second series of examples the air pressure applied was 7MPa. The desired product was again DFF. The reaction time was 2 hours. Dependent on the catalyst composition and amount, the yield of DFF varied significantly, viz. from 11.0 to 63.0%. The temperature was either 50 or 75 °C, wherein the higher conversion of HMF and the higher yield of DFF were obtained at higher temperatures. The examples did not indicate what the by-products were.
17. Comparison between various pairs of examples does not provide an unambiguous teaching; when the amount of catalyst is increased, the selectivity of HMF to the desired DFF product sometimes increases (cf. Ex. Nos. 9 + 10, 14 + 15), and sometimes decreases (cf. Ex. Nos. 7 + 8, 12 + 13). Although the conversion consistently increases at the higher temperature, the HMF selectivity to DFF decreases on at least one occasion (cf. Ex. Nos. 8 + 13). The only consistent feature appears to be that at higher catalyst concentrations the conversion of HMF is increased in the same reaction time.
18. Although there is no direct comparison possible between the first series of experiments and the second series of examples, the skilled person can see that at higher pressures the reaction seems to proceed faster. However, there is no indication whether and, if so, how the pressure affects the yield or selectivity.
19. The elaborate discussion of these two series of examples has been included since the Examining Division in its decision points to the passages in the description that refer to the “first process” as described in paragraph 6 hereof. It would seem that the Examining Division would agree with the applicant that at least for the first process D8 fails to provide a clear teaching on the effect of the pressure on yield or selectivity.
20. At the risk of laboring the obvious, it is submitted that the first and second series of examples in D8 do not provide any teaching on the influence of the reaction pressure on the conversion, selectivity or yield of FDCA in the second or third process, i.e. the reaction of HMF to FDCA.
21. In a third series of examples D8 shows the results of experiments wherein HMF was converted to FDCA. The experiments have been conducted in air at one pressure, viz. 7 MPa, and mostly at temperatures in the range of 100 – 125 °C. Three experiments have been conducted at staged temperatures, i.e. initially the temperature was held at 75 °C for two hours and then raised to 150 °C for two hours. It appeared that the yields of FDCA in these three experiments belonged to the four highest yields obtained in the third series of experiments. The Examining Division appears to have concluded that these yields have taught the skilled person that the higher yields are obtainable when the reaction is

conducted at higher reaction temperatures.

22. It is submitted that the Examining Division applied hindsight by drawing this conclusion. If the Examining Division would have compared the results of experiments 19 and 24, it would have concluded that at increasing temperatures the yields of FDCA from HMF with the same catalyst concentrations and with virtually the same amount of HMF as starting material for the same reaction duration would have made no difference.
23. In this respect we would submit the following. D8 relates to five different processes. The third process, as described in paragraph 8 hereof, relates to the conversion of HMF to DFF, to the subsequent oxidation of DFF to 5-formyl furoic acid, and the oxidation of the 5-formyl furoic acid to FDCA. From the first two series of examples the skilled person has been taught that the reaction of HMF at 75 °C yields DFF in yields up to values of 60% and more. It is in accordance with the teaching of the third process of D8 that the DFF formed in the first stage is subsequently converted to 5-formyl furoic acid and FDCA. Hence, the second stage at 150 °C does not relate to the conversion of HMF to FDCA, but relates to the conversion of DFF to (5-formyl furoic acid and) FDCA.
24. In summary, D8 may be considered the closest prior art in that it discloses a reaction starting with HMF and resulting in FDCA. The influence of reaction pressure and reaction temperature is unclear. Further, the reaction pathways in D8 are confusing in that allegedly the same reaction conditions may be applied to obtain different results. Moreover, D8 specifies two different pathways to arrive at FDCA without showing that any of these pathways will be followed and without indicating what to do to achieve either of these pathways.
25. The differences between the present invention and D8 include that the oxygen partial pressure is different and that the starting material is different when a reaction temperature in the range of 140 to 200 °C is applied.
26. The second step in the problem-solution approach is to establish the "objective technical problem" to be solved. The objective technical problem is to provide an improved process by applying reaction conditions that result in high yields of FDCA from HMF and certain HMF derivatives.
27. The technical problem is solved by contacting the HMF or the specified HMF derivative with an oxygen-containing gas in the presence of a catalyst which comprises at least one metal selected from Co and Mn in an acetic acid-comprising solvent, wherein the oxygen-containing gas is continuously fed and removed from the reactor in which the reactants are contacted. The reaction temperature is between 140 and 200 °C, and the oxygen partial pressure is from 1 to 10 bar.
28. One difference between D8 and the present invention is constituted by a lower pressure as expressed as oxygen partial pressure. Whereas the present invention applies an oxygen partial pressure of 1 to 10 bar, the process according to D8 applied a total air pressure of 7 MPa, boiling down to an oxygen partial pressure of about 14.5 bar. Another difference resides in that HMF is exposed to a temperature above 140 °C in the presently claimed process, whereas the prior art either exposed HMF to a lower temperature or converted HMF to DFF and exposed the DFF to the higher temperature.

29. The examples in the specification show that the technical problem is solved. The experiments in the examples were conducted at 180 °C and a total air pressure of 20 bar, i.e. an oxygen partial pressure of about 4.3 bar. The yield of FDCA from HMF alone varied from 76.7 to 67.9 % (cf. Experiment Nos. 1a, 1e, 1i and 1m of Table 1).
30. The final step in the problem-solution approach is to consider whether or not the claimed invention, starting from the closest prior art and the objective technical problem, would have been obvious to the skilled person.
31. As indicated above, the skilled person has been given confusing teachings from D8. The skilled person has received confusing information about the reaction temperature. He has been given no teaching on the optimal pressure. Further, he has been taught that the best way to conduct the conversion is to first convert HMF at low temperature, apparently leading to the forming of DFF, and subsequently convert the DFF formed to 5-formyl-furoic acid and FDCA at higher temperature. This would be in conformity with the only explicit teaching in D8 (cf. D8, page 8, line 27). In any case he would not have expected to obtain a yield of in the range of 70% and higher.
32. As to the higher reaction temperature, the Examining Division has decided that the high yield of FDCA could be expected based on the comparison of examples 33 and 39. It is acknowledged by the Examining Division that the examples 33 and 39 do not enable a direct comparison, with temperature as the only different feature. We have already shown (cf. paragraph 22) that the Examining Division used hindsight by picking these examples rather than others that showed more or less the opposite.
33. As to the lower oxygen partial pressure, the Examining Division argued that since the description did not explicitly mention that the oxygen partial pressure is essential and as the application did not contain a comparison with respect to the oxygen partial pressure, it can reasonably be expected that as long as the solvent is in liquid phase the pressure may vary.
34. It is observed that the Examining Division has made a number of assumptions that were not corroborated by prior art documents or evidence. The reaction under consideration involves the oxidation of HMF in the liquid phase. The catalyst is homogeneous, the metal salt(s) being dissolved in the solvent. The oxidant is oxygen. That means that in order to be effective, oxygen must be dissolved in the solvent so that it may react with HMF in solution. The skilled person would expect that it would be advantageous to apply high pressures so that as much oxygen as possible would be dissolved. As to the reaction temperature the skilled person would understand that whereas the reaction rate might be increased at higher temperatures, the solubility of oxygen would decrease at increasing temperatures. Therefore, he would expect that at high pressures such as those taught by D8, and at relatively low temperatures, e.g. such as those taught by examples 16-37, the best results would be obtainable. Examples 38-40 would teach the skilled person that a conversion of HMF to DFF should be carried out first at such high pressure and such low temperature and that the DFF formed can be subjected to somewhat higher temperatures to arrive at FDCA.
35. It is therefore surprising that when HMF is exposed to a high temperature while the



oxygen partial pressure is lowered, the yield of FDCA is higher than was achieved in the examples of D8.

36. In view of the above it is respectfully submitted that the Examining Division erred in considering the presently claimed invention obvious in view of D8.
37. The Examining Division also considered further prior art, viz. D7. D7 describes an overview of developments relating to the conversion of glucose to FDCA and associated products. In paragraph 4.2.2 concerning the oxidation of HMF to FDA (=FDCA) reference is made to an article by Ribeiro and Schuchardt wherein it is stated that cobalt was used as catalyst in the reaction of HMF to FDCA. Referring to this article D7 states that according to Ribeiro and Schuchardt (Catal. Commun., 4 (2003) 83-86) "*[u]sing cobalt acetylacetonate as a bifunctional acidic and redox catalyst encapsulated in silica in an autoclave at 160 °C, they obtained FDA from fructose via HMF formation, with 99% selectivity of HMF to FDCA at 72 % conversion of fructose*" (cf. D7, page 1323, right-hand column, third paragraph). Referring to D7 the Examining Division draws the conclusion that Ribeiro discloses the preparation of FDCA with  $\text{Co}(\text{acac})_3$  as a catalyst, deionized water as solvent, a temperature of 160 °C and a pressure of 20 bar of synthetic air, i.e. 4.2 bar oxygen partial pressure and achieving 99% selectivity of FDCA at 72 % conversion of fructose (cf. Decision dated 18.03.2014, point 2.5.4, page 7, third paragraph).
38. It is submitted that D7 does not provide the information on the solvent or the pressure in the process of the Ribeiro article as mentioned by the Examining Division. It would seem that the Examining Division has used information disclosed in the published article itself. Although a similar statement was made by the Examining Division in an earlier communication (cf. communication dated 16.04.2013, point 3), the Ribeiro article has not been introduced into the examination procedure. The question arises whether a decision that is partly based on a document that does not form part of the proceedings contravenes Article 113(1) EPC and constitutes a substantial procedural violation.
39. If the Board would find that a substantial procedural violation has taken place we request reimbursement of the appeal fee.
40. The Examining Division has referred to Ribeiro inter alia in point 2.4 of the impugned decision discussing the reaction pressure. The Examining Division refers to phrases in the specification wherein pressures of oxygen-containing gas of up to 80 or 100 bar are mentioned. It would seem that the Examining Division automatically converts these values to about 21 and 16.8 bar oxygen pressure, i.e. as if the oxygen-containing gas must be air. In this respect the Examining Division has overlooked the possibility that the oxygen-containing gas can also consist of lean air or any other oxygen-containing gas that contains a lower percentage of oxygen than air. It is deliberate that the present main claim mentions the oxygen partial pressure and not the total pressure as an essential feature.
41. Therefore the argument of the Examining Division on the suggested contradiction in the patent application is to be regarded as without merit.
42. In view of the argument by the Examining Division, we have obtained a copy of the journal article by Ribeiro and Schuchardt. We file this document herewith as D15.

43. D15 discloses that cobalt acetylacetonate encapsulated in sol-gel silica is shown to be a very efficient bifunctional acidic and redox catalyst, giving 2,5-furandicarboxylic acid with 99% selectivity directly from fructose at a conversion of 72%. A co-operative effect of the functions of the catalyst is operative, as the same reaction performed in two consecutive steps gives much lower conversions (cf. D15, abstract).
44. In the body of the article D15 discloses the conversions and selectivities of the one-pot synthesis of 2,5-furandicarboxylic acid (FDCA) from fructose in 6 ml deionized water, in an autoclave at 20 bar of synthetic air, at 160 °C for 65 min, using different catalyst systems (cf. D15, Table 2, page 85). On one occasion, viz. when  $\text{Co}(\text{acac})_3$  encapsulated in sol-gel silica is used as catalyst, the conversion of fructose is stated to be 72% and the selectivity towards FDCA is said to be 99%.
45. It is submitted that these results are obtained in the conversion of fructose. It is assumed that the reaction path proceeds via the formation of HMF, but such has not been shown. Moreover, as mentioned in the abstract, the same reaction in two consecutive steps, gives much lower conversions. It is even observed that none of the catalysts is appropriate for the conversion of HMF to FDCA (cf. D15, page 85, left-hand column, fourth paragraph).
46. From the above it is evident that Ribeiro does not provide any unambiguous teaching on the conversion of HMF to FDCA. Therefore, the presently claimed invention is also inventive over the combination of D8 and D7/D15.
47. When considering the prior art as a whole, it is submitted that D1 (W. Partenheimer, V.V. Grushin, *Adv. Synth. Catal.*, 2001; 1 102-111) would support the finding of an inventive step. The authors of D1 are the same persons as two of the three inventors of D8.
48. D1 discloses the synthesis of DFF and FDCA by oxidation of HMF, using a catalyst system comprising Co, Mn, Br and optionally Zr. A number of experiments are the same as those disclosed in D8. The experiments were run at a pressure of 70 bar of air and at temperatures ranging from 100 to 125 °C. The reaction duration was 2 or 3 hours. Four experiments were run at 50 °C for one hour and subsequently at 125 °C for another two hours. The yield of FDCA in the various experiments varied from 18.7 to 63.1 % (cf. D1, Table 3).
49. From Figure 7, it is apparent that the yield increases with increasing catalyst concentration. The authors conclude that extrapolation from Figure 7 suggests that the maximum obtainable 2,5-furandicarboxylic acid yield is about 70% using the Co/Mn/Zr/Br catalyst at the specified molar ratios of these elements.
50. In view of these teachings, it is surprising that the presently claimed invention has obtained yields above the expected maximum. Experiment Nos. 1a, 1e and 1i have resulted in a 100% conversion of HMF and a selectivity to FDCA in the range of 73.2 to 76.7% (cf. present application, Table 1). It is submitted that these yields were not to be expected by the skilled person based on the knowledge from the prior art documents.
51. In view of the above arguments it is submitted that the presently claimed invention involves an inventive step. That applies to claims 1-8 as well as to claims 9-12.

52. For completeness' sake it is observed that the Examining Division did not take any other HMF derivative as mentioned in the present claims into account in arguing the decision to refuse the application. We trust that the rebuttal of the objections based on the feature of HMF as component of the feed is sufficient to render the claims allowable.
53. If the Board would question the scope of the feed as claimed in the Main Request, it is observed that in the discussion of the Auxiliary Request this issue will be elaborated.

### **Auxiliary Request**

54. In the decision of 18.03.2015, the Examining Division raised an objection pursuant to Rule 43(4) EPC, paraphrasing claim 1 of the Auxiliary Request such that the compound to be oxidized is selected from 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. According to the Examining Division the wording of claim 1 in the Auxiliary request would not cover the oxidation of mixtures of the compounds mentioned herein and 5-hydroxymethylfurfural itself. Claim 2 is therefore considered not to be dependent on claim 1.
55. In this respect it is observed that the wording of claim 1 mentions "*a feed comprising a compound selected from the group consisting of an ester of 5-hydroxymethylfurfural, (...)*". The use of the "open" verb "*comprising*" indicates that other components, not mentioned in the list may be included in the feed. According to language conventional for patent claims in the field of chemistry, the wording "feed comprising a compound selected from a group" defines exclusively the mandatory presence of at least one compound from that group. Accordingly, the claim is completely open to further components; also components not belonging to that group (cf. e.g. T405/00, Reason 2.2). Claim 2 therefore describes an embodiment of the method of claim 1, wherein the feed comprises an ester of HMF or a mixture of an ester of HMF and HMF itself. The subject matter of claim 2 is embraced by the broader scope of claim 1 and claim 2 is thus a proper dependent claim.
56. It is, therefore, submitted that the Auxiliary Request fulfils the requirements of Rule 43(4) EPC.
57. If the Board would decide that the Auxiliary Request does not fulfil Rule 43(4) EPC we herewith submit a Second Auxiliary Request, wherein the subject matter of claim 2 has been made subject of the new claim 1, i.e. the method of the Second Auxiliary Request has been limited to the reaction of a feed that comprises esters of HMF and a mixture of esters of HMF and HMF. It is submitted that the subject matter of the Second Auxiliary request has been examined by the Examining Division. It is respectfully requested that the Board admits this Second Auxiliary Request using its discretion under Article 12(4) RPBA.
58. The Auxiliary Request has been found to fulfil the requirements as to Article 123 EPC. When discussing the objection under Rule 43(4) EPC we have shown that that Auxiliary request also complies with Article 84 EPC. From the Examining Division's decision it is concluded that the Auxiliary Request also fulfils the requirements as to sufficiency of disclosure and novelty.
59. The Examining Division based its decision to refuse the Auxiliary Request on two prior art

documents, viz. D8 and D2.

60. D8 has been extensively discussed in the above paragraphs. With relation to the third process D8 additionally discloses that after the oxidation of an alcohol/aldehyde compound to a dialdehyde compound and the subsequent oxidation of the dialdehyde to an acid/aldehyde compound, the acid/aldehyde compound is converted to an acetate ester before the acid/aldehyde compound is further oxidized to form the diacid. This reaction is not further elaborated. The only further reference to an acetate ester of HMF is in the product list of Table 2 in D8, which shows that when DFF is formed in acetic acid, between 0.4 and 8.4 % of acetoxymethyl furfural is formed as by-product.
61. D8 does not mention whether during the reaction of HMF to DFF at 7 MPa also acetoxymethyl furfural is formed. It is further silent about acetoxymethyl furfural in the reaction(s) of HMF to FDCA as shown in Table 4 of D8. It fails to provide any information about a deliberate conversion of an acid/aldehyde compound to the acetoxy ester thereof, let alone about the conversion of such an acetoxy ester to a diacid. The skilled person is left in the dark about what conditions should apply to prepare the acetoxy ester and to convert the acetoxy ester to a diacid.
62. The Examining Division erred in assuming that claims 20 and 21 of D8 disclose that HMF is completely converted to 5-acetoxymethyl furfural. The only teaching to acetoxymethyl furfural was as by-product in the preparation of DFF from HMF. There is no disclosure, teaching, or suggestion on the method to convert the acid/aldehyde, such as 5-formyl furoic acid, to acetoxymethyl furfural. Since the disclosure in claims 20 and 21 and the disclosure on page 4, lines 8-10 fail to provide an enabling teaching to the skilled person, such disclosures can be ignored (cf. e.g. T 755/91).
63. Therefore, the Auxiliary Request is inventive in view of the disclosures of D8.
64. As to D2 it would appear that the Examining Division considers the present Auxiliary Request obvious in view of Example 7 in D2 using the argumentation with relation to the Main Request.
65. D2 relates to a number of reactions. A first reaction is the conversion of a carbohydrate source to HMF, HMF ethers and HMF esters. HMF esters can be produced by heating a carbohydrate source with a solvent in a column and by making it continuously flow through a solid phase catalyst in the presence of an organic solvent (cf. D2, paragraph [0016]). Alternatively, HMF esters are formed by heating the carbohydrate source with an organic acid and a solid catalyst in a solvent (cf. D2, paragraph [0017]). A second reaction concerns the oxidation of an HMF ester or a mixture of HMF ester and HMF to FDCA over a catalyst that comprises Co, Mn and Br (cf. D2, paragraphs [0018] and [0019]). A third reaction is the reduction of an HMF ester by the addition of an alcohol, and a reducing agent under pressure (cf. D2, paragraph [0020]).
66. The specification of D2 further discloses other 'embodiments' relating to the production of citrate esters, HMF preparation via deacylation, and the synthesis of levulinic acid or levulinate esters. These embodiments have no relation to the presently claimed invention.
67. D2 discloses reaction conditions for a few of these reactions. In particular, it discloses that

the oxidation of HMF esters to FDCA can be conducted at a temperature of 85 to 110 °C and an oxygen pressure of 400 to 1000 psi (25.6 to 68.9 bar) for 100 to 150 minutes. The pressure is suitably 1000 psi and the temperature is suitably 100 °C (cf. D2, paragraph [0060]). Alternatively, an HMF ester or a mixture of an HMF ester and (residual) HMF can be oxidized to FDCA in an organic acid along with cobalt acetate, manganese acetate and sodium bromide. The mixture is pressurized with oxygen or air and heated to at least 100 °C for over an hour (cf. D2, paragraph [0062]). In an example 7, acetoxymethyl furfural (AcMF) in acetic acid with a Co, Mn and Br catalyst is subjected to 500-800 psi oxygen at 100 °C for 2 hours. The overall yield of FDCA is 54%.

68. In Example 9 a mixture of AcMF and HMF is subjected to oxidation with the addition of cobalt acetate, manganese acetate and sodium bromide. This mixture is pressurized with oxygen and heated to over 100 °C for over an hour. Upon filtration and evaporation, a product of FDCA is isolated. No exact reaction conditions nor product yield are given.
69. The use of the present tense in the description of, in particular, Example 9 of D2 gives the impression that Example 9 is a hypothetical example. The value of this example as practical evidence is therefore questionable.
70. For completeness' sake it is observed that the presently claimed method is to be conducted at a temperature in the range of 140 to 200 °C and an oxygen partial pressure of 1 to 10 bar. For these differences alone, it is evident that the presently claimed method is novel over D2. This is in addition to the feature that the oxygen-containing gas is continuously fed and removed from the reactor in which the reaction is conducted.
71. The presently claimed invention is also inventive over D2. Example 7 of D2 shows that when the oxidation reaction of AcMF is conducted at a temperature of 100 °C and an oxygen pressure of 500 – 800 psi (about 34 – 55 bar) for two hours, FDCA is obtained in a yield of 54 %.  
Assuming that Example 9 can be reproduced, Example 9 shows that, when a mixture of AcMF and HMF is pressurized with oxygen and heated for over an hour at a temperature of at least 100 °C, FDCA can be recovered in unknown yields.
72. In contradistinction therewith Table 1 of the present specification shows the results of experiments wherein at an air pressure of 20 bar, i.e. an oxygen partial pressure of about 4.3 bar, and at a temperature of 180 °C, higher selectivities for the oxidation of AcMF can be obtained, viz. in the range of 57 to 65 % (cf. Table 1, Experiment Nos. 1d, 1h and 1i). These higher selectivities were obtained in a reaction period of 1 hour which is considerably shorter than the reaction time of Example 7 of D2.  
For completeness' sake it is observed when the level of bromide in the catalyst system is reduced, the yield may be lower than 54% and thus be sub-optimal, but it is still at a level that might be found satisfactory.
73. When a mixture of AcMF and HMF is used at the reaction conditions of the experiments of Table 1, the yield of FDCA is even higher (cf. Table 1, Experiment Nos. 1b, 1c, 1f, 1g, 1j, 1k, 1n and 1o).
74. In addition, comparative experiments have been conducted wherein a lower temperature, viz. 100 °C, and a higher pressure, viz. 30 bar air, corresponding to about 6.5 bar oxygen,

were applied in the oxidation of AcMF. These conditions are similar to those in D2 (wherein for Example 9 the pressure is not specifically mentioned). Even when these conditions were maintained for two hours the yield of FDCA was found to be about 23 and 29%. Hence, the yield and selectivity of FDCA was found to be lower than those found in Example 7 of D2, when only the oxygen pressure was reduced from about 34 bar to about 6.5 bar.

75. Based on the prior art it could not be expected that the selectivity obtained at these low oxygen pressures would be increased to levels above the level in D2 when the temperature would be elevated to a value in the range of 140 to 200 °C. This is precisely what is shown by the results of the experiments of Example 1 of the present application. Since this advantage could not be expected it is respectfully submitted that the claimed method according to the Auxiliary Request involves an inventive step in view of D2 and D8, and hence is patentable.
76. Almost in passing the Examining Division also observes that the conversions of 5-methylfurfural and 2,5-dimethylfuran is considered so low that the objective technical problem cannot be regarded as solved over the entire breadth claimed.
77. We would submit that the prior art has not mentioned any oxidation process of 5-methylfurfural or 2,5-dimethylfuran. The claimed reaction for these compounds is therefore novel. Since nothing in the prior art teaches or suggests these reactions these reactions are to be considered inventive. The reaction conditions that feature in the claims are novel and inventive vis-à-vis feeds that contain HMF and AcMF. It is surprising that these conditions are also applicable to feeds that comprise other furan derivatives such as 5-methylfurfural or 2,5-dimethylfuran and that the oxidation of these furan derivatives results in interesting yields of FDCA. There is nothing in the prior art that teaches or suggests the use of these conditions for the oxidation of such furan derivatives. Therefore, it is submitted that the claims correctly cover these furan derivatives as potential feed components.
78. The Examining Division erred when it compared the yields of the oxidation of HMF or AcMF according to the prior art with the yields obtained in the oxidation of 5-methylfurfural and 2,5-dimethylfuran. The latter yields have no comparison in the prior art. Any yield therefore already represents an improvement over the prior art. Therefore, the main claim is considered to solve the technical problem over its entire breadth.
79. In view of the above arguments, the Auxiliary Request is novel and involves an inventive step.

### **Second Auxiliary Request**

80. The Second Auxiliary Request differs from the Auxiliary Request on file in that the subject matter of claim 2 of the Auxiliary Request has been incorporated into the main claim, and that the remaining claims have been renumbered. In renumbered claim 8 the scope of the feed has been brought into conformity with the new scope of claim 1. This Second Auxiliary Request is filed to overcome the Rule 43(4) EPC objection that was mentioned in the Examining Division's decision.
81. As the Auxiliary Request has been found to fulfil the requirements of Article 123 EPC,

Article 84 EPC, Article 83 EPC and Article 54 EPC, and as the sole substantive amendment of the Second Auxiliary Request is the incorporation of the subject matter of claim 2 of the Auxiliary Request into the main claim of the Second Auxiliary Request, it is submitted that also the Second Auxiliary Request complies with the requirements of Articles 123, 84, 83 and 54 EPC.

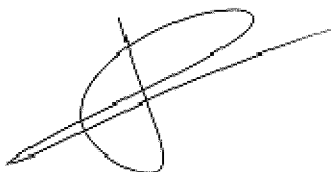
82. The Second Auxiliary Request is also related to the oxidation of AcMF and mixtures of AcMF and HMF. In the rebuttal of the refusal of the Auxiliary Request arguments have already been submitted to show the inventiveness of the claimed oxidation of AcMF and mixtures of AcMF and HMF. Therefore, it is submitted that the arguments that were presented in favour of the Auxiliary Request, also apply to the Second Auxiliary Request.
83. In addition, it is submitted that the scope of the Second Auxiliary Request no longer covers 5-methylfurfural, 5-(chloromethyl)furfural, 5-methylfuroic acid, 5-(chloromethyl)furoic acid or 2,5-dimethylfuran. Therefore, the Examining Division's observation regarding the alleged lack of solving the technical problem over the entire scope has become moot.
84. In view of the above arguments, it is submitted that the Second Auxiliary Request is novel and involves an inventive step. Therefore the Second Auxiliary Request is patentable.

#### **Requests**

85. Accordingly, the following requests are made:
- that the Examining Division's decision be set aside and a patent be granted on the basis of the Main Request;
  - if the Main request is found not to be patentable, that a patent be granted on the basis of the Auxiliary Request;
  - if the Auxiliary Request is found not to be patentable, that a patent be granted on the basis of the Second Auxiliary Request;
  - if the Board would contemplate to take any decision other than to allow the Main Request, that oral proceedings be arranged.

We look forward to receiving your further report on this case in due course.

Yours faithfully,  
EP&C



Robbert-Jan de Lang  
Association no. 497

Enclosures: Ribeiro and Schuchardt, Catal. Commun., 4 (2003) 83-86 (D15)  
Second Auxiliary Request

## Acknowledgement of receipt

We hereby acknowledge receipt of the following subsequently filed document(s):

Submission number	3503768	
Application number	EP10768600.8	
Date of receipt	18 May 2015	
Receiving Office	European Patent Office, The Hague	
Your reference	P30061EP00/RLA	
Applicant	All applicants as on file	
Documents submitted	package-data.xml  epf1038.pdf (2 p.)	ep-sfd-request.xml  APPEAL.pdf/Notice of Appeal.pdf (1 p.)
Submitted by	CN=Rene Raggars 13051	
Method of submission	Online	
Date and time receipt generated	18 May 2015, 14:44 (CEST)	
Message Digest	AB:CD:CF:BB:C5:44:2D:2F:C4:D5:02:8A:90:59:AA:6E:AF:6F:87:AC	

### Correction by the EPO of errors in debit instructions filed by eOLF

Errors in debit instructions filed by eOLF that are caused by the editing of Form 1038E entries or the continued use of outdated software (all forms) may be corrected automatically by the EPO, leaving the payment date unchanged (see decision T 152/82, OJ EPO 1984, 301 and point 6.3 ff ADA, Supplement to OJ EPO 10/2007).

/European Patent Office/





## Letter accompanying subsequently filed items

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The document(s) listed below is (are) subsequently filed documents pertaining to the following application:

Application number 10768600.8

Applicant's or representative's reference P30061EP00/RLA

	Description of document	Original file name	Assigned file name
1	Notice of appeal	Notice of Appeal.pdf	APPEAL.pdf

	Fees	Factor applied	Fee schedule	Amount to be paid
15-1	011 Fee for appeal	1	1 860.00	1 860.00
	<b>Total:</b>		<b>EUR</b>	<b>1 860.00</b>

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	Currency:	EUR
	The European Patent Office is hereby authorised, to debit from the deposit account with the EPO any fees and costs indicated on the fees page.	
	Deposit account number:	28090031
	Account holder:	Exter Polak & Charlouis B.V.
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	Reimbursement (if any) to be made to EPO deposit account:	28090031
	Account holder:	Exter Polak & Charlouis B.V.

### Signatures

Place: **Rijswijk**  
 Date: **18 May 2015**  
 Signed by: **Rene Raggars 13051**  
 Association: **EP&C**  
 Representative name: **Raggars**

Capacity:

(Representative)

EUROPEAN PATENT OFFICE  
P.O. Box 5818  
2280 HV RIJSWIJK (ZH)

Rijswijk, May 18, 2015

Your ref. : --  
Our ref. : P30061EP00/RLA/SDH  
Contact : Tel. 31-30-2737510/ email: Pasteur@epc.nl

Application no. : 10768600.8-1462  
Country : Europe  
In the name of : Furanix Technologies B.V.

Dear Madam, Sir,

The Proprietor, Furanix Technologies B.V. of Zekeringstraat 29, 1014 BV, Amsterdam, the Netherlands hereby appeals under Art 108 EPC from the decision of the Examining Division dated March 18, 2015 to the effect that the patent was refused.

It is requested that the Technical Board of Appeal will set aside the decision of the Examining division and decides that the subject matter of the claims of the patent meet the requirements of the EPC. Oral proceedings under Art 116 are requested in case the Technical Board of Appeal would be of the opinion that the request made herein cannot be met.

The Statement of Grounds will be filed in due course.

The Appeal fee can be debited from our deposit account nr. 28090031.

The professional representative,  
Association no. 497

  
Robbert-Jan de Lang Ph. D

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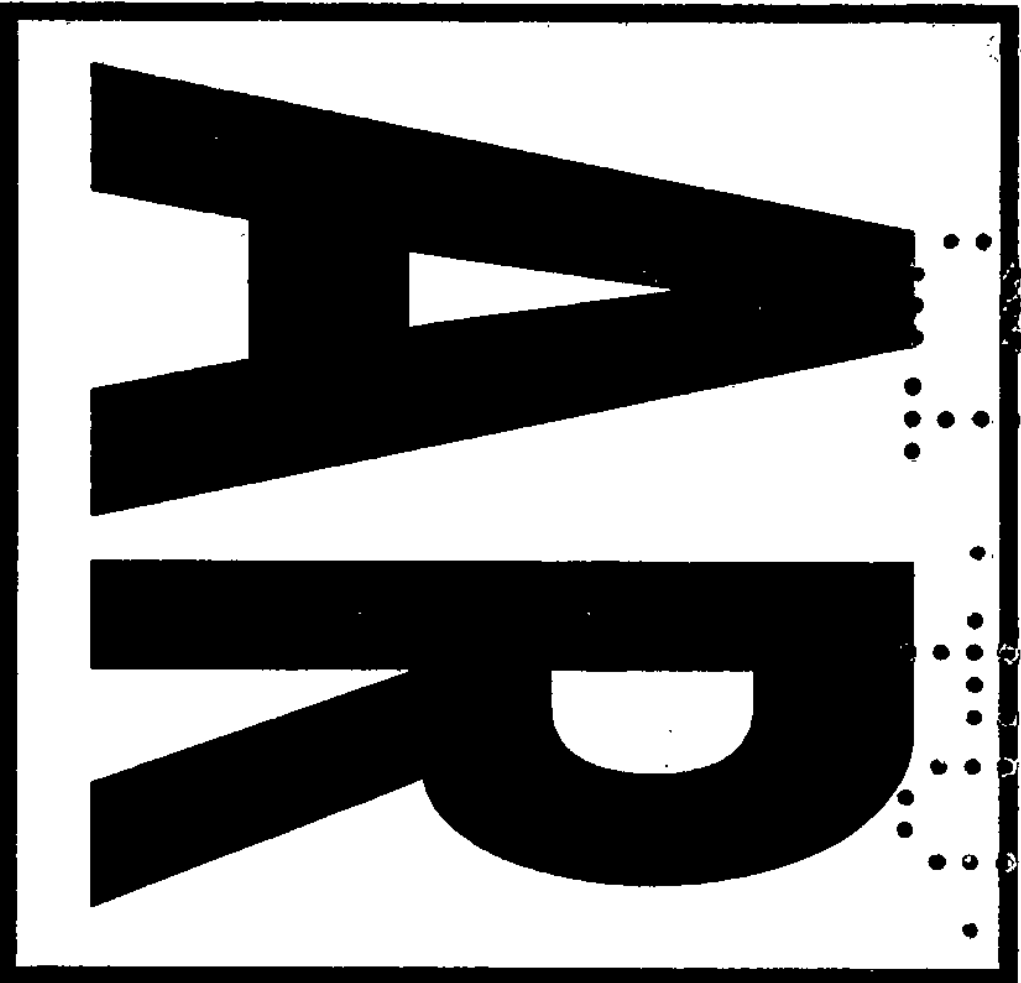
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28. März 2015

Date  
18-03-2015

Reference P30061EP00/AZE	Application No./Patent No. 10768600.8 - 1462 / 2486028
Applicant/Proprietor Furanix Technologies B.V	

EPA/EPO/OEB Formblatt/Form/Formulaire : F2007

**Empfangsbescheinigung über den Zugang des vorstehend bezeichneten Schriftstücks**  
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Date

18-03-2015

Reference P30061EP00/AZE	Application No./Patent No. 10768600.8 - 1462 / 2486028
Applicant/Proprietor Furanix Technologies B.V	

EPA/EPO/OEB Formblatt/Form/Formulaire : F2007

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**Acknowledgement of receipt of the document specified above**  
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Application No.:

10 768 600.8

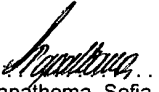
### Decision of the Examining Division


In the oral proceedings held on 24.02.2015, the examining division has decided:

**The European patent application is refused on the basis of Article 97(2) EPC. The reasons for the decision are attached (Form(s) 2916).**

*24.02.2015*  
Date

  
Fazzi, Raffaella  
Chairman

  
Papathoma, Sofia  
1st examiner

  
Wolf, Claudia  
2nd examiner

Enclosure(s): Form 2916





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Tel: +49 89 2399 - 7536

Application No. 10 768 600.8 - 1462	Ref. P30061EP00/AZE	Date 18.03.2015
Applicant Furanix Technologies B.V		

### Decision to refuse a European Patent application

The Examining Division - at the oral proceedings dated 24.02.2015 - has decided:

**European Patent application No. 10 768 600.8 is refused.**

#### Applicant/s:

Furanix Technologies B.V  
Zekeringstraat 29  
1014 BV Amsterdam  
NL

#### Title

METHOD FOR THE PREPARATION OF  
2,5-FURANDICARBOXYLIC ACID AND FOR THE PREPARATION  
OF THE DIALKYL ESTER OF 2,5-FURANDICARBOXYLIC ACID

The grounds for the decision are set out on the supplemental sheets annexed hereto.

#### Means of redress

This decision is open to appeal.  
Attention is drawn to the attached text of Articles 106 to 108 EPC and Rules 97 and 98 EPC.

**Examining Division:**

**Chairman:** Fazzi, Raffaella  
**2nd Examiner:** Wolf, Claudia  
**1st Examiner:** Papathoma, Sofia



Pfau, Andrea  
**Formalities Officer**  
Tel. No.: +49 89 2399-6731

Enclosure(s): 10 page/s reasons (Form 2916)  
Form 2019

to EPO postal service: 13.03.15

## **I. FACTS AND SUBMISSIONS**

- 1 The European Patent application No. 10768600.8 was filed on the 06.10.2010 claiming priority of the USP249395 filed on the 07.10.2009.  
  
The title of the application is "Method for the preparation of 2,5-furandicarboxylic acid and for the preparation of the dialkylester of 2,5-furadicarboxylic acid".  
  
The applicant is Furanix Technologies B.V..
- 2 With entry into the European Phase the applicant filed an amended set of 12 claims in reply to the novelty objections raised during the International Phase.  
  
With the Office Communication dated the 16.04.2013 the applicant was informed that the amendments carried out contravened Article 123(2) EPC. Further, it was stated that although the introduction of further technical features in the wording of claim 1 - i.e. of the oxidant, solvent, catalyst and pressure- could in principle differentiate the claimed scope from the disclosures of the cited prior art, the reader was left into doubt as to which is the special technical feature that defines the contribution of the claimed process over the prior art and leads to the claimed effect i.e. improved yield of FDCA. It was also considered that the claimed process was an obvious alternative to the process disclosed in the closest prior art D8.
- 3 With his letter of 01.08.2013 the applicant filed an amended set of 12 claims overcoming the objections under Article 123(2) EPC and argued in favor of inventive step.
- 4 With the Office Communication dated the 19.09.2014 the applicant was summoned to oral proceedings as the applicant's arguments as to inventive step were not deemed persuasive.
- 5 With his letter of 27.11.2014 the applicant provided further arguments in favor of inventive step and re-filed the same claim-set as on the 01.08.2013 being his Main Request as well as an Auxiliary Request. In the Main Request a typographical error was corrected in claim 7. Furthermore, he filed a description adapted to each one of the requests, respectively.
- 6 The applicant was informed with a telefax on the 11.02.2015 that the oral proceedings were maintained. With his letter of reply dated the 11.02.2015 the applicant informed the Examining Division that he would not be attending the oral proceedings.
- 7 The oral proceedings took place in the absence of the Applicant. The Examining Division decided to refuse the application.

## **II. REASONS FOR THE DECISION**

- 1 The applicant stated in his letter of 11.02.2015 that he would not be attending the oral proceedings.

According to the Notice from the European Patent Office concerning non-attendance at oral proceedings before the examining division (OJ 10/2008, p471) if an applicant who has been duly summoned to oral proceedings does not appear as summoned, oral proceedings may be conducted without him (Rule 115(2) EPC, Guidelines for Examination in the European Patent Office E-III, 8.3). The decision may be given orally in the absence of the applicant (Rule 111(1) EPC).

An applicant who files amended claims or other submissions in reply to the summons to oral proceedings has to expect that any objection relating to the amended claims and submissions will be dealt with at the oral proceedings. The fact that oral proceedings are maintained indicates that objections are still outstanding and they will be discussed at the oral proceedings.

The oral proceedings give the applicant the opportunity to present its comments, in accordance with Article 113(1) EPC. If the applicant decides not to attend the oral proceedings he chooses not to make use of the opportunity to comment at the oral proceedings on any of the objections, but relies on the arguments as set out in the written submissions. The applicant has thus to expect that a decision based on objections which arise against the amended claims during oral proceedings will be taken in his absence.

In decision G4/92 (OJ EPO 1994, 149) the Enlarged Board of Appeal interpreted the provisions of Article 113(1) EPC concerning the right to be heard and to present comments as meaning that a decision against a party which has been duly summoned but which fails to appear at oral proceedings may not be based on facts put forward for the first time during those oral proceedings. However, new arguments may - in principle - be used in the reasons based on the facts and evidence already put forward (see G4/92, especially conclusion 1).

Since the applicant filed in reply to the Summons to attend Oral Proceedings a Main Request, being identical to the claims-set filed the 01.08.2014, and an amended Auxiliary request, it should have been normally expected that the arguments presented by the Applicant in his last submissions would be discussed as well as the formal requirements such as of Article 123(2) EPC, Article 84 EPC and Rule 43 EPC for the amended Auxiliary Request.

The applicant informed with his letter of 11.02.2015 that he will not be attending the oral proceedings.

The oral proceedings were scheduled on 24.02.2015. Since the applicant was not represented, the proceedings were took place without them, as provided for in Rule 115(2) EPC.

The Examining Division's decision is based on:

- grounds, facts and evidence which were already known to the applicant from the proceedings before the Examining Division as well as on
- Articles 123(2) EPC and Article 84 EPC and Rule 43 EPC, grounds which would normally be expected to be discussed during the oral proceedings, when amended claims are filed.

Therefore, present decision does not conflict with the conclusions of the Enlarged Board of Appeal in decision G4/92 and does not contravene the applicant's procedural rights as laid down in Article 113(1) EPC, in spite of his absence during oral proceedings.

## 2 Main Request

- 2.1 The Main Request presently on file is identical to the claim-set filed the 01.08.2013. Said claim-set was acknowledged to fulfil the requirements of Article 123(2) EPC and Article 54 EPC (see Summons to oral proceedings dated the 19.09.2014).
- 2.2 With respect to inventive step, it was already pointed out in the Office Communication dated the 16.04.2013 that the introduction of various features (such as the oxidant, solvent, catalyst and pressure) in present claim 1 may render the claimed subject-matter novel over the disclosures of the cited prior art documents, but leaves the reader into doubt as to which is the special technical feature that defines the contribution of the claimed process over the prior art and leads to the claimed effect i.e. improved yield of FDCA.
- 2.3 The Examining Division observed- as stated in the Office Communications dated the 16.04.2013 and the 19.09.2014- that in the originally filed claim 1 only the temperature was identified as the special technical feature of the claimed process and not the pressure / oxygen partial pressure as said in the letters of the applicant for the later filed claim-sets.

This observation is also confirmed by the passage on page 2, lines 24-28 of the present application elucidating the solution to the technical problem underlying the present application: "*The present inventors have now surprisingly found that when using an oxidation catalyst, e.g., based on both cobalt and manganese and containing a bromide, at temperatures higher than 140 °C, derivatives of HMF, and in particular esters of HMF optionally in combination with HMF, such as for example 5-(acetoxymethyl)furfural (AMF) can be oxidized to FDCA in high yields .*"

In other words, it is understood from said passage that the contribution of the claimed process over the processes disclosed in the prior art is the use of temperatures higher than 140°C. This is also endorsed by the comparative data given in example 2 of the present application where the only parameter varied was the temperature (comparison of the yield of FDCA obtained at 180°C and 100°C).

Furthermore, it is also observed that the above cited passage makes no reference to the pressure that should be used in the claimed process or to the oxygen partial pressure for that matter. Even the examples of the present application do not make any reference to the oxygen partial pressure used therein. What is more, in the general description of the examples page 6, lines 34-36 it is stated that "*the reactors were sealed and pressurized to the desired air pressure ranging from 20-60 bars*"; said pressure being translated to 4-12.6 bars oxygen partial pressure, the end value 12.6 thereof being outside the claimed range.

- 2.4 The Examining Division also interpreted the passage relating to the pressure wherefrom the feature of "*oxygen partial pressure of 1 to 10 bar*" was deduced (see page 4, line 34 to page 5, line 10), to actually relate to existing commercial processes (see Office Communications dated the 16.04.2013 and the 19.09.2014). The applicant counter-argued in this respect that said passage relates to the adaptation of the claimed process on commercial scale.

However, the first phrase of said passage reads: "*The pressure in a commercial oxidation process may vary within wide ranges*". The following phrase that "*the pressure of the reaction mixture is preferably selected such that the solvent is mainly in the liquid phase*" is also found in document D8, page 7, lines 4-5. The following sentence "*In practice this means that pressures between 5 and 100 bar can be used with a preference for pressures between 10 and 80 bar.*" can thus only be interpreted as giving what order of pressure the person skilled in the art would normally expect in

order that the solvent is in the liquid phase. This is also confirmed by the most relevant disclosures of documents D7, D8 and D10 disclosing a reaction pressure of 20 bar (Ribeiro disclosure, see also reference thereto in the Office Communication dated the 16.04.2013), 70 bar and 10-400 bar, respectively.

In order that the claimed process "deviates" even more from the disclosures of the prior art, the applicant not only selected to refer to the oxygen partial pressure used in the claimed process (the range of 5-100 bar or 10-80 bar pressure would be converted to ~1-21 or ~2-17 bar oxygen partial pressure, respectively) but also to claim the narrower range of 1-10 bar oxygen partial pressure.

2.5 Assessing the inventiveness of the claimed process following is mentioned.

Document D8 disclosing a process for the preparation of FDCA is regarded to be the closest prior art (as also stated by the applicant). D8, in particular, discloses in the series of examples 16-40 the preparation of FDCA from HMF with an oxygen containing gas in acetic acid as a solvent and with a Co/Mn/Br/Zr catalyst at a temperature of 75°C / 150°C at 70 bar air pressure (14.7 bar oxygen partial pressure). In addition, the description states that for the preparation of the diacid the temperature should be between 50 and 250°C, preferably between 50 and 160°C (page 7, lines 2-7).

In view of the closest prior the technical problem underlying the present application is the provision of a further -if possible of an improved process for the preparation of FDCA.

As solution is claimed the process according to claim 1 which differs from the process according to D8 in the pressure of the oxidant used.

According to the Applicant (see letter of 27.11.2014 page 2, 5th paragraph):  
*"...the problem is solved by the feature, viz. the oxygen partial pressure that is different from the closest prior art, in combination with the feature, viz. the reaction temperature that is beyond what is explicitly exemplified in D8".*

The effect of the difference is that the claimed process leads to higher yields of FDCA due to 100% conversion of HMF.

2.5.1 Starting with the feature of the temperature it is mentioned that D8 teaches that the yield of the FDCA is improved by using higher temperatures (see examples 38-40 / in entry 28 a higher yield is obtained but after 12 hours of reaction time). In the present application a temperature range of 140-200°C is claimed for carrying out the reaction (the examples disclose only a temperature of 180°C). However, said range cannot be regarded as a narrow

selection of the range 50-250°C / 50-160° disclosed in D8; furthermore, the preferred end value 160°C disclosed in D8 as well as the 150°C reaction temperature disclosed in examples 38-40 of D8 fall within the presently claimed range.

- 2.5.2 The Applicant's Representative implied that the closest prior art D8 teaches that variations in pressure in the preparation of FDCA are immaterial.

This is not correct: the examples 1-15 cited by the applicant in this respect relate to the conversion of HMF to DFF, while it is examples 16-40 that relate to the conversion of HMF to FDCA. At no point of the passage relating to examples 1-15 was mentioned that the initial intention in said examples was to convert HMF to FDCA with the process described therein (see also in this respect, page 3, lines 1-15, page 5, lines 19-24, page 6, lines 36-38 etc. clearly stating as preferred embodiment the preparation of DFF).

D8 clearly teaches that the pressure is such to keep the solvent in the liquid phase (see page 7, lines 4-5). The claimed process acts within said teaching as it is evident from the examples on pages 6-7 of the present application where the solvent is also in the liquid phase.

- 2.5.3 Finally, the Applicant's Representative argued that the yield of the FDCA achieved by the claimed process is higher than in the closest prior art D8.

Examples 38-40 of D8 carried out within the temperature range presently claimed disclose a yield for the FDCA between 51.4 and 54.6%.

The Examining Division sees that when the substrate contains HMF higher yield is achieved; however such higher yields are to be expected, as also taught by document D8. In this respect, particular reference is made to example 39 in comparison with example 33 relating to the same amounts of catalyst and very similar amount of HMF. In example 39 there is a staging of the temperature: 2 hours at 75°C and 2 hours at 150°C while in example 33 the reaction is conducted at 105°C for 8 hours. Despite the longer reaction time (8 hours vs. 4 hours) the yield of FDCA is 41.0% in example 33 and 52.9% in example 39.

- 2.5.4 In view of the above, the Examining Division is of the opinion that the effect of the claimed process i.e. the higher yield of FDCA obtained can be reasonably expected since the claimed process is carried out in higher temperature.



As to the feature of the oxygen partial pressure, neither the description nor the examples unambiguously disclose it as essential for achieving the claimed effect. In this respect, it is also mentioned that while the description i.e. example 2 gives by means of a comparison the effect that the temperature has on the yield of FDCA, no similar comparison is made with respect to the oxygen partial pressure or the oxidant pressure for that matter.

It can be therefore reasonably expected that as long as the solvent is in liquid phase, the pressure may vary, and it would be the understanding of the person skilled in the art that when higher temperatures are used the pressure / oxygen partial pressure may be reduced i.e. lower than e.g. the 70 bar used in D8.

As a final point in this respect, reference is made to document D7 and in particular to the Ribeiro disclosure (see also same reference made in the Office Communication dated the 16.04.2013) disclosing the preparation of FDCA with  $\text{CO}(\text{acac})_3$  as a catalyst, deionized water as a solvent, a temperature of 160°C and a pressure of 20 bar of synthetic air, i.e. 4.2 bar oxygen partial pressure and achieving 99% selectivity of FDCA at 72% conversion of fructose.

In view of the above, the Examining Division is of the opinion that the subject-matter of the Main Request does not fulfil the requirements of Article 56 EPC.

### 3 Auxiliary Request

#### 3.1 Article 123(2) EPC

The Auxiliary Request filed with the letter of the applicant dated the 27.11.2014 is based on the Main Request, whereby the 5-hydroxymethylfurfural (HMF) is deleted from the group of compounds mentioned in claim 1.

Although -as also explained in the present application- a) fructose and glucose give in a first step HMF and b) HMF is the starting material for the preparation of its derivatives (see e.g. page 2, lines 1-3 or letter of the applicant dated the 27.11.2014 page 5, second paragraph), the present application contains examples where the substrate to be oxidized does not contain HMF (see examples 1d, 1h, 1l 1p and examples 2 and 3).

Thus, the deletion in claim 1 of one of the alternatives defining the compound to be oxidized does not contravene Article 123(2) EPC.

### 3.2 Rule 43(4) EPC

According to claim 1 of the Auxiliary Request the compound to be oxidized is "*selected from 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*".

Claims 2 refers to a preferred definition from the compound to be oxidized which is now "*selected from the group consisting of esters of 5-hydroxymethylfurfural ("HMF") and a mixture of esters of HMF and HMF.*" In other words the preferred definition of the compound to be oxidized now covers also a mixture of esters of HMF and HMF.

However, the list of compounds according to claim 1 covers only esters 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 and does not cover the 5-hydroxymethylfurfural, nor mixtures thereof.

As a consequence, claim 2 cannot be dependent on claim 1 and thus the requirements of Rule 43(4) EPC are not fulfilled.

### 3.3 Article 56 EPC

The intention of the amendments carried out in the Auxiliary Request was as mentioned in the letter of the applicant dated the 27.11.2014 "*that the starting material no longer comprises HMF as the sole compound that is to be oxidized*".

However, even when other components are present in the mixture to be oxidized from the moment that HMF is present, the same considerations as to inventive step apply as for the Main Request. In this respect, additional reference is made to the passage of D8, page 6, lines 33-35:

- "*it is contemplated that the processes of the invention is which DFF and/or FDA is prepared can be run using a biomass feedstock containing HMF such that only the final product need be isolated and purified*".

Furthermore, with respect to the preferred embodiment of claim 2 of the Auxiliary Request where HMF is not present in the mixture to be oxidized and the compound to be oxidized is an ester of 5-hydroxymethylfurfural, reference is made to claims 20 and 21 of D8:

- 20. *The process of Claim 16 wherein the process further comprises before step c converting the acid/aldehyde to an acetate ester of the formula  $CH_3(C=O)OCH_2-R'-(C=O)H$ .*
- 21. *The process of Claim 20 wherein the diacid is furan-2, 5-dicarboxylic acid and the alcohol/aldehyde is 5-(hydroxymethyl)furfural.*

Said claims of D8 disclose that HMF is completely converted to the 5-acetoxymethylfurfural before being further oxidized to FDCA, in other words in the reaction mixture only an ester of 5-hydroxymethylfurfural is present.

With respect to the subject-matter of the Auxiliary Request the applicant made reference to document D2 in his letter of 27.11.2014 (see also page 2 of the present application) and alleged that in D2 figure 8 relating to the "product" is identical to figure 7 (letter of 27.11.2014) and/or figure 6 (description page 2) which relates to the "starting material AMF". However, the Examining Division observes that already the reference to figure 8 in document D2 appears to contain an error (see page 3, paragraph 32: "*FIG. 8 is a <sup>1</sup>H NMR analysis graph showing substantially pure 2,5-diformylfuran, 2,5-furandicarboxylic acid (FDCA).*", figure 7 relates to substantially pure 5-propionoxymethylfurfural and figure 6 to substantially pure 5-acetoxymethylfurfural (AcHMF). Furthermore, the relevant example 7 of D2 does not refer to figure 8 for identifying the FDCA obtained by the process disclosed therein. Thus, similarly to D8, the information deduced from example 7 of D2 is that 5-acetoxymethylfurfural can be oxidized to FDCA directly and in the absence of HMF.

In view of the above disclosures and the argumentation set out for the inventiveness of the Main Request it is considered that the process according to the Auxiliary Request is an obvious alternative of the process disclosed in D8.

As a final point to the inventive step of the Auxiliary Request the Examining Division observes that when the substrate is a mixture containing HMF and in particular when the substrate does not contain HMF at all, the yields of FDCA obtained are much lower (see e.g. example 1p where FDCA in a 46.85% yield is obtained, or example 3 with 5-MF and DMF as a substrate where the maximum yield obtained is 42.62% FDCA while a yield of 7.19% FDCA is

Datum  
Date 18.03.2015  
Date

Blatt  
Sheet 10  
Feuille

Anmelde-Nr:  
Application No: 10 768 600.8  
Demande n°:

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also disclosed). Thus, the objective technical problem as set out by the applicant in his letter of 27.11.2014 of "*the provision of a process wherein FDCA is obtained ... in interesting yields*" cannot be regarded as solved or at least as solved over the whole breadth claimed.

In view of the above, the Auxiliary request does not fulfil the requirements of Article 56 EPC.

In view of the above, it is decided to refuse the application under Article 97(2) EPC.

**Article 106**  
**Decisions subject to appeal**

- (1) An appeal shall lie from decisions of the Receiving Section, Examining Divisions, Opposition Divisions and the Legal Division. It shall have suspensive effect.
- (2) A decision which does not terminate proceedings as regards one of the parties can only be appealed together with the final decision, unless the decision allows a separate appeal.
- (3) The right to file an appeal against decisions relating to the apportionment or fixing of costs in opposition proceedings may be restricted in the Implementing Regulations.

**Rule 97**  
**Appeal against apportionment and fixing of costs**

- (1) The apportionment of costs of opposition proceedings cannot be the sole subject of an appeal.
- (2) A decision fixing the amount of costs of opposition proceedings cannot be appealed unless the amount exceeds that of the fee for appeal.

**Rule 98**  
**Surrender or lapse of the patent**

The decision of an Opposition Division may be appealed even if the European patent has been surrendered in all the designated Contracting States or has lapsed in all those States.

**Article 107**  
**Persons entitled to appeal and to be parties to appeal proceedings**

Any party to proceedings adversely affected by a decision may appeal. Any other parties to the proceedings shall be parties to the appeal proceedings as of right.

**Article 108**  
**Time limit and form**

Notice of appeal shall be filed, in accordance with the Implementing Regulations, at the European Patent Office within **two months** of notification of the decision. Notice of appeal shall not be deemed to have been filed until the fee for appeal has been paid. Within **four months** of notification of the decision, a statement setting out the grounds of appeal shall be filed in accordance with the Implementing Regulations.

**Further information concerning the filing of an appeal**

- (a) Notice of appeal can be filed in accordance with Rule 1 and Rule 2(1) EPC, by delivery by hand, by post, or by technical means of communication. The filing has to comply with the details and conditions and, where appropriate, any special formal or technical requirements laid down by the President of the European Patent Office (R. 99(3) EPC).
- (b) The addresses of the filing offices of the European Patent Office are as follows:

(i) European Patent Office D-80298 Munich Germany  Fax: +49 89 2399-4465	(ii) European Patent Office Postbus 5818 NL-2280 HV Rijswijk (ZH) The Netherlands  Fax: +31 70 340-3016	(iii) European Patent Office D-10958 Berlin Germany  Fax: +49 30 259 01-840
--	--	---

- (c) The notice of appeal must contain the name and address of the appellant in accordance with the provisions of Rule 41(2)(c) EPC, an indication of the decision impugned, and a request defining the subject of the appeal. In the statement of grounds of appeal the appellant shall indicate the reasons for setting aside the decision impugned, or the extent to which it is to be amended, and the facts and evidence on which the appeal is based (R. 99(1) and (2) EPC). The notice of appeal and any subsequent submissions stating the grounds for appeal must be signed (R. 50(3) EPC).
- (d) The fee for appeal is laid down in the Rules relating to Fees. The schedule of fees and expenses of the EPO or a reference to the current version is regularly published in the Official Journal of the European Patent Office under the heading "Guidance for the payment of fees, expenses and prices". Fee information is also published on the EPO website under [www.epo.org/fees](http://www.epo.org/fees).

**Questions about this communication ?**  
Contact Customer Services at [www.epo.org/contact](http://www.epo.org/contact)



EP&C  
P.O. Box 3241  
2280 GE Rijswijk  
PAYS-BAS

By fax on 11.02.15

Date	17-02-2015
------	------------

Reference P30061EP00/AZE	Application No./Patent No. 10768600.8 - 1462 / 2486028
Applicant/Proprietor Furanix Technologies B.V	

**BRIEF COMMUNICATION**

**Oral Proceedings on 24.02.15**

Subject:  Your letter of 27.11.14

- Communication:
- The summons to attend oral proceedings on 24.02.15 has been cancelled.
  - The procedure will be continued in writing.
  - The date fixed for oral proceedings is maintained.
  - A new date will be set later.
  -

Please take note.

**For the Examining Division**



European patent application No. 10768600.8

**URGENT !**  
**To be completed (under II.) and returned to the formalities officer immediately**

**Maintenance / Change of date / Cancellation of oral proceedings  
 arranged for:  
 day 24.02.15 at 09.00 hrs**

**I. To the Examining / Opposition division**

1.  The proprietor has requested the revocation (or the like) of his patent (date: .....).
  
2.  The party / witness ..... has indicated (date: 11.02.15) that he / she
  - requests the date / time of oral proceedings to be changed.
  - withdraws the request for oral proceedings.
  - will not be attending.
  - wishes to be heard by a national court.
  - has filed amendments (in examination proceedings).
  - has requested that the oral proceedings be held as a videoconference (in examination proceedings).
  
3.  Two months before the oral proceedings the application is deemed to be withdrawn (in examination proceedings). The oral proceedings have to be cancelled.

12-02-2015

Pfau, Andrea

\_\_\_\_\_  
 Date

\_\_\_\_\_  
 Formalities Officer



**II. To the Formalities Officer**

- 1.  The date / time fixed for oral proceedings is maintained.  
 (if necessary) The reasons are indicated on enclosed EPO Form 2906/2906O, which is to be dispatched to the party with EPO Form 2008A/2310A.
- 2.  At the instigation of the division the oral proceedings cannot take place on the arranged date for the reasons indicated on enclosed EPO Form 2906, which is to be dispatched to the party with EPO Form 2008A/2310A.

\_\_\_\_\_  
Date

\_\_\_\_\_  
Director

- 3.  The summons to attend oral proceedings on 24.02.15 should be cancelled.
  - 3.1  The proceedings will be continued in writing.
  - 3.2  A new date will be set later.
  - 3.3  A new date/time is set as follows:  
date ..... at ..... hrs.  
Parties' written submissions and amendments in preparation for the oral proceedings, if any, should be made not later than  
..... month(s) before the date of the oral proceedings.

- 4.  The request for the oral proceedings to be held as a videoconference
  - 4.1  is allowed.
  - 4.2  is rejected for the reasons indicated on enclosed EPO Form 2906, which is to be dispatched to the party with EPO Form 2008A.

- 5.  The application is deemed to be withdrawn. The oral proceedings are cancelled.

\_\_\_\_\_  
Date

\_\_\_\_\_  
Chairman

\_\_\_\_\_  
Second member

\_\_\_\_\_  
Primary Examiner

\_\_\_\_\_  
Legal member

**III. Action taken by the formalities officer**

- EPO Form 2008A/2310A has been dispatched, if applicable (see point II above) together with EPO Form 2906/2906O.
- A new summons has been dispatched.
- .....

\_\_\_\_\_  
Date

\_\_\_\_\_  
Formalities Officer

## Acknowledgement of receipt

We hereby acknowledge receipt of the following subsequently filed document(s):

Submission number	3305136	
Application number	EP10768600.8	
Date of receipt	11 February 2015	
Receiving Office	European Patent Office, The Hague	
Your reference	P30061EP00/RLA	
Applicant	All applicants as on file	
Documents submitted	package-data.xml  epf1038.pdf (1 p.)	ep-sfd-request.xml  ORAL-1.pdf\letter to EPO re Oral Proc.pdf (2 p.)
Submitted by	CN=Rene Raggars 13051	
Method of submission	Online	
Date and time receipt generated	11 February 2015, 15:10 (CET)	
Message Digest	B1:25:79:4A:00:F7:30:F5:56:B9:F1:74:78:39:12:C3:9D:B5:94:8F	

### Correction by the EPO of errors in debit instructions filed by eOLF

Errors in debit instructions filed by eOLF that are caused by the editing of Form 1038E entries or the continued use of outdated software (all forms) may be corrected automatically by the EPO, leaving the payment date unchanged (see decision T 152/82, OJ EPO 1984, 301 and point 6.3 ff ADA, Supplement to OJ EPO 10/2007).

/European Patent Office/



## Letter accompanying subsequently filed items

Representative:

**EP&C  
497**

**P.O. Box 3241  
2280 GE Rijswijk  
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80298 Munich  
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Tel. +49(0)89 2399-0 | Fax -4465

P.O. Box 5818  
NL-2280 HV Rijswijk  
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Tel. +31(0)70 340-2040 | Fax -3016

10958 Berlin  
Germany  
Tel. +49(0)30 25901-0 | Fax -840

The document(s) listed below is (are) subsequently filed documents pertaining to the following application:

Application number

10768600.8

Applicant's or representative's reference

P30061EP00/RLA

	Description of document	Original file name	Assigned file name
1	Letter dealing with Oral proceedings	letter to EPO re Oral Proc.pdf	ORAL-1.pdf

### Signatures

Place: **Rijswijk**  
Date: **11 February 2015**  
Signed by: **Rene Raggars 13051**  
Association: **EP&C**  
Capacity: **(Representative)**

EUROPEAN PATENT OFFICE  
P.O. Box 5818  
2280 HV RIJSWIJK (ZH)

Rijswijk, February 11, 2015

**ORAL PROCEEDINGS FEBRUARY 24, 2015**

Our ref. : P30061EP00/RLA/wee  
Contact : Tel. 31-30-2737510/ email: Pasteur@epc.nl

Application no. : 10768600.8 - 1462  
Country : Europe  
In the name of : Furanix Technologies B.V.

Dear Sirs,

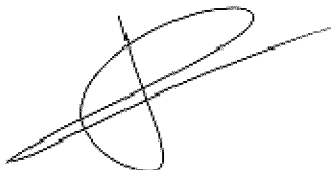
This is further to the Summons to Oral proceedings in the matter of the above-mentioned patent application.

The efforts of the examiner to consult the file and determine whether our latest submissions were sufficient to continue the further proceedings writing are appreciated.

This is to inform you that we will NOT attend the Oral proceedings of February 24, 2015. We request that a decision is made based on the current state of the file. The main request and auxiliary requests are all maintained.

We expect a reasoned decision in due time.

The professional representative  
EP&C



Robbert-Jan de Lang, PhD  
Association no: 497



European patent application No. 10768600.8

**URGENT !**  
**To be completed (under II.) and returned to the formalities officer immediately**

**Maintenance / Change of date / Cancellation of oral proceedings  
 arranged for:  
 day 02.15 at 09.00 hrs**

**I. To the Examining / Opposition division**

1.  The proprietor has requested the revocation (or the like) of his patent (date: .....).
  
2.  The party / witness ..... has indicated (date: 27.11.14) that he / she
  - requests the date / time of oral proceedings to be changed.
  - withdraws the request for oral proceedings.
  - will not be attending.
  - wishes to be heard by a national court.
  - has filed amendments (in examination proceedings).
  - has requested that the oral proceedings be held as a videoconference (in examination proceedings).
  
3.  Two months before the oral proceedings the application is deemed to be withdrawn (in examination proceedings). The oral proceedings have to be cancelled.

04-12-2014

\_\_\_\_\_  
 Date

Pfau, Andrea

\_\_\_\_\_  
 Formalities Officer

European patent application No. 10768600.8

**II. To the Formalities Officer**

- 1.  The date / time fixed for oral proceedings is maintained.
  - (if necessary) The reasons are indicated on enclosed EPO Form 2906/2906O, which is to be dispatched to the party with EPO Form 2008A/2310A.
- 2.  At the instigation of the division the oral proceedings cannot take place on the arranged date for the reasons indicated on enclosed EPO Form 2906, which is to be dispatched to the party with EPO Form 2008A/2310A.

\_\_\_\_\_  
Date

\_\_\_\_\_  
Director

- 3.  The summons to attend oral proceedings on 24.02.15 should be cancelled.
  - 3.1  The proceedings will be continued in writing.
  - 3.2  A new date will be set later.
  - 3.3  A new date/time is set as follows:  
 date ..... at ..... hrs.  
 Parties' written submissions and amendments in preparation for the oral proceedings, if any, should be made not later than  
 ..... month(s) before the date of the oral proceedings.
- 4.  The request for the oral proceedings to be held as a videoconference
  - 4.1  is allowed.
  - 4.2  is rejected for the reasons indicated on enclosed EPO Form 2906, which is to be dispatched to the party with EPO Form 2008A.
- 5.  The application is deemed to be withdrawn. The oral proceedings are cancelled.

04.02.14

Date  
[Signature]  
Chairman

[Signature]  
Second member

[Signature]  
Primary Examiner

\_\_\_\_\_  
Legal member

**III. Action taken by the formalities officer**

- EPO Form 2008A/2310A has been dispatched, if applicable (see point II above) together with EPO Form 2906/2906O.
- A new summons has been dispatched.
- .....

10.02.15  
Date

[Signature]  
Formalities Officer

## Acknowledgement of receipt

We hereby acknowledge receipt of the following subsequently filed document(s):

Submission number	3151795	
Application number	EP08773872.0	
Date of receipt	27 November 2014	
Receiving Office	European Patent Office, The Hague	
Your reference	P30061PE00/RLA	
Applicant	All applicants as on file	
Documents submitted	package-data.xml  epf1038.pdf (1 p.)  DESC-HWA-1.pdf\FUR 19b EP text 1 main request marked up.pdf (11 p.)  CLMS-1.pdf\FUR 19b Amended claims Main request.pdf (2 p.)  DESC-2.pdf\FUR 19b EP text 1 Aux Req clean.pdf (11 p.)	ep-sfd-request.xml  ORAL-1.pdf\Response to a communication P30061EP00.pdf (7 p.)  DESC-1.pdf\FUR 19b EP text 1 Main Request clean.pdf (10 p.)  DESC-HWA-2.pdf\FUR 19b EP text 1 Aux Req marked up.pdf (12 p.)  CLMS-2.pdf\FUR 19b Aux Req claims.pdf (2 p.)
Submitted by	CN=Johan Volmer 36336	
Method of submission	Online	
Date and time receipt generated	27 November 2014, 14:17 (CET)	
Message Digest	DA:DE:F9:81:74:D5:29:D0:39:E4:0A:80:4F:D4:35:74:CB:D2:41:71	



Errors in debit instructions filed by eOLF that are caused by the editing of Form 1038E entries or the continued use of outdated software (all forms) may be corrected automatically by the EPO, leaving the payment date unchanged (see decision T 152/82, OJ EPO 1984, 301 and point 6.3 ff ADA, Supplement to OJ EPO 10/2007).

*/European Patent Office/*

Auxiliary Request

Title: Method for the preparation of 2,5-furandicarboxylic acid and for the preparation of the dialkyl ester of 2,5-furandicarboxylic acid

5           The present invention relates to a method for the preparation of 2,5-furandicarboxylic acid ("FDCA") from 5-hydroxymethylfurfural ("HMF") and/or derivatives thereof. FDCA can be produced in particular from esters of HMF, such as for example 5-acetoxymethylfurfural (AMF) or a mixture of one or more of these compounds with HMF, such as for example from a mixture of AMF and HMF. The invention further relates to a process for the preparation of  
10 the dialkyl ester of 2,5-furandicarboxylic acid.

          2,5-Furandicarboxylic acid, also known as dehydromucic acid is a furan derivative. This organic compound was first obtained by Fittig and Heinzelmann in 1876. The first review, by Henry Hill was published in 1901 (Am. Chem. Journ. 25, 439). FDCA was more than 125  
15 years later identified by the US Department of Energy as one of 12 priority chemicals for establishing the "green" chemistry industry of the future. However, to date, no commercial process exists for its production. On laboratory scale it is often synthesized from 5-hydroxymethylfurfural (HMF), which in turn can be obtained from carbohydrate containing sources such as glucose, fructose, sucrose and starch. From fructose and glucose HMF is  
20 obtained by acidic elimination of three moles of water.

          The derivatives of HMF are identified as potential and versatile fuel components and precursors for the production of plastics. The polyester from FDCA dimethyl diester and ethylene glycol was first reported in 1946 (GB 621,971).

          WO 01/72732 describes the oxidation of HMF to FDCA. The maximum FDCA yield  
25 reported is 59%, obtained at 105 °C. The oxidation of HMF in an aqueous medium with oxygen using a catalyst from the Pt-group is described in US 4977283. Taarning et al. described the oxidation of HMF over gold based catalysts (ChemSusChem, 2008, 1, 1-4).

          Partenheimer et al (Adv. Synth. Catal. **2001**, 343, pp 102-11) describe the synthesis of 2,5-furandicarboxylic acid by catalytic air-oxidation of 5-hydroxymethylfurfural with  
30 metal/bromide catalysts such as Co/Mn/Br in acetic acid at temperatures ranging from 50 to 125 °C. With the Co/Mn/Br catalyst the highest FDCA yield obtained is 35.2% (Table 3, experiment 4). On page 103 of the same paper, under the header "products formed" it is stated: "A side reaction is the esterification of the alcohols to form the more oxidatively stable  
35 acetate ...." As apparently 5-hydroxymethylfurfural reacts with acetic acid a loss of the starting material takes place. Further, in the reaction scheme given in Figure 1 on page 103, it is indicated that 5-(acetoxymethyl)furfural is an end-point. There is no further reaction of

this compound indicated to FDCA (in contrast to the ester of the intermediate product 5-

(acetoxymethyl)furan-2-carboxylic acid). In other words, the 5-(acetoxymethyl)furfural (AMF) formed through reaction of HMF with acetic acid solvent, is not oxidized to FDCA and its formation leads therefore to yield loss.

This result was confirmed in US 2009/0156841. Although the intention of the process according to US 2009/0156841 was to obtain FDCA, the product isolated and erroneously characterized as being FDCA was in fact the starting material acetoxymethyl furfural (AMF). Under the low temperature conditions deployed (100 °C), AMF is quite stable, as was already reported by Partenheimer (see above).

In US 2009/0156841 a <sup>1</sup>H NMR spectrum is shown in Figure 8 and suggested that it is the spectrum of the product that was identified as FDCA. However, this is not the case. The <sup>1</sup>H NMR spectrum of the product shown in Figure 8 is the same as that in Figure 6 and represents the starting material AMF. The <sup>1</sup>H NMR spectrum of FDCA shows a singlet at a shift of about 7.26 ppm. Moreover, the product is described as a tan solid. In the experience of the present inventors, AMF is a tan solid, while FDCA is a white solid. It would seem that no FDCA was obtained in the experiments according to US 2009/0156841.

The experiments executed under the conditions of US 2009/0156841 were repeated. These comparative experiments confirm the low reactivity of AMF under conditions given in US 2009/0156841. Thus, a person skilled in the art would therefore have concluded that FDCA cannot be obtained in interesting yields from AMF using the conditions that are reported in US 2009/0156841, i.e., using a Co/Mn/Br catalyst in acetic acid at between 85 and 110 °C within a time frame of from 100 and 150 minutes. In Example 7 of US 2009/0156841, slightly more than 50% of the starting material was the only product isolated from the reaction.

In the method according to WO 01/72732, FDCA is prepared by contacting HMF with an oxygen-containing gas in the presence of an oxidation catalyst comprising Co and Mn in a solvent comprising acetic acid. The reaction temperature may be between 50 and 250 °C, e.g. from 50 to 160 °C. Although in examples the reaction temperatures were generally in the range from 100 to 125 °C, a reaction stage in some examples was conducted at a temperature of 150 °C. WO 01/72732 is directed to five different processes, one of which is directed to a process for preparing a diacid, such as FDCA, from an alcohol/aldehyde, such as HMF. According to the examples, a yield on the desired diacid FDCA of up to 58.8% was obtainable.

Boisen et al., Chem Eng. Research Design, 87 (2009) 1318-1327 describes the conversion of sugars to FDCA in general terms. In particular it discusses the conversion of

HMF to FDCA referring to the work by the inventors of WO 01/72732. It concludes that the oxidation with Co/Mn/Zr/Br is conducted at atmospheric pressure and at 70 bar. It also refers to an oxidation over Pt on alumina, wherein the reaction temperature is 60 °C and a partial oxygen pressure of 0.2 bar.

5 WO 2008/054804 relates to the oxidation of HMF using air or O<sub>2</sub> as oxidant over a platinum-supported catalyst; the temperature ranges from about 50 to about 200 °C. A suitable pressure is 150 - 500 psi (about 10 to 34.5 bar). JP 2009 001519 discloses the oxidation of HMF over a catalyst containing Ru, Co and Ce with molecular oxygen. The temperature may be from 50 to 200 °C. The pressure is 10 – 400 bar. RU 636233 discloses  
10 the oxidation of HMF over a catalyst comprising CuO.Ag<sub>2</sub>O.Ce<sub>2</sub>O<sub>3</sub> on alumina. The oxidant is oxygen or air, the pressure is 25 - 30 atm and the temperature is 110 - 150 °C.

The present inventors have now surprisingly found that when using an oxidation catalyst, e.g., based on both cobalt and manganese and containing a bromide, at temperatures higher than 140 °C, derivatives of HMF, and in particular esters of HMF  
15 optionally in combination with HMF, such as for example 5-(acetoxymethyl)furfural (AMF) can be oxidized to FDCA in high yields.

Thus, in a first aspect the invention provides a method for the preparation of 2,5-furan  
20 dicarboxylic acid comprising the step of contacting in a reactor 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 oxygen-containing gas being continuously fed and removed to  
25 and from the reactor, in the presence of an oxidation catalyst comprising at least one metal selected from Co and Mn, at a temperature higher than between 140 and 200°C at an oxygen partial pressure of 1 to 10 bar, wherein a solvent or solvent mixture comprising acetic acid or acetic acid and water mixtures is present. The feed may optionally comprise 5-hydroxymethylfurfural as a further compound.

30 The invention described hereinafter may use any of the compounds described above in the feed. A preferred ester of HMF contains an ester moiety of an alkyl carboxylic acid

wherein the alkyl group contains up to 6 carbon atoms, preferably from 1 to 5 carbon atoms, i.e. methyl, ethyl, propyl, isopropyl, butyl, 2-butyl, tert-butyl, pentyl, 2-pentyl, neopentyl and 3-

5 pentyl. Particularly preferred are alkyl groups with 1 to 4 carbon atoms. There is a preference for methyl, giving (5-acetoxymethyl)furfural. Hence, 5-acetoxymethylfurfural is the preferred feedstock, by itself or in combination with HMF.

10 In another aspect of the invention, we have also investigated the oxidation of other furan-based substrates under the process conditions according to the current invention. We have been able to convert 5-(chloromethyl)furfural, 5-(chloromethyl)furoic acid, 5-methylfurfural, 5-methylfuroic acid and 2,5-dimethylfuran all to FDCA in very interesting yields.

15 In WO 2007/104515 and WO 2009/030512, the synthesis of esters of HMF such as 5-acetoxymethylfurfural (AMF) from biomass sources is described. Given the higher stability of the HMF esters than HMF and hence improved production pathways and given the fact that upon oxidation in acetic acid the acetoxy functionality that was obtained from acetic acid is now liberated as acetic acid and given the green reputation of these esters, they were considered by the present inventors as interesting starting point in the preparation of furan-20 based monomers that could be used for the production of furandicarboxylic acid-based polyesters, for instance as an alternative for PET or FDCA-based polyamids (nylons). The most important conventional, oil-based, polyester monomer to produce PET is Purified Terephthalic acid (PTA) and its dialkyl ester DiMethyl Terephthalate (DMT).

25 AMF can be obtained from biomass sources as described in WO 2007/104515 and WO 2009/030512. Depending on the process conditions the product obtained in accordance with the process of these references may also contain HMF.

30 FDCA, the product of the reaction can be used in the preparation of a polyester, by reaction of FDCA or its dialkyl ester with a suitable diol. Such polyester preparations are preferably performed by transesterification, whereby the di-methyl ester or di-ethyl ester of FDCA is used and wherein the methyl or ethyl groups are exchanged in the form of a volatile alcohol during the transesterification with the diol.

The oxidation catalyst can be selected from a variety of oxidation catalysts, but is preferably a catalyst based on both cobalt and manganese and suitably containing a source of bromine, preferably a bromide.

35 The bromine source can be any compound that produces bromide ions in the reaction mixture. These compounds include hydrogen bromide, sodium bromide, elemental bromine,

benzyl bromide and tetrabromoethane. Also other bromine salts, such as an alkali or alkaline earth metal bromide or another metal bromide such as  $ZnBr_2$  can be used. There is a preference for hydrobromic acid or sodium bromide. The amount of bromine mentioned in here relates to the amount measured as Br relative to cobalt.

5

Suitable metal bromide catalysts employed in all of the processes of this invention comprise a cobalt compound and a manganese compound and a bromine-containing compound. Preferably these compounds are soluble in the reaction mixture.

Preferably, the catalyst comprises both Co and Mn. The metal and bromide catalyst contains, in addition to bromide, Co and Mn and optionally may contain one or more additional metals, in particular Zr and/or Ce. Alternative and suitable catalysts are described in W. Partenheimer, *Catalysis Today* 23(2), 69-158 (1995) in particular on pages 89-99, included herein by reference.

Each of the metal components can be provided in any of their known ionic forms. Preferably the metal or metals are in a form that is soluble in the reaction solvent. Examples of suitable counterions for cobalt and manganese include, but are not limited to, carbonate, acetate, acetate tetrahydrate and halide, with bromide being the preferred halide.

As described in Partenheimer, *ibid*, pages 86-88, suitable solvents for use in the processes of the present invention, described above, preferably have at least one component that contains a monocarboxylic acid functional group. The solvent may also function as one of the reagents. The processes may be run in a solvent or solvent mixture that does not contain an acid group. In that case, preferably one of the reagents does contain a monocarboxylic acid functional group. Suitable solvents can also be aromatic acids

such as benzoic acid and derivatives thereof. ~~A preferred~~The solvent in the present process comprises ~~is an aliphatic C<sub>2</sub>-C<sub>6</sub> monocarboxylic acid, such as but not limited to acetic acid, propionic acid, n-butylric acid, isobutyric acid, n-valeric acid, trimethylacetic acid, and caproic acid and mixtures thereof. Said~~ A ~~mixtures~~ may also include benzene, acetonitrile, heptane, acetic anhydride, chlorobenzene, o-dichlorobenzene, and water. The most preferred solvent is acetic acid ("AcOH").

The oxidant in the processes of the present invention is preferably an oxygen-containing gas or gas mixture, such as, but not limited to air and oxygen-enriched air. Oxygen by itself is also a preferred oxidant.

The processes of the instant invention described above can be conducted in a batch, semi-continuous or continuous mode. Especially for the manufacture of FDCA, 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 desirable. For example, variation of the catalyst composition during the reaction can be accomplished by addition of cobalt and/or manganese and/or zirconium, and/or cerium, and/or bromide at specified times.



\_\_\_\_ The pressure in a commercial oxidation process may vary within wide ranges. ~~When~~ As  
a  
diluent is present, and in particular with acetic acid as diluent, the temperature and the  
pressure in such a process are not independent. The pressure is determined by the solvent

5

(e.g., acetic acid) pressure at a certain temperature. The pressure of the reaction mixture is preferably selected such that the solvent is mainly in the liquid phase. In practice this means that pressures between 5 and 100 bar can be used with a preference for pressures between 10 and 80 bar. In ~~case the oxidant is the process according to the present invention an~~ oxygen-containing gas, such as air, the gas ~~can be~~ is continuously fed to and removed from the reactor, ~~or the gas can be supplied all at the start of the reaction. In the latter case, the pressure of the system will depend on the headspace volume and the amount of gas required to convert the starting material. It is clear that in the latter case, the pressure of the system may be significantly higher than the pressure in a process wherein an oxygen~~ containing gas is continuously fed and removed. In the case of continuously feeding and removing the oxidant gas to and from the reactor, the oxygen partial pressure will suitably be between 1 and 30 bar or more preferably between 1 and 10 bar.

The temperature of the reaction mixture is ~~at least 140 °C,~~ preferably from 140 and 200 °C, most preferably between 160 and 190 °C. Temperatures higher than 180 °C may lead to decarboxylation and to other degradation products. Good results to FDCA have been achieved at a temperature of about 180 °C.

Molar ratios of cobalt to manganese (Co/Mn) are typically 1/1000 - 100/1, preferably 1/100 - 10/1 and more preferably 1/10 - 4/1.

Molar ratios of bromine to metals (e.g. Br/(Co+Mn)) are typically 0.001-5.00, preferably 0.01 - 2.00 and more preferably 0.1 - 0.9.

Catalyst concentration (Co + Mn) is typically from 0.1 to 10 mol %, relative to the substrate, with a preference for concentrations from 2 to 6 mol %. Good results were obtained in general with catalyst concentrations of around 4 mol %.

The starting materials for the production of FDCA may originate from a carbohydrate source as described above. Examples of such disclosures are WO 2007/104515 and WO 2009/030512. Accordingly, the invention also provides a method for the preparation of 2,5-furandicarboxylic acid wherein a carbohydrate source is converted in the presence of an alkyl carboxylic acid into products comprising an HMF ester and optionally 5-hydroxymethyl furfural, from which is isolated a feed comprising the ester of HMF and optionally 5-hydroxymethyl furfural, and which method further comprises the subsequent step of contacting the feed with an oxidant in the presence of an oxidation catalyst, in particular a cobalt and manganese and bromide-containing catalyst, under appropriate reaction conditions, in particular at temperatures higher than 140 °C

In another aspect, the FDCA obtained according to the process of the present invention can be transformed using common esterification reactions to a diester by contacting the starting material under appropriate conditions with the relevant alcohol. Thus, in one aspect, the invention also relates to the use of FDCA obtained according to the

process of the current invention in the preparation of a dialkylester of 2,5-dicarboxylic acid by reaction of the FDCA with a C<sub>1</sub>-C<sub>5</sub> alkyl alcohol, preferably methanol to prepare the dimethyl ester of FDCA.

5           Accordingly, the present invention also provides a process for the preparation of a dialkyl ester of 2,5,-furan dicarboxylic acid, comprising the step of contacting in a reactor 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  
10           more  
of these compounds with an oxidant oxygen-containing gas being continuously fed and removed to and from the reactor in the presence of an oxidation catalyst comprising at least one metal selected from Co and Mn, at a temperature higher than between 140 and 200 °C, at an oxygen partial pressure of 1 to 10 bar, wherein a solvent or solvent mixture comprising  
15           acetic acid or acetic acid and water mixtures is present and esterifying the thus obtained product. Preferably, the product is esterified with an alkyl alcohol, suitably having 1 to 5 carbon atoms.

                  The esterification of 2,5-furan dicarboxylic acid is known. As a specific example for the  
20           manufacture of these esters, reference is made to US 2673860 wherein the diester is obtained by transesterification of another dicarboxylic acid ester in the presence of sulphuric acid. A more general description for the esterification of dicarboxylic acids is presented in US 2628249.

                  In a further aspect of the invention, the di-methylester can be used in the preparation  
25           of polyester polymers by reaction with a diol. Reacting the di-methylester with a diol will result in the formation of methanol that quickly vaporises. In 1946 the polymerization of FDCA dimethyl ester with ethylene glycol was described as a first example of such a polymerization  
30           in GB 621,971.

                  Indeed, polyesters are generally made by a combined esterification/polycondensation reaction between monomer units of a diol (e.g., ethylene glycol (EG)) and a dicarboxylic acid.

                  Additives such as catalysts and stabilizers may be added to facilitate the process and  
35           stabilize the polyester towards degradation.

                  Examples:

Experiments were carried out in parallel 8 ml magnetically stirred stainless steel batch reactors. The reactors are grouped in blocks containing 12 batch reactors. The standard procedure for all the reactions was as follows:

5           0.5 ml of starting material stock solution in acetic acid (0.78 mmol/ml) were added into a reactor lined with a Teflon insert. To the reactor 1 ml of a catalyst stock solution in acetic acid was subsequently added. In a typical experiment, a catalyst composition Co/Mn/Br with a relative 1-x-y ratio, the concentration of  $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$  was varied. As a Mn source, 10  $\text{Mn}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$  was used and as a bromine source NaBr was used. The reactors were closed with a rubber septum, after which the reactors were sealed and pressurized to the desired air pressure, ranging from 20-60 bars. After pressurization, the block with 12 reactors 15 was placed in the test unit which was preheated at the desired temperature, ranging from

ranging from 100 to 220 °C. After the desired reaction time, ranging from 0.5 hr to 24 hrs, the block is placed into an ice bath for 20 minutes. When the block had cooled down, it was depressurized. After opening, HPLC samples were prepared. First 5 ml of a saccharine solution in DMSO (11.04 mg/ml) was added to each reactor and the mixture was stirred for 5 minutes. Then 10 µl of this mixture was diluted to 1000 µl with water in a HPLC vial. The samples were analyzed using HPLC.

#### Example 1

Example 1 shows the selectivity of FDCA in the oxidation of HMF, of a HMF/AMF 3/2 mixture, of a HMF/AMF 2/3 mixture and of AMF, respectively, with 2.7 mol% Co catalyst (relative to substrate), and Co/Mn molar ratio of 1/1, so that the catalyst concentration (Co + Mn) amounted to 5.4 mol%. The Br/(Co+Mn) molar ratio was 1.0; 0.7; 0.4 and 0.1 at 0.26 M substrate concentration in acetic acid at 180 [deg.]C for 1 hr with 20 bar air. The amount of oxygen was 2.69 mol oxygen per mol substrate. Under these conditions, higher Br amounts give higher yields but when Br/(Co+Mn) > 1, corrosion will be a problem on commercial scale. HMF gives slightly higher yields than AMF at one hour reaction time. The results of these experiments are given in Table 1.

#### Example 2

Example 2 shows the selectivity to FDCA for the AMF oxidation of Example 1, together with the comparative examples based on the experimental conditions described in US 2009/0156841. In those comparative experiments (2a and 2b) 10 wt/wt% AMF in acetic acid was oxidized with 1.75 and 2.65 mol % Co catalyst and a fixed Br/(Co + Mn) molar ratio of 1.0 and a Co/Mn molar ratio of 1.0 at 100 °C and 30 bar for 2 hours. The amount of oxygen was 2.88 mol oxygen per mol substrate. Under these conditions, the yield of FDCA was lower than the result suggested in US 2009/0156841 and also lower than the results obtained at higher temperature. The results of these experiments are given in Table 2.

#### Example 3

Example 3 shows the yield of FDCA in the oxidation of 5-methylfurfural (5MF) and 2,5-dimethylfuranfural (DMF) at 180 °C with 2.7 mol% Co catalyst (relative to substrate), and Co/Mn ratio of 1/1, so that the catalyst concentration (Co + Mn) amounted to 5.4 mol%. The Br/(Co+Mn) molar ratio was 1.0, 0.7, 0.4 and 0.1. The substrate concentration was 0.26 M in acetic acid. The reaction temperature was at 180 °C and the reaction was conducted with 50 bars air. The amount of oxygen was 6.7 mol oxygen per mol substrate. Under these conditions, higher Br amounts give higher yields but when Br/(Co+Mn) > 1, corrosion will be a problem on commercial scale. Reactions with 5-MF give higher yields than reactions with DMF. The results of these experiments are also given in Table 3.

Title: Method for the preparation of 2,5-furandicarboxylic acid and for the preparation of the dialkyl ester of 2,5-furandicarboxylic acid

The present invention relates to a method for the preparation of 2,5-furandicarboxylic acid ("FDCA") from 5-hydroxymethylfurfural ("HMF") and/or derivatives thereof. FDCA can be produced in particular from esters of HMF, such as for example 5-acetoxymethylfurfural (AMF) or a mixture of one or more of these compounds with HMF, such as for example from a mixture of AMF and HMF. The invention further relates to a process for the preparation of the dialkyl ester of 2,5-furandicarboxylic acid.

2,5-Furandicarboxylic acid, also known as dehydromucic acid is a furan derivative. This

organic compound was first obtained by Fittig and Heinzelmann in 1876. The first review, by Henry Hill was published in 1901 (Am. Chem. Journ. 25, 439). FDCA was more than 125 years later identified by the US Department of Energy as one of 12 priority chemicals for establishing the "green" chemistry industry of the future. However, to date, no commercial process exists for its production. On laboratory scale it is often synthesized from 5-hydroxymethylfurfural (HMF), which in turn can be obtained from carbohydrate containing sources such as glucose, fructose, sucrose and starch. From fructose and glucose HMF is obtained by acidic elimination of three moles of water.

The derivatives of HMF are identified as potential and versatile fuel components and precursors for the production of plastics. The polyester from FDCA dimethyl diester and ethylene glycol was first reported in 1946 (GB 621,971).

WO 01/72732 describes the oxidation of HMF to FDCA. The maximum FDCA yield reported is 59%, obtained at 105 °C. The oxidation of HMF in an aqueous medium with oxygen using a catalyst from the Pt-group is described in US 4977283. Taarning et al. described the oxidation of HMF over gold based catalysts (ChemSusChem, 2008, 1, 1-4).

Partenheimer et al (Adv. Synth. Catal. **2001**, 343, pp 102-11) describe the synthesis of 2,5-furandicarboxylic acid by catalytic air-oxidation of 5-hydroxymethylfurfural with metal/bromide catalysts such as Co/Mn/Br in acetic acid at temperatures ranging from 50 to 125 °C. With the Co/Mn/Br catalyst the highest FDCA yield obtained is 35.2% (Table 3, experiment 4). On page 103 of the same paper, under the header "products formed" it is stated: "A side reaction is the esterification of the alcohols to form the more oxidatively stable

acetate ...." As apparently 5-hydroxymethylfurfural reacts with acetic acid a loss of the starting material takes place. Further, in the reaction scheme given in Figure 1 on page 103, it is indicated that 5-(acetoxymethyl)furfural is an end-point. There is no further reaction of this compound indicated to FDCA (in contrast to the ester of the intermediate product 5-

(acetoxymethyl)furan-2-carboxylic acid). In other words, the 5-(acetoxymethyl)furfural (AMF) formed through reaction of HMF with acetic acid solvent, is not oxidized to FDCA and its formation leads therefore to yield loss.

This result was confirmed in US 2009/0156841. Although the intention of the process according to US 2009/0156841 was to obtain FDCA, the product isolated and erroneously characterized as being FDCA was in fact the starting material acetoxymethyl furfural (AMF). Under the low temperature conditions deployed (100 °C), AMF is quite stable, as was already reported by Partenheimer (see above).

In US 2009/0156841 a  $^1\text{H}$  NMR spectrum is shown in Figure 8 and suggested that it is the spectrum of the product that was identified as FDCA. However, this is not the case. The  $^1\text{H}$  NMR spectrum of the product shown in Figure 8 is the same as that in Figure 6 and represents the starting material AMF. The  $^1\text{H}$  NMR spectrum of FDCA shows a singlet at a shift of about 7.26 ppm. Moreover, the product is described as a tan solid. In the experience of the present inventors, AMF is a tan solid, while FDCA is a white solid. It would seem that no FDCA was obtained in the experiments according to US 2009/0156841.

The experiments executed under the conditions of US 2009/0156841 were repeated. These comparative experiments confirm the low reactivity of AMF under conditions given in US 2009/0156841. Thus, a person skilled in the art would therefore have concluded that FDCA cannot be obtained in interesting yields from AMF using the conditions that are reported in US 2009/0156841, i.e., using a Co/Mn/Br catalyst in acetic acid at between 85 and 110 °C within a time frame of from 100 and 150 minutes. In Example 7 of US 2009/0156841, slightly more than 50% of the starting material was the only product isolated from the reaction.

In the method according to WO 01/72732, FDCA is prepared by contacting HMF with an oxygen-containing gas in the presence of an oxidation catalyst comprising Co and Mn in a solvent comprising acetic acid. The reaction temperature may be between 50 and 250 °C, e.g. from 50 to 160 °C. Although in examples the reaction temperatures were generally in the range from 100 to 125 °C, a reaction stage in some examples was conducted at a temperature of 150 °C. WO 01/72732 is directed to five different processes, one of which is directed to a process for preparing a diacid, such as FDCA, from an alcohol/aldehyde, such as HMF. According to the examples, a yield on the desired diacid FDCA of up to 58.8% was obtainable.

Boisen et al., Chem Eng. Research Design, 87 (2009) 1318-1327 describes the conversion of sugars to FDCA in general terms. In particular it discusses the conversion of

HMF to FDCA referring to the work by the inventors of WO 01/72732. It concludes that the oxidation with Co/Mn/Zr/Br is conducted at atmospheric pressure and at 70 bar. It also refers to an oxidation over Pt on alumina, wherein the reaction temperature is 60 °C and a partial oxygen pressure of 0.2 bar.

5 WO 2008/054804 relates to the oxidation of HMF using air or O<sub>2</sub> as oxidant over a platinum-supported catalyst; the temperature ranges from about 50 to about 200 °C. A suitable pressure is 150 - 500 psi (about 10 to 34.5 bar). JP 2009 001519 discloses the oxidation of HMF over a catalyst containing Ru, Co and Ce with molecular oxygen. The temperature may be from 50 to 200 °C. The pressure is 10 – 400 bar. RU 636233 discloses  
10 the oxidation of HMF over a catalyst comprising CuO.Ag<sub>2</sub>O.Ce<sub>2</sub>O<sub>3</sub> on alumina. The oxidant is oxygen or air, the pressure is 25 - 30 atm and the temperature is 110 - 150 °C.

The present inventors have now surprisingly found that when using an oxidation catalyst, e.g., based on both cobalt and manganese and containing a bromide, at temperatures higher than 140 °C, derivatives of HMF, and in particular esters of HMF  
15 optionally in combination with HMF, such as for example 5-(acetoxymethyl)furfural (AMF) can be oxidized to FDCA in high yields.

Thus, in a first aspect the invention provides a method for the preparation of 2,5-furan  
20 dicarboxylic acid comprising the step of contacting in a reactor 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~~ oxygen-containing gas being continuously fed and removed to  
25 and from the reactor, in the presence of an oxidation catalyst comprising at least one metal selected from Co and Mn, at a temperature higher than between 140 and 200 °C at an oxygen partial pressure of 1 to 10 bar, wherein a solvent or solvent mixture comprising acetic acid or acetic acid and water mixtures is present. The feed may optionally comprise 5-hydroxymethylfurfural as a further compound.

30 The invention described hereinafter may use any of the compounds described above in the feed. A preferred ester of HMF contains an ester moiety of an alkyl carboxylic acid



wherein the alkyl group contains up to 6 carbon atoms, preferably from 1 to 5 carbon atoms, i.e. methyl, ethyl, propyl, isopropyl, butyl, 2-butyl, tert-butyl, pentyl, 2-pentyl, neopentyl and 3-

5 pentyl. Particularly preferred are alkyl groups with 1 to 4 carbon atoms. There is a preference for methyl, giving (5-acetoxymethyl)furfural. Hence, 5-acetoxymethylfurfural is the preferred feedstock, by itself or in combination with HMF.

10 In another aspect of the invention, we have also investigated the oxidation of other furan-based substrates under the process conditions according to the current invention. We have been able to convert 5-(chloromethyl)furfural, 5-(chloromethyl)furoic acid, 5-methylfurfural, 5-methylfuroic acid and 2,5-dimethylfuran all to FDCA in very interesting yields.

15 In WO 2007/104515 and WO 2009/030512, the synthesis of esters of HMF such as 5-acetoxymethylfurfural (AMF) from biomass sources is described. Given the higher stability of the HMF esters than HMF and hence improved production pathways and given the fact that upon oxidation in acetic acid the acetoxy functionality that was obtained from acetic acid is now liberated as acetic acid and given the green reputation of these esters, they were considered by the present inventors as interesting starting point in the preparation of furan-20 based monomers that could be used for the production of furandicarboxylic acid-based polyesters, for instance as an alternative for PET or FDCA-based polyamids (nylons). The most important conventional, oil-based, polyester monomer to produce PET is Purified Terephthalic acid (PTA) and its dialkyl ester DiMethyl Terephthalate (DMT).

25 AMF can be obtained from biomass sources as described in WO 2007/104515 and WO 2009/030512. Depending on the process conditions the product obtained in accordance with the process of these references may also contain HMF.

30 FDCA, the product of the reaction can be used in the preparation of a polyester, by reaction of FDCA or its dialkyl ester with a suitable diol. Such polyester preparations are preferably performed by transesterification, whereby the di-methyl ester or di-ethyl ester of FDCA is used and wherein the methyl or ethyl groups are exchanged in the form of a volatile alcohol during the transesterification with the diol.

The oxidation catalyst can be selected from a variety of oxidation catalysts, but is preferably a catalyst based on both cobalt and manganese and suitably containing a source of bromine, preferably a bromide.

35 The bromine source can be any compound that produces bromide ions in the reaction mixture. These compounds include hydrogen bromide, sodium bromide, elemental bromine,

benzyl bromide and tetrabromoethane. Also other bromine salts, such as an alkali or alkaline earth metal bromide or another metal bromide such as  $ZnBr_2$  can be used. There is a preference for hydrobromic acid or sodium bromide. The amount of bromine mentioned in here relates to the amount measured as Br relative to cobalt.

5

Suitable metal bromide catalysts employed in all of the processes of this invention comprise a cobalt compound and a manganese compound and a bromine-containing compound. Preferably these compounds are soluble in the reaction mixture.

Preferably, the catalyst comprises both Co and Mn. The metal and bromide catalyst contains, in addition to bromide, Co and Mn and optionally may contain one or more additional metals, in particular Zr and/or Ce. Alternative and suitable catalysts are described in W. Partenheimer, *Catalysis Today* 23(2), 69-158 (1995) in particular on pages 89-99, included herein by reference.

Each of the metal components can be provided in any of their known ionic forms. Preferably the metal or metals are in a form that is soluble in the reaction solvent. Examples of suitable counterions for cobalt and manganese include, but are not limited to, carbonate, acetate, acetate tetrahydrate and halide, with bromide being the preferred halide.

As described in Partenheimer, *ibid*, pages 86-88, suitable solvents for use in the processes of the present invention, described above, preferably have at least one component that contains a monocarboxylic acid functional group. The solvent may also function as one of the reagents. The processes may be run in a solvent or solvent mixture that does not contain an acid group. In that case, preferably one of the reagents does contain a monocarboxylic acid functional group. Suitable solvents can also be aromatic acids

such as benzoic acid and derivatives thereof. ~~A preferred~~ The solvent in the present process is an ~~comprises~~ aliphatic C<sub>2</sub>-C<sub>6</sub> monocarboxylic acid, such as but not limited to acetic acid, propionic acid, n-butylric acid, isobutyric acid, n-valeric acid, trimethylacetic acid, and caproic acid and mixtures thereof. Said ~~A~~ mixtures may also include benzene, acetonitrile, heptane, acetic anhydride, chlorobenzene, o-dichlorobenzene, and water. The most preferred solvent is acetic acid ("AcOH").

The oxidant in the processes of the present invention is preferably an oxygen-containing gas or gas mixture, such as, but not limited to air and oxygen-enriched air. Oxygen by itself is also a preferred oxidant.

The processes of the instant invention described above can be conducted in a batch, semi-continuous or continuous mode. Especially for the manufacture of FDCA, 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 desirable. For example, variation of the catalyst composition during the reaction can be accomplished by addition of cobalt and/or manganese and/or zirconium, and/or cerium, and/or bromide at specified times.

\_\_\_\_ The pressure in a commercial oxidation process may vary within wide ranges. ~~When~~ As  
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diluent is present, and in particular with acetic acid as diluent, the temperature and the  
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(e.g., acetic acid) pressure at a certain temperature. The pressure of the reaction mixture is preferably selected such that the solvent is mainly in the liquid phase. In practice this means that pressures between 5 and 100 bar can be used with a preference for pressures between 10 and 80 bar. In ~~case the oxidant is the process according to the present invention an~~ oxygen-containing gas, such as air, the gas ~~can be~~ is continuously fed to and removed from the reactor, ~~or the gas can be supplied all at the start of the reaction. In the latter case, the pressure of the system will depend on the headspace volume and the amount of gas required to convert the starting material. It is clear that in the latter case, the pressure of the system may be significantly higher than the pressure in a process wherein an oxygen~~ containing gas is continuously fed and removed. In the case of continuously feeding and removing the oxidant gas to and from the reactor, the oxygen partial pressure will suitably be between 1 and 30 bar or more preferably is between 1 and 10 bar.

The temperature of the reaction mixture is ~~at least 140 °C,~~ preferably from 140 and 200 °C, most preferably between 160 and 190 °C. Temperatures higher than 180 °C may lead to decarboxylation and to other degradation products. Good results to FDCA have been achieved at a temperature of about 180 °C.

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Molar ratios of bromine to metals (e.g. Br/(Co+Mn)) are typically 0.001-5.00, preferably 0.01 - 2.00 and more preferably 0.1 - 0.9.

Catalyst concentration (Co + Mn) is typically from 0.1 to 10 mol %, relative to the substrate, with a preference for concentrations from 2 to 6 mol %. Good results were obtained in general with catalyst concentrations of around 4 mol %.

The starting materials for the production of FDCA may originate from a carbohydrate source as described above. Examples of such disclosures are WO 2007/104515 and WO 2009/030512. Accordingly, the invention also provides a method for the preparation of 2,5-furandicarboxylic acid wherein a carbohydrate source is converted in the presence of an alkyl carboxylic acid into products comprising an HMF ester and optionally 5-hydroxymethyl furfural, from which is isolated a feed comprising the ester of HMF and optionally 5-hydroxymethyl furfural, and which method further comprises the subsequent step of contacting the feed with an oxidant in the presence of an oxidation catalyst, in particular a cobalt and manganese and bromide-containing catalyst, under appropriate reaction conditions, in particular at temperatures higher than 140 °C

In another aspect, the FDCA obtained according to the process of the present invention can be transformed using common esterification reactions to a diester by contacting the starting material under appropriate conditions with the relevant alcohol. Thus, in one aspect, the invention also relates to the use of FDCA obtained according to the

process of the current invention in the preparation of a dialkylester of 2,5-dicarboxylic acid by reaction of the FDCA with a C<sub>1</sub>-C<sub>5</sub> alkyl alcohol, preferably methanol to prepare the dimethyl ester of FDCA.

5           Accordingly, the present invention also provides a process for the preparation of a dialkyl ester of 2,5,-furan dicarboxylic acid, comprising the step of contacting in a reactor 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  
10 more of these compounds with an oxidant oxygen-containing gas being continuously fed and removed to and from the reactor in the presence of an oxidation catalyst comprising at least one metal selected from Co and Mn, at a temperature higher than between 140 and 200 °C at an oxygen partial pressure of 1 to 10 bar, wherein a solvent or solvent mixture comprising  
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          The esterification of 2,5-furan dicarboxylic acid is known. As a specific example for the  
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          Additives such as catalysts and stabilizers may be added to facilitate the process and  
35 stabilize the polyester towards degradation.

          Examples:

Experiments were carried out in parallel 8 ml magnetically stirred stainless steel batch reactors. The reactors are grouped in blocks containing 12 batch reactors. The standard procedure for all the reactions was as follows:

5           0.5 ml of starting material stock solution in acetic acid (0.78 mmol/ml) were added into a reactor lined with a Teflon insert. To the reactor 1 ml of a catalyst stock solution in acetic acid was subsequently added. In a typical experiment, a catalyst composition Co/Mn/Br with a relative 1-x-y ratio, the concentration of  $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$  was varied. As a Mn source, 10  $\text{Mn}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$  was used and as a bromine source NaBr was used. The reactors were closed with a rubber septum, after which the reactors were sealed and pressurized to the desired air pressure, ranging from 20-60 bars. After pressurization, the block with 12 reactors 15 was placed in the test unit which was preheated at the desired temperature, ranging from

ranging from 100 to 220 °C. After the desired reaction time, ranging from 0.5 hr to 24 hrs, the block is placed into an ice bath for 20 minutes. When the block had cooled down, it was depressurized. After opening, HPLC samples were prepared. First 5 ml of a saccharine solution in DMSO (11.04 mg/ml) was added to each reactor and the mixture was stirred for 5 minutes. Then 10 µl of this mixture was diluted to 1000 µl with water in a HPLC vial. The samples were analyzed using HPLC.

#### Example 1

Example 1 shows the selectivity of FDCA in the oxidation of HMF, of a HMF/AMF 3/2 mixture, of a HMF/AMF 2/3 mixture and of AMF, respectively, with 2.7 mol% Co catalyst (relative to substrate), and Co/Mn molar ratio of 1/1, so that the catalyst concentration (Co + Mn) amounted to 5.4 mol%. The Br/(Co+Mn) molar ratio was 1.0; 0.7; 0.4 and 0.1 at 0.26 M substrate concentration in acetic acid at 180 °C for 1 hr with 20 bar air. The amount of oxygen was 2.69 mol oxygen per mol substrate. Under these conditions, higher Br amounts give higher yields but when Br/(Co+Mn) > 1, corrosion will be a problem on commercial scale. HMF gives slightly higher yields than AMF at one hour reaction time. The results of these experiments are given in Table 1.

#### Example 2

Example 2 shows the selectivity to FDCA for the AMF oxidation of Example 1, together with the comparative examples based on the experimental conditions described in US 2009/0156841. In those comparative experiments (2a and 2b) 10 wt/wt% AMF in acetic acid was oxidized with 1.75 and 2.65 mol % Co catalyst and a fixed Br/(Co + Mn) molar ratio of 1.0 and a Co/Mn molar ratio of 1.0 at 100 °C and 30 bar for 2 hours. The amount of oxygen was 2.88 mol oxygen per mol substrate. Under these conditions, the yield of FDCA was lower than the result suggested in US 2009/0156841 and also lower than the results obtained at higher temperature. The results of these experiments are given in Table 2.

#### Example 3

Example 3 shows the yield of FDCA in the oxidation of 5-methylfurfural (5MF) and 2,5-dimethylfuranfural (DMF) at 180 °C with 2.7 mol% Co catalyst (relative to substrate), and Co/Mn ratio of 1/1, so that the catalyst concentration (Co + Mn) amounted to 5.4 mol%. The Br/(Co+Mn) molar ratio was 1.0, 0.7, 0.4 and 0.1. The substrate concentration was 0.26 M in acetic acid. The reaction temperature was at 180 °C and the reaction was conducted with 50 bars air. The amount of oxygen was 6.7 mol oxygen per mol substrate. Under these conditions, higher Br amounts give higher yields but when Br/(Co+Mn) > 1, corrosion will be a problem on commercial scale. Reactions with 5-MF give higher yields than reactions with DMF. The results of these experiments are also given in Table 3.



## CLAIMS

1. Method for the preparation of 2,5-furan dicarboxylic acid comprising the step of  
5 contacting in a reactor 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 oxygen-containing gas being  
continuously fed and removed to and from the reactor in the presence of an oxidation catalyst  
10 comprising at least one metal selected from Co and Mn, at a temperature between 140 and  
200 °C at an oxygen partial pressure of 1 to 10 bar, wherein a solvent or solvent mixture  
comprising acetic acid or acetic acid and water mixtures is present.

2. Method according to claim 1, wherein the feed comprises a compound selected  
15 from the group consisting of 5-hydroxymethylfurfural ("HMF"), esters of HMF and a mixture  
thereof.

3. Method according to claim 1 or 2, wherein the oxidation catalyst comprises a  
source of bromine.  
20

4. Method according to claim 3, wherein the oxidation catalyst contains both Co and  
Mn.

5. Method according to claim 4, wherein the oxidation catalyst comprises at least one  
25 additional metal.

6. Method according to claim 5, wherein the additional metal is Zr and/or Ce.

7. Method according to claims 1-6, wherein the oxygen-containing gas is selected  
30 from oxygen, air or other oxygen-containing gases.

8. Method according to any of the previous claims wherein the temperature is  
between 160 and 190 °C.

35 9. Method according to any of the previous claims, wherein the feed comprises an  
ester of HMF containing an ester moiety of an alkyl carboxylic acid wherein the alkyl group  
contains up to 6 carbon atoms, preferably from 1 to 5 carbon atoms.

10. Process for the preparation of a dialkyl ester of 2,5-furan dicarboxylic acid, comprising the step of contacting in a reactor a feed comprising a compound selected from the group consisting of 5-hydroxymethyl-furfural ("HMF"), an ester of 5-hydroxymethyl-  
5 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 oxygen-containing gas being continuously fed and removed to and from the reactor, in the presence of an oxidation catalyst comprising at least one metal selected from Co and Mn, at a temperature between 140 and 200 °C at an oxygen partial pressure of 1 to 10 bar wherein a  
10 solvent or solvent mixture comprising acetic acid or acetic acid and water mixtures, is present, and esterifying the thus obtained product.

11. Process according to claim 10, wherein the product is esterified with a C<sub>1</sub>-C<sub>5</sub> alkyl alcohol.  
15

12. Process according to claim 11, wherein the C<sub>1</sub>-C<sub>5</sub> alkyl alcohol is methanol and the dialkyl ester is the dimethylester of 2,5-furan dicarboxylic acid.

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## Auxiliary Request

## CLAIMS

1. Method for the preparation of 2,5-furan dicarboxylic acid comprising the step of  
5 contacting in a reactor a feed comprising a compound selected from the group consisting of  
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 oxygen-containing gas being continuously fed and removed to and from  
10 the reactor in the presence of an oxidation catalyst comprising at least one metal selected  
from Co and Mn, at a temperature between 140 and 200 °C at an oxygen partial pressure of  
1 to 10 bar, wherein a solvent or solvent mixture comprising acetic acid or acetic acid and  
water mixtures is present.

2. Method according to claim 1, wherein the feed comprises a compound selected  
15 from the group consisting of esters of 5-hydroxymethylfurfural ("HMF") and a mixture of  
esters of HMF and HMF.

3. Method according to claim 1 or 2, wherein the oxidation catalyst comprises a  
source of bromine.

20

4. Method according to claim 3, wherein the oxidation catalyst contains both Co and  
Mn.

5. Method according to claim 4, wherein the oxidation catalyst comprises at least one  
25 additional metal.

6. Method according to claim 5, wherein the additional metal is Zr and/or Ce.

7. Method according to claims 1-6, wherein the oxygen-containing gas is selected  
30 from oxygen, air or other oxygen-containing gases.

8. Method according to any of the previous claims wherein the temperature is  
between 160 and 190 °C.

35 9. Method according to any of the previous claims, wherein the feed comprises an  
ester of HMF containing an ester moiety of an alkyl carboxylic acid wherein the alkyl group  
contains up to 6 carbon atoms, preferably from 1 to 5 carbon atoms.

10. Process for the preparation of a dialkyl ester of 2,5-furan dicarboxylic acid, comprising the step of contacting in a reactor a feed comprising a compound selected from the group

5 consisting of 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 oxygen-containing gas being continuously fed and removed to and from the reactor, in the presence of an oxidation catalyst comprising at least one metal selected from Co and Mn, at a temperature between 140 and 200 °C at an  
10 oxygen partial pressure of 1 to 10 bar wherein a solvent or solvent mixture comprising acetic acid or acetic acid and water mixtures, is present, and esterifying the thus obtained product.

11. Process according to claim 10, wherein the product is esterified with a C<sub>1</sub>-C<sub>5</sub> alkyl alcohol.

15

12. Process according to claim 11, wherein the C<sub>1</sub>-C<sub>5</sub> alkyl alcohol is methanol and the dialkyl ester is the dimethylester of 2,5-furan dicarboxylic acid.

Auxiliary Request

Title: Method for the preparation of 2,5-furandicarboxylic acid and for the preparation of the dialkyl ester of 2,5-furandicarboxylic acid

5           The present invention relates to a method for the preparation of 2,5-furandicarboxylic acid ("FDCA") from 5-hydroxymethylfurfural ("HMF") and/or derivatives thereof. FDCA can be produced in particular from esters of HMF, such as for example 5-acetoxymethylfurfural (AMF) or a mixture of one or more of these compounds with HMF, such as for example from a mixture of AMF and HMF. The invention further relates to a process for the preparation of  
10 the dialkyl ester of 2,5-furandicarboxylic acid.

          2,5-Furandicarboxylic acid, also known as dehydromucic acid is a furan derivative. This organic compound was first obtained by Fittig and Heinzelmann in 1876. The first review, by Henry Hill was published in 1901 (Am. Chem. Journ. 25, 439). FDCA was more than 125  
15 years later identified by the US Department of Energy as one of 12 priority chemicals for establishing the "green" chemistry industry of the future. However, to date, no commercial process exists for its production. On laboratory scale it is often synthesized from 5-hydroxymethylfurfural (HMF), which in turn can be obtained from carbohydrate containing sources such as glucose, fructose, sucrose and starch. From fructose and glucose HMF is  
20 obtained by acidic elimination of three moles of water.

          The derivatives of HMF are identified as potential and versatile fuel components and precursors for the production of plastics. The polyester from FDCA dimethyl diester and ethylene glycol was first reported in 1946 (GB 621,971).

          WO 01/72732 describes the oxidation of HMF to FDCA. The maximum FDCA yield  
25 reported is 59%, obtained at 105 °C. The oxidation of HMF in an aqueous medium with oxygen using a catalyst from the Pt-group is described in US 4977283. Taarning et al. described the oxidation of HMF over gold based catalysts (ChemSusChem, 2008, 1, 1-4).

          Partenheimer et al (Adv. Synth. Catal. **2001**, 343, pp 102-11) describe the synthesis of 2,5-furandicarboxylic acid by catalytic air-oxidation of 5-hydroxymethylfurfural with  
30 metal/bromide catalysts such as Co/Mn/Br in acetic acid at temperatures ranging from 50 to 125 °C. With the Co/Mn/Br catalyst the highest FDCA yield obtained is 35.2% (Table 3, experiment 4). On page 103 of the same paper, under the header "products formed" it is stated: "A side reaction is the esterification of the alcohols to form the more oxidatively stable  
35 acetate ...." As apparently 5-hydroxymethylfurfural reacts with acetic acid a loss of the starting material takes place. Further, in the reaction scheme given in Figure 1 on page 103, it is indicated that 5-(acetoxymethyl)furfural is an end-point. There is no further reaction of

this compound indicated to FDCA (in contrast to the ester of the intermediate product 5-

(acetoxymethyl)furan-2-carboxylic acid). In other words, the 5-(acetoxymethyl)furfural (AMF) formed through reaction of HMF with acetic acid solvent, is not oxidized to FDCA and its formation leads therefore to yield loss.

This result was confirmed in US 2009/0156841. Although the intention of the process according to US 2009/0156841 was to obtain FDCA, the product isolated and erroneously characterized as being FDCA was in fact the starting material acetoxymethyl furfural (AMF). Under the low temperature conditions deployed (100 °C), AMF is quite stable, as was already reported by Partenheimer (see above).

In US 2009/0156841 a  $^1\text{H}$  NMR spectrum is shown in Figure 8 and suggested that it is the spectrum of the product that was identified as FDCA. However, this is not the case. The  $^1\text{H}$  NMR spectrum of the product shown in Figure 8 is the same as that in Figure 6 and represents the starting material AMF. The  $^1\text{H}$  NMR spectrum of FDCA shows a singlet at a shift of about 7.26 ppm. Moreover, the product is described as a tan solid. In the experience of the present inventors, AMF is a tan solid, while FDCA is a white solid. It would seem that no FDCA was obtained in the experiments according to US 2009/0156841.

The experiments executed under the conditions of US 2009/0156841 were repeated. These comparative experiments confirm the low reactivity of AMF under conditions given in US 2009/0156841. Thus, a person skilled in the art would therefore have concluded that FDCA cannot be obtained in interesting yields from AMF using the conditions that are reported in US 2009/0156841, i.e., using a Co/Mn/Br catalyst in acetic acid at between 85 and 110 °C within a time frame of from 100 and 150 minutes. In Example 7 of US 2009/0156841, slightly more than 50% of the starting material was the only product isolated from the reaction.

In the method according to WO 01/72732, FDCA is prepared by contacting HMF with an oxygen-containing gas in the presence of an oxidation catalyst comprising Co and Mn in a solvent comprising acetic acid. The reaction temperature may be between 50 and 250 °C, e.g. from 50 to 160 °C. Although in examples the reaction temperatures were generally in the range from 100 to 125 °C, a reaction stage in some examples was conducted at a temperature of 150 °C. WO 01/72732 is directed to five different processes, one of which is directed to a process for preparing a diacid, such as FDCA, from an alcohol/aldehyde, such as HMF. According to the examples, a yield on the desired diacid FDCA of up to 58.8% was obtainable.

Boisen et al., Chem Eng. Research Design, 87 (2009) 1318-1327 describes the conversion of sugars to FDCA in general terms. In particular it discusses the conversion of

HMF to FDCA referring to the work by the inventors of WO 01/72732. It concludes that the oxidation with Co/Mn/Zr/Br is conducted at atmospheric pressure and at 70 bar. It also refers to an oxidation over Pt on alumina, wherein the reaction temperature is 60 °C and a partial oxygen pressure of 0.2 bar.

5 WO 2008/054804 relates to the oxidation of HMF using air or O<sub>2</sub> as oxidant over a platinum-supported catalyst; the temperature ranges from about 50 to about 200 °C. A suitable pressure is 150 - 500 psi (about 10 to 34.5 bar). JP 2009 001519 discloses the oxidation of HMF over a catalyst containing Ru, Co and Ce with molecular oxygen. The temperature may be from 50 to 200 °C. The pressure is 10 – 400 bar. RU 636233 discloses  
10 the oxidation of HMF over a catalyst comprising CuO.Ag<sub>2</sub>O.Ce<sub>2</sub>O<sub>3</sub> on alumina. The oxidant is oxygen or air, the pressure is 25 - 30 atm and the temperature is 110 - 150 °C.

The present inventors have now surprisingly found that when using an oxidation catalyst, e.g., based on both cobalt and manganese and containing a bromide, at temperatures higher than 140 °C, derivatives of HMF, and in particular esters of HMF  
15 optionally in combination with HMF, such as for example 5-(acetoxymethyl)furfural (AMF) can be oxidized to FDCA in high yields.

Thus, in a first aspect the invention provides a method for the preparation of 2,5-furan  
20 dicarboxylic acid comprising the step of contacting in a reactor a feed comprising a compound selected from the group consisting of 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 oxygen-containing gas being continuously fed and removed to and from the reactor, in the presence of an  
25 oxidation catalyst comprising at least one metal selected from Co and Mn, at a temperature between 140 and 200°C at an oxygen partial pressure of 1 to 10 bar, wherein a solvent or solvent mixture comprising acetic acid or acetic acid and water mixtures is present.. The feed may optionally comprise 5-hydroxymethylfurfural as a further compound.

The invention described hereinafter may use any of the compounds described above  
30 in the feed. A preferred ester of HMF contains an ester moiety of an alkyl carboxylic acid



wherein the alkyl group contains up to 6 carbon atoms, preferably from 1 to 5 carbon atoms, i.e. methyl, ethyl, propyl, isopropyl, butyl, 2-butyl, tert-butyl, pentyl, 2-pentyl, neopentyl and 3-

5 pentyl. Particularly preferred are alkyl groups with 1 to 4 carbon atoms. There is a preference for methyl, giving (5-acetoxymethyl)furfural. Hence, 5-acetoxymethylfurfural is the preferred feedstock, by itself or in combination with HMF.

10 In another aspect of the invention, we have also investigated the oxidation of other furan-based substrates under the process conditions according to the current invention. We have been able to convert 5-(chloromethyl)furfural, 5-(chloromethyl)furoic acid, 5-methylfurfural, 5-methylfuroic acid and 2,5-dimethylfuran all to FDCA in very interesting yields.

15 In WO 2007/104515 and WO 2009/030512, the synthesis of esters of HMF such as 5-acetoxymethylfurfural (AMF) from biomass sources is described. Given the higher stability of the HMF esters than HMF and hence improved production pathways and given the fact that upon oxidation in acetic acid the acetoxy functionality that was obtained from acetic acid is now liberated as acetic acid and given the green reputation of these esters, they were considered by the present inventors as interesting starting point in the preparation of furan-20 based monomers that could be used for the production of furandicarboxylic acid-based polyesters, for instance as an alternative for PET or FDCA-based polyamids (nylons). The most important conventional, oil-based, polyester monomer to produce PET is Purified Terephthalic acid (PTA) and its dialkyl ester DiMethyl Terephthalate (DMT).

25 AMF can be obtained from biomass sources as described in WO 2007/104515 and WO 2009/030512. Depending on the process conditions the product obtained in accordance with the process of these references may also contain HMF.

30 FDCA, the product of the reaction can be used in the preparation of a polyester, by reaction of FDCA or its dialkyl ester with a suitable diol. Such polyester preparations are preferably performed by transesterification, whereby the di-methyl ester or di-ethyl ester of FDCA is used and wherein the methyl or ethyl groups are exchanged in the form of a volatile alcohol during the transesterification with the diol.

The oxidation catalyst can be selected from a variety of oxidation catalysts, but is preferably a catalyst based on both cobalt and manganese and suitably containing a source of bromine, preferably a bromide.

35 The bromine source can be any compound that produces bromide ions in the reaction mixture. These compounds include hydrogen bromide, sodium bromide, elemental bromine,

benzyl bromide and tetrabromoethane. Also other bromine salts, such as an alkali or alkaline earth metal bromide or another metal bromide such as  $ZnBr_2$  can be used. There is a preference for hydrobromic acid or sodium bromide. The amount of bromine mentioned in here relates to the amount measured as Br relative to cobalt.

5

Suitable metal bromide catalysts employed in all of the processes of this invention comprise a cobalt compound and a manganese compound and a bromine-containing compound. Preferably these compounds are soluble in the reaction mixture.

5 Preferably, the catalyst comprises both Co and Mn. The metal and bromide catalyst contains, in addition to bromide, Co and Mn and optionally may contain one or more additional metals, in particular Zr and/or Ce. Alternative and suitable catalysts are described in W. Partenheimer, *Catalysis Today* 23(2), 69-158 (1995) in particular on pages 89-99.

10 Each of the metal components can be provided in any of their known ionic forms. Preferably the metal or metals are in a form that is soluble in the reaction solvent. Examples of suitable counterions for cobalt and manganese include, but are not limited to, carbonate, acetate, acetate tetrahydrate and halide, with bromide being the preferred halide.

15 As described in Partenheimer, *ibid*, pages 86-88, suitable solvents for use in the processes of the present invention, described above, preferably have at least one component that contains a monocarboxylic acid functional group. The solvent may also function as one of the reagents. The processes may be run in a solvent or solvent mixture that does not contain an acid group. In that case, preferably one of the reagents does contain a monocarboxylic acid functional group. Suitable solvents can also be aromatic acids  
20 such as benzoic acid and derivatives thereof. The solvent in the present process comprises acetic acid . A mixture may also include water. The most preferred solvent is acetic acid ("AcOH").

The oxidant in the processes of the present invention is an oxygen-containing gas or gas mixture, such as, but not limited to air and oxygen-enriched air. Oxygen by itself is also a preferred oxidant.

25 The processes of the instant invention described above can be conducted in a batch, semi-continuous or continuous mode. Especially for the manufacture of FDCA, 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  
30 the catalyst composition during the reaction is desirable. For example, variation of the catalyst composition during the reaction can be accomplished by addition of cobalt and/or manganese and/or zirconium, and/or cerium, and/or bromide at specified times.

35 The pressure in a commercial oxidation process may vary within wide ranges. As a diluent is present, and in particular with acetic acid as diluent, the temperature and the pressure in such a process are not independent. The pressure is determined by the solvent

(e.g., acetic acid) pressure at a certain temperature. The pressure of the reaction mixture is preferably selected such that the solvent is mainly in the liquid phase. In practice this means that pressures between 5 and 100 bar can be used with a preference for pressures between 10 and 80 bar. In the process according to the present invention an oxygen-containing gas, such as air, the gas is continuously fed to and removed from the reactor. In the case of continuously feeding and removing the oxidant gas to and from the reactor, the oxygen partial pressure will suitably be between 1 and 30 bar or more preferably between 1 and 10 bar.

The temperature of the reaction mixture is from 140 and 200 °C, most preferably between 160 and 190 °C. Temperatures higher than 180 °C may lead to decarboxylation and to other degradation products. Good results to FDCA have been achieved at a temperature of about 180 °C.

Molar ratios of cobalt to manganese (Co/Mn) are typically 1/1000 - 100/1, preferably 1/100 - 10/1 and more preferably 1/10 - 4/1.

Molar ratios of bromine to metals (e.g. Br/(Co+Mn)) are typically 0.001-5.00, preferably 0.01 - 2.00 and more preferably 0.1 - 0.9.

Catalyst concentration (Co + Mn) is typically from 0.1 to 10 mol %, relative to the substrate, with a preference for concentrations from 2 to 6 mol %. Good results were obtained in general with catalyst concentrations of around 4 mol %.

The starting materials for the production of FDCA may originate from a carbohydrate source as described above. Examples of such disclosures are WO 2007/104515 and WO 2009/030512. Accordingly, the invention also provides a method for the preparation of 2,5-furandicarboxylic acid wherein a carbohydrate source is converted in the presence of an alkyl carboxylic acid into products comprising an HMF ester and optionally 5-hydroxymethyl furfural, from which is isolated a feed comprising the ester of HMF and optionally 5-hydroxymethyl furfural, and which method further comprises the subsequent step of contacting the feed with an oxidant in the presence of an oxidation catalyst, in particular a cobalt and manganese and bromide-containing catalyst, under appropriate reaction conditions, in particular at temperatures higher than 140 °C

In another aspect, the FDCA obtained according to the process of the present invention can be transformed using common esterification reactions to a diester by contacting the starting material under appropriate conditions with the relevant alcohol. Thus, in one aspect, the invention also relates to the use of FDCA obtained according to the

process of the current invention in the preparation of a dialkylester of 2,5-dicarboxylic acid by reaction of the FDCA with a C<sub>1</sub>-C<sub>5</sub> alkyl alcohol, preferably methanol to prepare the dimethyl ester of FDCA.

5           Accordingly, the present invention also provides a process for the preparation of a dialkyl ester of 2,5,-furan dicarboxylic acid, comprising the step of contacting in a reactor a feed comprising a compound selected from the group consisting of 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  
10 more of these compounds with an oxygen-containing gas being continuously fed and removed to and from the reactor in the presence of an oxidation catalyst comprising at least one metal selected from Co and Mn, at a temperature between 140 and 200 °C, at an oxygen partial pressure of 1 to 10 bar, wherein a solvent or solvent mixture comprising acetic acid or acetic  
15 acid and water mixtures is present and esterifying the thus obtained product. Preferably, the product is esterified with an alkyl alcohol, suitably having 1 to 5 carbon atoms.

The esterification of 2,5-furan dicarboxylic acid is known. As a specific example for the manufacture of these esters, reference is made to US 2673860 wherein the diester is  
20 obtained by transesterification of another dicarboxylic acid ester in the presence of sulphuric acid. A more general description for the esterification of dicarboxylic acids is presented in US 2628249.

In a further aspect of the invention, the di-methylester can be used in the preparation of polyester polymers by reaction with a diol. Reacting the di-methylester with a diol will  
25 result in the formation of methanol that quickly vaporises. In 1946 the polymerization of FDCA dimethyl ester with ethylene glycol was described as a first example of such a polymerization in GB 621,971.

30           Indeed, polyesters are generally made by a combined esterification/polycondensation reaction between monomer units of a diol (e.g., ethylene glycol (EG)) and a dicarboxylic acid.

Additives such as catalysts and stabilizers may be added to facilitate the process and stabilize the polyester towards degradation.

35           Examples:

Experiments were carried out in parallel 8 ml magnetically stirred stainless steel batch

reactors. The reactors are grouped in blocks containing 12 batch reactors. The standard procedure for all the reactions was as follows:

0.5 ml of starting material stock solution in acetic acid (0.78 mmol/ml) were added into

- 5 a reactor lined with a Teflon insert. To the reactor 1 ml of a catalyst stock solution in acetic acid was subsequently added. In a typical experiment, a catalyst composition Co/Mn/Br with a relative 1-x-y ratio, the concentration of  $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$  was varied. As a Mn source,  $\text{Mn}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$  was used and as a bromine source NaBr was used. The reactors were
- 10 closed with a rubber septum, after which the reactors were sealed and pressurized to the desired air pressure, ranging from 20-60 bars. After pressurization, the block with 12 reactors
- was placed in the test unit which was preheated at the desired temperature, ranging from

100 to 220 °C. After the desired reaction time, ranging from 0.5 hr to 24 hrs, the block is placed into an ice bath for 20 minutes. When the block had cooled down, it was depressurized. After opening, HPLC samples were prepared. First 5 ml of a saccharine solution in DMSO (11.04 mg/ml) was added to each reactor and the mixture was stirred for 5 minutes. Then 10 µl of this mixture was diluted to 1000 µl with water in a HPLC vial. The samples were analyzed using HPLC.

#### Example 1

Example 1 shows the selectivity of FDCA in the oxidation of HMF, of a HMF/AMF 3/2 mixture, of a HMF/AMF 2/3 mixture and of AMF, respectively, with 2.7 mol% Co catalyst (relative to substrate), and Co/Mn molar ratio of 1/1, so that the catalyst concentration (Co + Mn) amounted to 5.4 mol%. The Br/(Co+Mn) molar ratio was 1.0; 0.7; 0.4 and 0.1 at 0.26 M substrate concentration in acetic acid at 180 [deg.]C for 1 hr with 20 bar air. The amount of oxygen was 2.69 mol oxygen per mol substrate. Under these conditions, higher Br amounts give higher yields but when Br/(Co+Mn) > 1, corrosion will be a problem on commercial scale. HMF gives slightly higher yields than AMF at one hour reaction time. The results of these experiments are given in Table 1.

#### Example 2

Example 2 shows the selectivity to FDCA for the AMF oxidation of Example 1, together with the comparative examples based on the experimental conditions described in US 2009/0156841. In those comparative experiments (2a and 2b) 10 wt/wt% AMF in acetic acid was oxidized with 1.75 and 2.65 mol % Co catalyst and a fixed Br/(Co + Mn) molar ratio of 1.0 and a Co/Mn molar ratio of 1.0 at 100 °C and 30 bar for 2 hours. The amount of oxygen was 2.88 mol oxygen per mol substrate. Under these conditions, the yield of FDCA was lower than the result suggested in US 2009/0156841 and also lower than the results obtained at higher temperature. The results of these experiments are given in Table 2.

#### Example 3

Example 3 shows the yield of FDCA in the oxidation of 5-methylfurfural (5MF) and 2,5-dimethylfuran (DMF) at 180 °C with 2.7 mol% Co catalyst (relative to substrate), and Co/Mn ratio of 1/1, so that the catalyst concentration (Co + Mn) amounted to 5.4 mol%. The Br/(Co+Mn) molar ratio was 1.0, 0.7, 0.4 and 0.1. The substrate concentration was 0.26 M in acetic acid. The reaction temperature was at 180 °C and the reaction was conducted with 50 bars air. The amount of oxygen was 6.7 mol oxygen per mol substrate. Under these conditions, higher Br amounts give higher yields but when Br/(Co+Mn) > 1, corrosion will be a problem on commercial scale. Reactions with 5-MF give higher yields than reactions with DMF. The results of these experiments are also given in Table 3.

Title: Method for the preparation of 2,5-furandicarboxylic acid and for the preparation of the dialkyl ester of 2,5-furandicarboxylic acid

The present invention relates to a method for the preparation of 2,5-furandicarboxylic acid ("FDCA") from 5-hydroxymethylfurfural ("HMF") and/or derivatives thereof. FDCA can be produced in particular from esters of HMF, such as for example 5-acetoxymethylfurfural (AMF) or a mixture of one or more of these compounds with HMF, such as for example from a mixture of AMF and HMF. The invention further relates to a process for the preparation of the dialkyl ester of 2,5-furandicarboxylic acid.

2,5-Furandicarboxylic acid, also known as dehydromucic acid is a furan derivative. This

organic compound was first obtained by Fittig and Heinzelmann in 1876. The first review, by Henry Hill was published in 1901 (Am. Chem. Journ. 25, 439). FDCA was more than 125 years later identified by the US Department of Energy as one of 12 priority chemicals for establishing the "green" chemistry industry of the future. However, to date, no commercial process exists for its production. On laboratory scale it is often synthesized from 5-hydroxymethylfurfural (HMF), which in turn can be obtained from carbohydrate containing sources such as glucose, fructose, sucrose and starch. From fructose and glucose HMF is obtained by acidic elimination of three moles of water.

The derivatives of HMF are identified as potential and versatile fuel components and precursors for the production of plastics. The polyester from FDCA dimethyl diester and ethylene glycol was first reported in 1946 (GB 621,971).

WO 01/72732 describes the oxidation of HMF to FDCA. The maximum FDCA yield reported is 59%, obtained at 105 °C. The oxidation of HMF in an aqueous medium with oxygen using a catalyst from the Pt-group is described in US 4977283. Taarning et al. described the oxidation of HMF over gold based catalysts (ChemSusChem, 2008, 1, 1-4).

Partenheimer et al (Adv. Synth. Catal. **2001**, 343, pp 102-11) describe the synthesis of 2,5-furandicarboxylic acid by catalytic air-oxidation of 5-hydroxymethylfurfural with metal/bromide catalysts such as Co/Mn/Br in acetic acid at temperatures ranging from 50 to 125 °C. With the Co/Mn/Br catalyst the highest FDCA yield obtained is 35.2% (Table 3, experiment 4). On page 103 of the same paper, under the header "products formed" it is stated: "A side reaction is the esterification of the alcohols to form the more oxidatively stable

acetate ...." As apparently 5-hydroxymethylfurfural reacts with acetic acid a loss of the starting material takes place. Further, in the reaction scheme given in Figure 1 on page 103, it is indicated that 5-(acetoxymethyl)furfural is an end-point. There is no further reaction of this compound indicated to FDCA (in contrast to the ester of the intermediate product 5-



(acetoxymethyl)furan-2-carboxylic acid). In other words, the 5-(acetoxymethyl)furfural (AMF) formed through reaction of HMF with acetic acid solvent, is not oxidized to FDCA and its formation leads therefore to yield loss.

This result was confirmed in US 2009/0156841. Although the intention of the process according to US 2009/0156841 was to obtain FDCA, the product isolated and erroneously characterized as being FDCA was in fact the starting material acetoxymethyl furfural (AMF). Under the low temperature conditions deployed (100 °C), AMF is quite stable, as was already reported by Partenheimer (see above).

In US 2009/0156841 a  $^1\text{H}$  NMR spectrum is shown in Figure 8 and suggested that it is the spectrum of the product that was identified as FDCA. However, this is not the case. The  $^1\text{H}$  NMR spectrum of the product shown in Figure 8 is the same as that in Figure 6 and represents the starting material AMF. The  $^1\text{H}$  NMR spectrum of FDCA shows a singlet at a shift of about 7.26 ppm. Moreover, the product is described as a tan solid. In the experience of the present inventors, AMF is a tan solid, while FDCA is a white solid. It would seem that no FDCA was obtained in the experiments according to US 2009/0156841.

The experiments executed under the conditions of US 2009/0156841 were repeated. These comparative experiments confirm the low reactivity of AMF under conditions given in US 2009/0156841. Thus, a person skilled in the art would therefore have concluded that FDCA cannot be obtained in interesting yields from AMF using the conditions that are reported in US 2009/0156841, i.e., using a Co/Mn/Br catalyst in acetic acid at between 85 and 110 °C within a time frame of from 100 and 150 minutes. In Example 7 of US 2009/0156841, slightly more than 50% of the starting material was the only product isolated from the reaction.

In the method according to WO 01/72732, FDCA is prepared by contacting HMF with an oxygen-containing gas in the presence of an oxidation catalyst comprising Co and Mn in a solvent comprising acetic acid. The reaction temperature may be between 50 and 250 °C, e.g. from 50 to 160 °C. Although in examples the reaction temperatures were generally in the range from 100 to 125 °C, a reaction stage in some examples was conducted at a temperature of 150 °C. WO 01/72732 is directed to five different processes, one of which is directed to a process for preparing a diacid, such as FDCA, from an alcohol/aldehyde, such as HMF. According to the examples, a yield on the desired diacid FDCA of up to 58.8% was obtainable.

Boisen et al., Chem Eng. Research Design, 87 (2009) 1318-1327 describes the conversion of sugars to FDCA in general terms. In particular it discusses the conversion of

HMF to FDCA referring to the work by the inventors of WO 01/72732. It concludes that the oxidation with Co/Mn/Zr/Br is conducted at atmospheric pressure and at 70 bar. It also refers to an oxidation over Pt on alumina, wherein the reaction temperature is 60 °C and a partial oxygen pressure of 0.2 bar.

5 WO 2008/054804 relates to the oxidation of HMF using air or O<sub>2</sub> as oxidant over a platinum-supported catalyst; the temperature ranges from about 50 to about 200 °C. A suitable pressure is 150 - 500 psi (about 10 to 34.5 bar). JP 2009 001519 discloses the oxidation of HMF over a catalyst containing Ru, Co and Ce with molecular oxygen. The temperature may be from 50 to 200 °C. The pressure is 10 – 400 bar. RU 636233 discloses  
10 the oxidation of HMF over a catalyst comprising CuO.Ag<sub>2</sub>O.Ce<sub>2</sub>O<sub>3</sub> on alumina. The oxidant is oxygen or air, the pressure is 25 - 30 atm and the temperature is 110 - 150 °C.

The present inventors have now surprisingly found that when using an oxidation catalyst, e.g., based on both cobalt and manganese and containing a bromide, at temperatures higher than 140 °C, derivatives of HMF, and in particular esters of HMF  
15 optionally in combination with HMF, such as for example 5-(acetoxymethyl)furfural (AMF) can be oxidized to FDCA in high yields.

Thus, in a first aspect the invention provides a method for the preparation of 2,5-furan  
20 dicarboxylic acid comprising the step of contacting in a reactor 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 oxygen-containing gas being continuously fed and removed to and from  
25 the reactor, in the presence of an oxidation catalyst comprising at least one metal selected from Co and Mn, at a temperature between 140 and 200 °C at an oxygen partial pressure of 1 to 10 bar, wherein a solvent or solvent mixture comprising acetic acid or acetic acid and water mixtures is present.

The invention described hereinafter may use any of the compounds described above  
30 in the feed. A preferred ester of HMF contains an ester moiety of an alkyl carboxylic acid

wherein the alkyl group contains up to 6 carbon atoms, preferably from 1 to 5 carbon atoms, i.e. methyl, ethyl, propyl, isopropyl, butyl, 2-butyl, tert-butyl, pentyl, 2-pentyl, neopentyl and 3-

5 pentyl. Particularly preferred are alkyl groups with 1 to 4 carbon atoms. There is a preference for methyl, giving (5-acetoxymethyl)furfural. Hence, 5-acetoxymethylfurfural is the preferred feedstock, by itself or in combination with HMF.

10 In another aspect of the invention, we have also investigated the oxidation of other furan-based substrates under the process conditions according to the current invention. We have been able to convert 5-(chloromethyl)furfural, 5-(chloromethyl)furoic acid, 5-methylfurfural, 5-methylfuroic acid and 2,5-dimethylfuran all to FDCA in very interesting yields.

15 In WO 2007/104515 and WO 2009/030512, the synthesis of esters of HMF such as 5-acetoxymethylfurfural (AMF) from biomass sources is described. Given the higher stability of the HMF esters than HMF and hence improved production pathways and given the fact that upon oxidation in acetic acid the acetoxy functionality that was obtained from acetic acid is now liberated as acetic acid and given the green reputation of these esters, they were considered by the present inventors as interesting starting point in the preparation of furan-20 based monomers that could be used for the production of furandicarboxylic acid-based polyesters, for instance as an alternative for PET or FDCA-based polyamids (nylons). The most important conventional, oil-based, polyester monomer to produce PET is Purified Terephthalic acid (PTA) and its dialkyl ester DiMethyl Terephthalate (DMT).

25 AMF can be obtained from biomass sources as described in WO 2007/104515 and WO 2009/030512. Depending on the process conditions the product obtained in accordance with the process of these references may also contain HMF.

30 FDCA, the product of the reaction can be used in the preparation of a polyester, by reaction of FDCA or its dialkyl ester with a suitable diol. Such polyester preparations are preferably performed by transesterification, whereby the di-methyl ester or di-ethyl ester of FDCA is used and wherein the methyl or ethyl groups are exchanged in the form of a volatile alcohol during the transesterification with the diol.

The oxidation catalyst can be selected from a variety of oxidation catalysts, but is preferably a catalyst based on both cobalt and manganese and suitably containing a source of bromine, preferably a bromide.

35 The bromine source can be any compound that produces bromide ions in the reaction mixture. These compounds include hydrogen bromide, sodium bromide, elemental bromine,

benzyl bromide and tetrabromoethane. Also other bromine salts, such as an alkali or alkaline earth metal bromide or another metal bromide such as  $ZnBr_2$  can be used. There is a preference for hydrobromic acid or sodium bromide. The amount of bromine mentioned in here relates to the amount measured as Br relative to cobalt.

5

Suitable metal bromide catalysts employed in all of the processes of this invention comprise a cobalt compound and a manganese compound and a bromine-containing compound. Preferably these compounds are soluble in the reaction mixture.

Preferably, the catalyst comprises both Co and Mn. The metal and bromide catalyst  
5 contains, in addition to bromide, Co and Mn and optionally may contain one or more additional metals, in particular Zr and/or Ce. Alternative and suitable catalysts are described in W. Partenheimer, *Catalysis Today* 23(2), 69-158 (1995) in particular on pages 89-99.

Each of the metal components can be provided in any of their known ionic forms. Preferably the metal or metals are in a form that is soluble in the reaction solvent. Examples  
10 of suitable counterions for cobalt and manganese include, but are not limited to, carbonate, acetate, acetate tetrahydrate and halide, with bromide being the preferred halide.

As described in Partenheimer, *ibid*, pages 86-88, suitable solvents for use in the processes of the present invention, described above, preferably have at least one component that contains a monocarboxylic acid functional group. The solvent may also  
15 function as one of the reagents. The processes may be run in a solvent or solvent mixture that does not contain an acid group. In that case, preferably one of the reagents does contain a monocarboxylic acid functional group. Suitable solvents can also be aromatic acids such as benzoic acid and derivatives thereof. The solvent in the present process comprises  
20 acetic acid . A mixture may also include water. The most preferred solvent is acetic acid ("AcOH").

The oxidant in the processes of the present invention is an oxygen-containing gas or gas mixture, such as, but not limited to air and oxygen-enriched air. Oxygen by itself is also a preferred oxidant.

25 The processes of the instant invention described above can be conducted in a batch, semi-continuous or continuous mode. Especially for the manufacture of FDCA, 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  
30 the catalyst composition during the reaction is desirable. For example, variation of the catalyst composition during the reaction can be accomplished by addition of cobalt and/or manganese and/or zirconium, and/or cerium, and/or bromide at specified times.

The pressure in a commercial oxidation process may vary within wide ranges. As a diluent is present, and in particular with acetic acid as diluent, the temperature and the  
35 pressure in such a process are not independent. The pressure is determined by the solvent

(e.g., acetic acid) pressure at a certain temperature. The pressure of the reaction mixture is preferably selected such that the solvent is mainly in the liquid phase. In practice this means that pressures between 5 and 100 bar can be used with a preference for pressures between 10 and 80 bar. In the process according to the present invention an oxygen-containing gas, such as air, the gas is continuously fed to and removed from the reactor. In the case of continuously feeding and removing the oxidant gas to and from the reactor, the oxygen partial pressure is between 1 and 10 bar.

The temperature of the reaction mixture is from 140 and 200 °C, most preferably between 160 and 190 °C. Temperatures higher than 180 °C may lead to decarboxylation and to other degradation products. Good results to FDCA have been achieved at a temperature of about 180 °C.

Molar ratios of cobalt to manganese (Co/Mn) are typically 1/1000 - 100/1, preferably 1/100 - 10/1 and more preferably 1/10 - 4/1.

Molar ratios of bromine to metals (e.g. Br/(Co+Mn)) are typically 0.001-5.00, preferably 0.01 - 2.00 and more preferably 0.1 - 0.9.

Catalyst concentration (Co + Mn) is typically from 0.1 to 10 mol %, relative to the substrate, with a preference for concentrations from 2 to 6 mol %. Good results were obtained in general with catalyst concentrations of around 4 mol %.

The starting materials for the production of FDCA may originate from a carbohydrate source as described above. Examples of such disclosures are WO 2007/104515 and WO 2009/030512. Accordingly, the invention also provides a method for the preparation of 2,5-furandicarboxylic acid wherein a carbohydrate source is converted in the presence of an alkyl carboxylic acid into products comprising an HMF ester and optionally 5-hydroxymethyl furfural, from which is isolated a feed comprising the ester of HMF and optionally 5-hydroxymethyl furfural, and which method further comprises the subsequent step of contacting the feed with an oxidant in the presence of an oxidation catalyst, in particular a cobalt and manganese and bromide-containing catalyst, under appropriate reaction conditions, in particular at temperatures higher than 140 °C

In another aspect, the FDCA obtained according to the process of the present invention can be transformed using common esterification reactions to a diester by contacting the starting material under appropriate conditions with the relevant alcohol. Thus, in one aspect, the invention also relates to the use of FDCA obtained according to the

process of the current invention in the preparation of a dialkylester of 2,5-dicarboxylic acid by reaction of the FDCA with a C<sub>1</sub>-C<sub>5</sub> alkyl alcohol, preferably methanol to prepare the dimethyl ester of FDCA.

5           Accordingly, the present invention also provides a process for the preparation of a dialkyl ester of 2,5,-furan dicarboxylic acid, comprising the step of contacting in a reactor 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  
10 more of these compounds with an oxygen-containing gas being continuously fed and removed to and from the reactor in the presence of an oxidation catalyst comprising at least one metal selected from Co and Mn, at a temperature between 140 and 200 °C at an oxygen partial pressure of 1 to 10 bar, wherein a solvent or solvent mixture comprising acetic acid or acetic  
15 acid and water mixtures is present, and esterifying the thus obtained product. Preferably, the product is esterified with an alkyl alcohol, suitably having 1 to 5 carbon atoms.

The esterification of 2,5-furan dicarboxylic acid is known. As a specific example for the manufacture of these esters, reference is made to US 2673860 wherein the diester is  
20 obtained by transesterification of another dicarboxylic acid ester in the presence of sulphuric acid. A more general description for the esterification of dicarboxylic acids is presented in US 2628249.

In a further aspect of the invention, the di-methylester can be used in the preparation of polyester polymers by reaction with a diol. Reacting the di-methylester with a diol will  
25 result in the formation of methanol that quickly vaporises. In 1946 the polymerization of FDCA dimethyl ester with ethylene glycol was described as a first example of such a polymerization in GB 621,971.

30           Indeed, polyesters are generally made by a combined esterification/polycondensation reaction between monomer units of a diol (e.g., ethylene glycol (EG)) and a dicarboxylic acid.

Additives such as catalysts and stabilizers may be added to facilitate the process and stabilize the polyester towards degradation.

35           Examples:

Experiments were carried out in parallel 8 ml magnetically stirred stainless steel batch

reactors. The reactors are grouped in blocks containing 12 batch reactors. The standard procedure for all the reactions was as follows:

0.5 ml of starting material stock solution in acetic acid (0.78 mmol/ml) were added into

- 5 a reactor lined with a Teflon insert. To the reactor 1 ml of a catalyst stock solution in acetic acid was subsequently added. In a typical experiment, a catalyst composition Co/Mn/Br with a relative 1-x-y ratio, the concentration of  $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$  was varied. As a Mn source,  $\text{Mn}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$  was used and as a bromine source NaBr was used. The reactors were closed with a rubber septum, after which the reactors were sealed and pressurized to the
- 10 desired air pressure, ranging from 20-60 bars. After pressurization, the block with 12 reactors
- was placed in the test unit which was preheated at the desired temperature, ranging from



100 to 220 °C. After the desired reaction time, ranging from 0.5 hr to 24 hrs, the block is placed into an ice bath for 20 minutes. When the block had cooled down, it was depressurized. After opening, HPLC samples were prepared. First 5 ml of a saccharine solution in DMSO (11.04 mg/ml) was added to each reactor and the mixture was stirred for 5 minutes. Then 10 µl of this mixture was diluted to 1000 µl with water in a HPLC vial. The samples were analyzed using HPLC.

#### Example 1

Example 1 shows the selectivity of FDCA in the oxidation of HMF, of a HMF/AMF 3/2 mixture, of a HMF/AMF 2/3 mixture and of AMF, respectively, with 2.7 mol% Co catalyst (relative to substrate), and Co/Mn molar ratio of 1/1, so that the catalyst concentration (Co + Mn) amounted to 5.4 mol%. The Br/(Co+Mn) molar ratio was 1.0; 0.7; 0.4 and 0.1 at 0.26 M substrate concentration in acetic acid at 180 °C for 1 hr with 20 bar air. The amount of oxygen was 2.69 mol oxygen per mol substrate. Under these conditions, higher Br amounts give higher yields but when Br/(Co+Mn) > 1, corrosion will be a problem on commercial scale. HMF gives slightly higher yields than AMF at one hour reaction time. The results of these experiments are given in Table 1.

#### Example 2

Example 2 shows the selectivity to FDCA for the AMF oxidation of Example 1, together with the comparative examples based on the experimental conditions described in US 2009/0156841. In those comparative experiments (2a and 2b) 10 wt/wt% AMF in acetic acid was oxidized with 1.75 and 2.65 mol % Co catalyst and a fixed Br/(Co + Mn) molar ratio of 1.0 and a Co/Mn molar ratio of 1.0 at 100 °C and 30 bar for 2 hours. The amount of oxygen was 2.88 mol oxygen per mol substrate. Under these conditions, the yield of FDCA was lower than the result suggested in US 2009/0156841 and also lower than the results obtained at higher temperature. The results of these experiments are given in Table 2.

#### Example 3

Example 3 shows the yield of FDCA in the oxidation of 5-methylfurfural (5MF) and 2,5-dimethylfuran (DMF) at 180 °C with 2.7 mol% Co catalyst (relative to substrate), and Co/Mn ratio of 1/1, so that the catalyst concentration (Co + Mn) amounted to 5.4 mol%. The Br/(Co+Mn) molar ratio was 1.0, 0.7, 0.4 and 0.1. The substrate concentration was 0.26 M in acetic acid. The reaction temperature was at 180 °C and the reaction was conducted with 50 bars air. The amount of oxygen was 6.7 mol oxygen per mol substrate. Under these conditions, higher Br amounts give higher yields but when Br/(Co+Mn) > 1, corrosion will be a problem on commercial scale. Reactions with 5-MF give higher yields than reactions with DMF. The results of these experiments are also given in Table 3.



## Letter accompanying subsequently filed items

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The document(s) listed below is (are) subsequently filed documents pertaining to the following application:

Application number

08773872.0

Applicant's or representative's reference

P30061PE00/RLA

	Description of document	Original file name	Assigned file name
1	Letter dealing with Oral proceedings	Response to a communication P30061EP00.pdf	ORAL-1.pdf
2	Amended description with annotations	FUR 19b EP text 1 main request marked up.pdf	DESC-HWA-1.pdf
3	Amended description (clean copy)	FUR 19b EP text 1 Main Request clean.pdf	DESC-1.pdf
4	Amended claims (clean copy)	FUR 19b Amended claims Main request.pdf	CLMS-1.pdf
5	Amended description with annotations	FUR 19b EP text 1 Aux Req marked up.pdf	DESC-HWA-2.pdf
6	Amended description (clean copy)	FUR 19b EP text 1 Aux Req clean.pdf	DESC-2.pdf
7	Amended claims (clean copy)	FUR 19b Aux Req claims.pdf	CLMS-2.pdf

### Signatures

Place: **Rijswijk**  
 Date: **27 November 2014**  
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Rijswijk, November 27, 2014

Your ref. :  
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Application no. : 10768600.8 - 1462  
Country : Europe  
In the name of : Furanix Technologies B.V.  
Title : Method for the preparation of 2,5-furandicarboxylic acid from 5-hydroxymethylfurfural and/or derivatives thereof, and th

Dear Madam or Sir,

Reference is made to the summons to attend oral proceedings in connection with the above-mentioned patent application.

We are pleased to note that the Examining Division agrees that the pending amended claims fulfill the requirements of Article 123(2) EPC, and also the requirements as to novelty under Article 54 EPC.

In this letter we shall explain the arguments as to inventive step in more detail. In doing so we shall apply the problem-solution approach.

The first step of the problem-solution approach consists of the determination of the closest prior art. We agree with the Examining Division that D8 (WO 01/72732) represents the closest prior art, as D8 discloses the combination of features which constitutes the most promising starting point for a development leading to the invention. D8 is directed to a similar purpose or effect as the invention, and requires the minimum of structural and functional modifications to arrive at the claimed invention (see T 606/89).

D8 is directed to five different processes, one of which is directed to a process for preparing a diacid, such as FDCA, from an alcohol/aldehyde, such as HMF. In the method according to D8, 2,5-furandicarboxylic acid (FDCA) is prepared by contacting 5-hydroxymethylfurfural (HMF) with an oxygen-containing gas in the presence of an oxidation catalyst comprising Co and Mn in a solvent comprising acetic acid. The reaction temperature may be between 50 and 250 °C, preferably from 50 to 160 °C. Although in examples the reaction temperatures were generally in

the range from 100 to 125 °C, a reaction stage in some examples was conducted at a temperature of 150 °C. The pressure at the reaction is such to keep the solvent mostly in the liquid phase. No further information on the pressure is provided. The examples are conducted at either atmospheric pressure or at 70 bar. According to the examples, a yield on the desired diacid FDCA (at 70 bar ) of up to 58.8% is obtainable.

The objective technical problem is to optimize the yield of FDCA.

The problem is solved by operating the method at such a pressure that the oxygen partial pressure is in the range of 1 to 10 bar, whilst the reaction temperature is relatively high, viz. in the range of 140 to 200°C.

Experiments 1a,1e, 1i and 1m show that yields in the range of about 68 to about 78% are obtainable when the reaction temperature is in the range of 140 to 200 °C, viz. 180 °C, and the oxygen partial pressure is in the range of 1 to 10 bar, viz. about 4 bar.

Hence, the problem is solved by the feature, viz. the oxygen partial pressure, that is different from the closest prior art, in combination with a feature, viz. the reaction temperature, that is beyond what is explicitly exemplified in D8.

In this context it is observed that the Examining Division seems to be of the opinion that the skilled person is in doubt which technical feature leads to the claimed effect. From the above analysis it is apparent that the combination of a relatively high temperature with an undisclosed pressure level leads to the high yield of FDCA. A reaction temperature of at least 140 °C is indispensable, and also an oxygen partial pressure of 1 to 10 bar is essential to obtain the high yields. It is respectfully submitted that the skilled person is clearly taught what the distinguishing features are.

The final step in the problem-solution approach is considering whether the claimed invention, starting from the closest prior art and the objective technical problem, would have been obvious to the skilled person.

According to the Examining Division, D8 teaches that the yield of FDCA can be enhanced by using higher temperatures. To support this statement, the Examining Division points towards Examples 38-40 in D8. However, we would draw the Division's attention to Example 28 in D8, wherein a higher yield is obtained than in Examples 38-40. Example 28 is conducted at a lower temperature than Examples 38-40 for a longer period. Hence, the skilled person would be encouraged to use moderate temperatures, certainly temperatures below 150 °C, and, optionally, to prolong the reaction duration.

If the Examining Division would observe that the high yield of Example 28 is obtained by a very high catalyst concentration it is observed that a comparison between the conditions and results of Examples 39 and 40 teaches the skilled person that a higher yield is obtainable at a lower catalyst concentration. Therefore, if the skilled person would want to obtain the optimal yield of FDCA he would use lower temperatures and optionally prolong the reaction duration and decrease the catalyst concentration.

The teaching on the reaction pressure in D8 is limited to the statement that the pressure is such to keep the solvent, i.e. acetic acid, mostly in the liquid phase and that the reaction time, the

pressure, the temperature and the catalyst concentration are to be determined such that a maximum yield of diacid is obtained (cf. D8, page 7, lines 4-7).

The skilled person would know that the boiling point of acetic acid is about 117.9°C. Hence, the reaction according to D8 can easily be conducted at atmospheric pressure. Therefore, D8 merely shows that any pressure from atmospheric can be used.

In this context it is observed that the statements on pressure in D8 relate to the total pressure, not the oxygen partial pressure. Whereas the pressure according to D8 serves to prevent vaporization of the solvent, the oxygen partial pressure in the method according to the present invention is relevant vis-à-vis the reaction selectivity. The exemplified pressures in D8 are atmospheric pressure and 70 bar. This means that the exemplified oxygen partial pressures are 0.2 and 14 bar, wherein the FDCA synthesis has only been shown at 14 bar oxygen pressure.

In the absence of any teaching about the oxygen partial pressure in D8, the skilled person would not expect that the above-mentioned objective technical problem would be solved by applying an oxygen partial pressure in the claimed range.

The other prior art documents on file also fail to render the claimed oxygen pressures obvious. In the annex to the summons the Examining Division specifically refers to D7-D11, which documents allegedly show that the oxygen partial pressure ranges are common in the field.

First, it is necessary to determine what “the field” is. It would seem that the Examining Division regards any oxidation of HMF to FDCA, irrespective of the catalyst system used, as “the field”. It is submitted that such generalization is inappropriate. The homogeneous catalysts such as dissolved Co and Mn salts on the one hand are completely different from heterogeneous catalysts such as Pt on alumina on the other hand.

D7 (*Boisen et al., Chem Eng. Research Design, 87 (2009) 1318-1327*) describes the conversion of sugars to FDCA in general terms. In particular it discusses the conversion of HMF to FDCA referring to the work by the inventors of D8. It concludes that the oxidation with Co/Mn/Zr/Br is conducted at atmospheric pressure and at 70 bar. It also refers to an oxidation over Pt on alumina, wherein the reaction temperature is 60 °C and a partial oxygen pressure of 0.2 bar. Hence, it is clear that D7 does not teach an oxygen pressure regime that is applicable to any oxidation of HMF, let alone that such an oxygen pressure regime will be in the range of 1 to 10 bar.

Other prior art documents confirm this finding.

As discussed, D8 discloses an oxygen partial pressure of 14 bar in the oxidation of HMF to FDCA using a Co/MnZr/Br catalyst.

D9 (*WO 2008/054804*) relates to the oxidation of HMF using air or O<sub>2</sub> as oxidant over a platinum-supported catalyst; the temperature ranges from about 50 to about 200 °C. A suitable pressure is 150 - 500 psi (about 10.3 to 34.5 bar).

D10 (*JP 2009 001519*) discloses the oxidation of HMF over a catalyst containing Ru, Co and Ce with molecular oxygen. The temperature may be from 50 to 200 °C. The pressure is 10 – 400 bar.

D11 (*RU 636233*) discloses the oxidation of HMF over a catalyst comprising  $\text{CuO} \cdot \text{Ag}_2\text{O} \cdot \text{Ce}_2\text{O}_3$  on alumina. The oxidant is oxygen or air, the pressure is 25 - 30 atm and the temperature is 110 - 150 °C.

The above data show that there is a wide spread of potentially suitable pressures that should be applied in the oxidation of HMF. It is evident that suitable reaction conditions for one oxidation reaction using one particular catalyst system are not automatically also suitable for the oxidation using a different catalyst system.

Hence, there is no clear teaching or suggestion to the skilled person which oxygen pressure would yield the best results.

The Examining Division also points to the phrase in the application on page 4, line 35 ff. It is observed that this phrase is discussing the process according to the present invention. The paragraph in question discusses the pressure in future commercial oxidation plants that operate the process according to the present invention. The lower limit of the pressure is preferably such that the solvent, i.e. acetic acid, is in the liquid phase. In that respect the teaching is similar to that in D8. However, since the reaction temperature in the method according to the present invention is above 140 °C, and thus above the atmospheric boiling point of acetic acid, the pressure is suitably above 1 bar, preferably from 5 to 100, more preferably from 10 to 80 bar. These pressure ranges relate to the total pressure, not to the oxygen partial pressure. Hence, this paragraph does not represent the skilled person's common general knowledge relating to the oxygen partial pressure in the specific oxidation process according to the present invention.

The claimed range of oxygen partial pressures is therefore not clearly taught to the skilled person by any of the above-mentioned prior art references.

In view of the above arguments it is respectfully submitted that the presently claimed method is patentable over the teachings of D8, taken alone or in combination with the common general knowledge of the skilled person.

D1 (Partenheimer et al, *Adv. Synth. Catal.*, 343 (2001) 102-11) also discloses Co/Mn/Zr/Br catalyst systems and their use in the oxidation of HMF to FDCA. D1 repeats several of the experiments in D8. The oxidation experiments of HMF to FDCA have been conducted at 70 bar air pressure. The reaction temperatures vary between 100 and 125 °C. The yields are the same or similar to those obtained in some of the Examples 16 – 40 of D8.

If the skilled person would combine the teachings of D1 and D8 he would conclude that the best results would be obtainable at a temperature of 125°C and an air pressure of 70 bar. He would therefore not be encouraged to increase the temperature and decrease the oxygen partial pressure.

Therefore, it is submitted that the presently claimed method would also be patentable in view of the combined teachings of D8 and D1. Reconsideration and withdrawal of the present objections are respectfully requested.

The Examining Division refers to Experiments 3a-37 in Table 3 of the present application. The yields of FDCA in these experiments vary from 7.19 to 42.62%. These values are lower than the yields obtained in the examples of D8.

It is respectfully submitted that the Examining Division is not making an appropriate comparison. The starting materials in Experiments 3a-3f are 5-methylfuran and 2,5-dimethylfuran, respectively. The different yields show that the nature of the starting material is influencing the eventual product. That is also confirmed by experiments 1d, 1h, 1l and 1p, wherein the starting material was acetoxymethylfurfural, resulting in different yield from the oxidation of HMF itself.

In this context it is observed that D8 does not contain any reference to the oxidation of these starting materials. For this reason alone, the currently claimed process concerning the oxidation of these starting materials should be considered patentable over D8.

In anticipation of a positive response to our request we enclose a revised description which has been brought into agreement with the present claims. The amended pages include the correction of the typographical errors on page 7. For your convenience we enclose a version with annotations as well as a clean version.

We also enclose a set of amended claims. In the enclosed set of amended claims a typographical error in claim 7 (viz. the word "is" has been inserted) has been corrected.

#### **Auxiliary Request**

If the Examining Division would decide to refuse the present application we herewith file an auxiliary request. We request that the claims and description as per this auxiliary request be granted in case the pending claims and corresponding description are considered non-patentable.

#### **Claims**

The claims of the auxiliary request differ from those of the originally filed application in that the reference to HMF has been deleted from claim 1, so that the starting material no longer comprises HMF as the sole compound that is to be oxidized. All other features in claim 1 are the same as those in the main request.

In claim 2 the wording has been slightly amended to exclude HMF as sole compound to be oxidized.

Claim 10 has been brought in conformity with the scope of claim 1.

It is submitted that the auxiliary request fulfils the requirements of Article 123(2) EPC.

As claims 1 and 10 of the main request are novel, we trust that claims 1 and 10 of the auxiliary request are novel, too. If the Examining Division intends to refuse the application, it is expected that this is done on the basis of the contents of D8. By deleting HMF as the sole compound to be oxidized D8 has lost its particular relevance. Hence, the auxiliary request is remedying a deficiency in response to the annex to the summons. It is therefore respectfully submitted that the auxiliary request is to be considered admissible.

The invention is now directed to the oxidation of a compound selected from the group consisting of an ester of 5-hydroxymethyl-furfural (HMF), 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 to FDCA. The oxidation is established in a reactor by means of an oxygen-containing gas in the presence of a catalyst system comprising at least one of Co and Mn in an acetic acid-containing solvent or solvent mixture at a temperature of 140 to 200 °C and at an oxygen partial pressure of 1 to 10 bar. The oxygen-containing gas is continuously fed and removed to and from the reactor.

It is submitted that the closest prior art is now represented by D2 (US 2009/156841). D2 relates to a number of processes including the conversion of carbohydrates to HMF and derivatives thereof. One of the processes relate to the oxidation of esters of HMF with cobalt acetate, manganese acetate and sodium bromide at 400 -1000 oxygen pressure (27.6 -68.9 bar O<sub>2</sub>) at 85 -110 °C (cf. D2, column 6, [0060]). The document also describes experiments wherein acetoxymethyl furfural (AMF) and a mixture of AMF and HMF are oxidized over a Co/Mn/Br catalyst in acetic acid at 500-800 psi oxygen (about 34.5 to about 55 bar O<sub>2</sub>) at 100 °C for 2 hours.

In the description of the present application we have explained that the product of the example method in D2 is identified by reference to an NMR spectrum (viz. Fig. 8) that is identical to another NMR spectrum (viz. FIG. 7) which probably is the NMR spectrum of the starting material AMF, rather than FDCA. D2 therefore does not have a direct and unambiguous disclosure of the preparation of FDCA from AMF.

The objective technical problem is thus the provision of a process wherein FDCA is obtained by the oxidation of AMF in interesting yields.

This problem is solved by the method according to the present invention, viz. by conducting the oxidation at a temperature of 140 to 200 °C and a lower oxygen pressure of 1 to 10 bar.

It is submitted that D2 does not provide any teaching which would lead the skilled person to this method. D2 teaches that a temperature of 85-110°C and a high oxygen pressure (27.6 -68.9 bar) are required. When the skilled person starts from the teachings of D2, he comes to the conclusion that D2 teaches that the original starting compound is recovered. That will deter him from doing further experiments.

Even if he would conduct further experiments at a lower oxygen pressure, he finds that the conversion to FDCA is relatively low. It is not until he enhances the reaction temperature to values in the range 140 to 200 °C in addition to lowering the oxygen partial pressure, that he obtains satisfactorily high yields of FDCA (cf. present application, experiments 1d, 1h, 1l and 1p on the one hand and 2a and 2b on the other hand).

This clearly shows the inventivity of the present method over D2.

Since the other prior art documents on file do not relate to the oxidation of AMF or any of the HMF-derivatives mentioned in claim 1, these documents do not seem relevant to the extent that the skilled person would consult any of those. The only other documents that describe a similar oxidation catalyst system are D1 and D8. D1 relates to a high pressure, low temperature oxidation of HMF. Therefore, it fails to add any teachings in addition to D2. D8 has been



discussed extensively hereinabove. Also D8 discloses the oxidation of HMF to FDCA under application of high pressures and, in principle, low temperatures.

Since both D1 and D8 relate to the oxidation of HMF instead of AMF, a skilled person would not consult D1 or D8 when he tries to solve the objective technical problem starting from D2. Even if he would consult these documents, he would be taught to apply high pressures and relatively low temperatures. Thus, he would not arrive at the currently claimed process.

The inventivity of the process according to the auxiliary request is further illustrated by experiments 1c, 1g, 1k and 1o. In these experiments mixtures of AMF and HMF are oxidized. The results obtained show that the yields of these mixtures are significantly higher than the proportional yields, based on the oxidation of HMF alone and the oxidation of AMF alone. This synergism is completely unexpected.

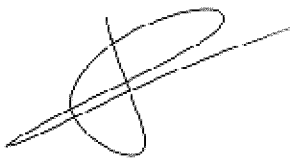
Therefore, the method according to the auxiliary request also involves an inventive step.

In order to expedite the proceedings and also in response to the explicit request by the Examining Division, an amended description for the claims of the auxiliary request is enclosed, both in a marked-up version and a clean version.

If the above arguments would persuade the Examining Division to cancel the oral proceedings in view of the allowability of at least one of the requests, it would be appreciated if the Examining Division would inform the applicant accordingly.

Also, if only minor deficiencies are to be corrected, the Examining Division is invited to contact the applicant by telephone, email or further written communication to arrange for the appropriate action.

Yours faithfully,  
EP&C



Robbert-Jan de Lang  
Association no. 497

Enclosed.: Description (pages 1-7) (marked-up and clean version) and claims for Main Request  
Claims and description (pages 1-7) for Auxiliary Request (marked-up and clean version)

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EP 10 768 600.8

19.09.14

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26. Sep. 2014

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GERMANY

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Zeestraten, Albertus W. J.  
Exter Polak & Charlouis B.V. (EP&C)  
P.O. Box 3241  
NL-GE Rijswijk  
PAYS-BAS

Formalities officer: Ms Andrea Pfau

Please specify the name of the formalities officer when  
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Date  
19-09-2014

Reference P30061EP00/AZE	Application No / Patent No. 10768600.8 - 1462 / 2486028
Applicant/Proprietor Furanix Technologies B.V	

EPA/EPO/OEB Formblatt/Form/Formulaire : F2008, F2906

**Empfangsbescheinigung über den Zugang des vorstehend bezeichneten Schriftstücks**  
**Acknowledgement of receipt of the document specified above**  
**Récépissé du document spécifié ci-dessus**

Unter Bezugnahme auf die Mitteilung im ABI EPA 7/2010, 377 wird gebeten, die Empfangsbescheinigung mit Empfangsdatum und Unterschrift zu versehen und umgehend an das EPA zurückzusenden:

With reference to the Notice in OJ EPO 7/2010, 377, you are requested to date and sign the acknowledgement of receipt and return it to the EPO immediately:

Conformément au communiqué paru au JO OEB 7/2010, 377, vous êtes prié d'indiquer sur le récépissé la date de réception du document, de signer le récépissé et de le renvoyer sans délai à l' OEB:

- über die Online-Dienste des EPA (als Anlage zu EPA Form 1038) / through EPO Online Services (as annex to EPO Form 1038) / par les services en ligne de l'OEB (en tant que pièce jointe au formulaire OEB 1038),
- per Fax / by fax / par téléfax (+49 (0) 89 2399-4465 or +31 (0) 70 340-3016)
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24 SEP 2014

**EP&C**

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EP&C  
P.O. Box 3241  
2280 GE Rijswijk  
PAYS-BAS

Date 24.09.14
------------------

Reference P30061EP00/AZE	Application No./Patent No. 10768600.8 - 1462 / 2486028
Applicant/Proprietor Furanix Technologies B.V	

**Communication of amended entries concerning the representative (R. 143(1)(h) EPC)**

As requested, for the above-mentioned European patent application / European patent the entries concerning the representative have been amended as follows:

EP&C  
P.O. Box 3241  
2280 GE Rijswijk  
NL

The amendment will be recorded in the Register of European Patents.

**For the Examining Division**





European Patent Office  
80298 MUNICH  
GERMANY



Zeestraten, Albertus W. J.  
Exter Polak & Charlouis B.V. (EP&C)  
P.O. Box 3241  
NL-GE Rijswijk  
PAYS-BAS

**Questions about this communication ?**

Contact Customer Services at [www.epo.org/contact](http://www.epo.org/contact)

Formalities officer: Ms Andrea Pfau

Please specify the name of the formalities officer when contacting Customer Services by contact form or phone.

Date

19-09-2014

Reference P30061EP00/AZE	Application No./Patent No. 10768600.8 - 1462 / 2486028
Applicant/Proprietor Furanix Technologies B.V	

EPA/EPO/OEB Formblatt/Form/Formulaire : F2008, F2906

**Empfangsbescheinigung über den Zugang des vorstehend bezeichneten Schriftstücks**  
**Acknowledgement of receipt of the document specified above**  
**Récépissé du document spécifié ci-dessus**

Unter Bezugnahme auf die Mitteilung im ABI EPA 7/2010, 377 wird gebeten, die Empfangsbescheinigung mit Empfangsdatum und Unterschrift zu versehen und **umgehend** an das EPA zurückzusenden:

With reference to the Notice in OJ EPO 7/2010, 377, you are requested to date and sign the acknowledgement of receipt and return it to the EPO **immediately**:

Conformément au communiqué paru au JO OEB 7/2010, 377, vous êtes prié d'indiquer sur le récépissé la date de réception du document, de signer le récépissé et de le renvoyer **sans délai** à l' OEB:

- **über die Online-Dienste des EPA** (als Anlage zu EPA Form 1038) / **through EPO Online Services** (as annex to EPO Form 1038) / **par les services en ligne de l'OEB** (en tant que pièce jointe au formulaire OEB 1038),
- **per Fax / by fax / par télécopie (+49 (0) 89 2399-4465 or +31 (0) 70 340-3016)**
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**Europäisches Patentamt**

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The Oral Proceedings will be carried out on the **following application documents**

**Description, Pages**

1-9 as published

**Claims, Numbers**

1-12 filed in electronic form on 01-08-2013

Since the Applicant has requested that Oral Proceedings be held before any adverse decision is given, and since the Examining Division remains of the opinion that the application does not contain any subject-matter which would be suitable to form the basis of an allowable claim, it is considered to be expedient to hold such proceedings at this stage of the procedure. The Applicant should note that it is intended to reach a final conclusion of the examination during the Oral Proceedings, that is either to agree on the text to be recommended for grant or to refuse the application. Hence, any requests to continue the examination in writing are unlikely to be granted.

In order to prepare the Oral Proceedings the whole case has been carefully reviewed taking all submissions and requests of the Applicant into account. The arguments, submitted by the Applicant with letters of 01.08.2013 and 07.02.2012 in favour of patentability of the set of claims are not deemed persuasive. The main issue to be discussed at the Oral Proceedings would appear to be that of inventive step (Article 56 EPC), in particular in the light of the document D8.

1) First of all, the amendments filed with the letter of the Applicant dated the 01.08.2013 fulfil the requirements of Article 123(2) EPC.

Similar to the claim-set filed the 07.02.2012 the claim-set filed the 01.08.2013 also fulfils the requirements of Novelty under Article 54 EPC.

2a) With respect to inventive step, it was already pointed out in the Official Communication dated the 16.04.2013 that the introduction of various features (such as the solvent, catalyst and pressure) in present claim 1 although rendering the claimed subject-matter novel over the disclosure of the cited prior art documents, leave the reader into doubt which is actually the special technical feature of the claimed process that leads to the claimed effect, i.e improved yield of FDCA.

It is pointed out that in the originally filed claim 1 it was only the temperature that was identified as the special technical feature of the claimed process and not the pressure as identified in the letters of the Applicant for the later filed claim-sets.

2b) The Applicant's Representative objected in his letter of 01.08.2013 that the paragraph on page 4, line 34 to page 5, line 10 cited by the Examiner in her inventive-step-argumentation does to refer to existing commercial processes.

However, already the first phrase of said paragraph refers to a commercial oxidation process "*The pressure in a commercial oxidation process may vary within wide ranges*". The following phrase that "*the pressure of the reaction mixture is preferably selected such that the solvent is mainly in the liquid phase*" is also found in document D8, page 7, lines 4-5. The following sentence "*In practice this means that pressures between 5 and 100 bar can be used with a preference for pressures between 10 and 80 bar.*" just gives what order of pressure the person skilled in the art would normally expect in order that the solvent is in the liquid phase. These ranges of pressure are common in the field as it can be seen by documents D7-D11 (in D7 20 bar, in D8 14 bar, in D10 10-400 bar and in D11 25-30 bar). Converting the common in the field 5-100 bar or 10-80 bar pressure to partial oxygen pressure the values residing would normally be ~1-21 or ~2-17 bar respectively. Presently is claimed a range of 1-10 bar partial oxygen pressure.

2c) The Applicant's Representative implied that the closest prior art D8 teaches that variations in pressure in the preparation of FDCA are immaterial. This is not correct: examples 1-15 relate to the conversion of HMF to DFF; at no point of said examples it was mentioned that it was intended to convert HMF to FDCA with the process described therein. In this respect, reference is also made to page 3, lines 1-15, page 5, lines 19-24, page 6, lines 36-38 etc. clearly stating as preferred embodiment the preparation of DFF.

D8 clearly teaches that the pressure is such to keep the solvent in the liquid phase (see page 7, lines 4-5). The claimed process acts within said teaching as it is evident from the examples on page 6-7 of the present application that the solvent is also in the liquid phase.

Furthermore, the closest prior art D8 teaches that the yield of the FDCA is improved by using higher temperatures (see examples 38-40). In the present application a temperature range of 140-200 °C is claimed for carrying out the reaction. However, said range cannot be regarded as a narrow selection of the range 50-250 °C / 50-160 ° disclosed in D8; furthermore, the preferred end value 160 °C disclosed in D8 as well as the 150 °C reaction temperature disclosed in examples 38-40 of D8 fall within the presently claimed range.



Finally, the Applicant's Representative argued that the yield of the FDCA achieved by the claimed process and in particular due to the partial oxygen pressure of 1-10 bar is higher than in the closest prior art D8. Examples 38-40 carried out within the temperature range presently claimed disclose a yield for the FDCA between 51.4 and 54.6%. On the other hand, example 3 of the present application discloses a yield for the FDCA lower than 43% which reaches 7.19%.

3) As a consequence, it is still not clear which is the special technical feature characterising the claimed process, which is the effect residing therefrom and if the effect can be proven over the whole breadth presently claimed.

In this respect, it is also pointed out that in all examples carried out according to the presently claimed process, the temperature was set at 180 °C.

4) As in the previous Communications it is repeated that :

- Claim 9 uses the wording "preferably". This wording has no limiting effect on the scope of a claim; that is to say, the feature following any such expression is to be regarded as entirely optional.
- In example 3 it is erroneously referred to 2,5-dimethylfurfural. The correct reference is to 2,5-dimethylfuran (DMF).

5) Concluding remarks

As a preliminary, non-binding opinion the Examining Division considers that the Applicant's request for a patent based on the claims filed with letter of 01.08.2013 has to be refused.

As requested the Applicant is invited to Oral Proceedings during which the above objections will have to be overcome and at the end of which a final decision about patentability will be taken.

In order to expedite the examination procedure, the Applicant is invited to submit a final set of claims which overcome all the objections mentioned in the previous communications which are still valid (Rule 137(3) EPC).

Attention is drawn to the fact that an Applicant who files amended claims before Oral Proceedings and choose not attend them must expect a decision based on objections which might arise against such claims in his absence. The fact that Oral Proceedings are maintained indicates that objections are still pending and need to be discussed at the Oral Proceedings. Consequently, the Applicant must expect that any problems and objections relating to the requests filed in reply to the summons to Oral

Proceedings are dealt with at the Oral Proceedings. If the Applicant decides not to attend the Oral Proceedings he chooses not to make use of the opportunity to comment at the Oral Proceedings on any of the objections but relies on the arguments as set out in the written submissions. The decision may be given orally in his absence.

According to Rule 116 EPC, the final date for making written submission in preparation for the Oral Proceedings is fixed in the summons. The Examining Division will exercise its discretion regarding the consideration of new submissions presented after that date and may not admit such submissions according to Rule 116 EPC.

In exercising its discretionary power for treating late filed requests during the proceedings, the Examining Division will apply the criterion of "clear allowability", that is, said requests will be considered, but they will not be admitted into the proceedings under Rules 116(2) EPC if they clearly give rise to new objections under the EPC, or if they do not clearly meet all outstanding objections under the EPC.

If a patentable set of claims is submitted before the end of Oral Proceedings, the Applicant will have to amend the description accordingly before the end of Oral Proceedings. Failure to do so may lead to refusal of the application under Article 84 EPC (see e.g. T2294/08).

Application No.: 10 768 600.8

### Preparation for oral proceedings - Instructions to Support Service

Oral proceedings are to be held in connection with the above patent application

1. The matters to be discussed are set out in the annex (Form 2906)
2. Dispatch the summons using Form 2008/2310 and Form 2906 for the parties to attend on:

Day 24.02.2015 Time 09:00

#### ROOMS

Room 1999 booked

ORAL 01, 02, 03 and 05 coded

11.09.14 AP  
 Date Initials

- 2.1 Parties' submissions in preparation for the oral proceedings, if any, should be made no later than

**1 month(s)**

before the date of the oral proceedings  
(transfer to Form 2008.1 / 2310.1)

- 2.2 Encode ORAL(04)

coded

11.09.14 AP  
 Date Initials

- 2.3 Dispatch Form 2008.7 / 2310.7 to division

11.09.14 AP  
 Date Initials

Date Initials

3.  Arrange for the following special equipment to be provided in the conference room:

.....  
 Date Initials

4. Request language service to provide simultaneous interpretation facilities as necessary

.....  
Date Initials

5. Return the dossier to primary examiner with Form 2041 (15 days before the oral proceedings)

.....  
Date Initials

6. Check that summons has been received (Form 2936 / advice of delivery)

7. 15 days before the oral proceedings:  
- dispatch the dossier to the primary examiner.

08.09.14

.....  
Date

  
 Fazzi, Raffaella  
 Chairman

  
 Wolf, Claudia  
 2nd examiner

  
 Papathoma, Sofia  
 1st examiner

.....  
Legal member

Enclosure(s):



European Patent Office  
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GERMANY



Zeestraten, Albertus W. J.  
Exter Polak & Charlouis B.V. (EP&C)  
P.O. Box 3241  
NL-GE Rijswijk  
PAYS-BAS

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Formalities officer: Ms Andrea Pfau

Please specify the name of the formalities officer when contacting Customer Services by contact form or phone.

Date

19-09-2014

Reference P30061EP00/AZE	Application No./Patent No. 10768600.8 - 1462 / 2486028
Applicant/Proprietor Furanix Technologies B.V	

**Summons to attend oral proceedings pursuant to Rule 115(1) EPC**

You are hereby summoned to attend oral proceedings arranged in connection with the above-mentioned European patent application.

The matters to be discussed are set out in the communication accompanying this summons (EPO Form 2906).

The oral proceedings, which will not be public, will take place before the Examining Division

on 24.02.15 at 09.00 hrs at the EPO,  
PschorrHöfe, Bayerstr. 34, D-80335 München

No changes to the date of the oral proceedings can be made, except on serious grounds (see OJ EPO 1/2009, 68). If you do not appear as summoned, the oral proceedings may continue without you (R. 115(2) EPC, see also OJ EPO 10/2008, 471).

Your attention is drawn to Rule 4 EPC, regarding the language of the oral proceedings, and to the Special edition No. 3 OJ EPO 2007, L.1., concerning the filing of authorisations for company employees and lawyers acting as representatives before the EPO.

**The final date for making written submissions and/or amendments (R. 116 EPC) is 23.01.15.**

The actual room number as well as the waiting room numbers will be given to you by the porter in the foyer at the above EPO address.

Parking is available in the underground car park, accessible only via the entrance "Grasserstrasse 2/6". On presentation of the summons to oral proceedings at one of the porters' lodges in the PschorrHöfe, the parking ticket will be revoked.

1st Examiner:  
Papathoma S

2nd Examiner:  
Wolf C

Chairman:  
Fazzi R

**For the Examining Division**



Annexes:

Confirmation of receipt (Form 2936)  
Communication (EPO Form 2906)

Petitioners' Exhibit 1010, Page 125 of 231

Date: 17 september 2014  
To: Ms. Claudia Weber  
Company: European Patent Office  
From: EP&C, vestiging Rijswijk  
Pages: 3 (including this sheet)

Clean-up for starting mailbox / my files



European Patent Office  
Attn. Ms Claudia Weber/Eric Bihl  
Dir. 523 - Legal Division - CVU  
Patent Administration  
80298 Munich  
Germany

Fax +49 89 2399 4465

Rijswijk, September 16, 2014

Your ref. : --  
Our ref. : EOF  
Contact : Tel.31-70-4145442/ email : ellen.offenberg@epc.nl  
  
Re : Clean-up for Mailbox/My files – association 497

Dear Ms. Weber,

Thank you for your telephone call yesterday morning with my colleague Ellen Offenberg.  
We herewith provide you with the necessary details for conducting a search and clean-up of  
our files before we start working with the Mailbox/My files.

**Description**

The correct name of our association (497) is **EP&C**.  
This is the only name by which we wish to be registered.

**Address**

The address of our association is:

P.O. Box 3241  
2280 GE RIJSWIJK

Sir Winston Churchilllaan 295a  
2288 DC RIJSWIJK

**Pending applications**

All pending applications should be moved to the association with the address mentioned above.

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**List of EP attorneys being part of the association EP&C**

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If you need any further information for starting the search, please do not hesitate to contact Ellen Offenberg at telephone number: 0031-70-414 5442.

We await your further notification.

With kind regards,  
On behalf of EP&C

A handwritten signature in black ink, appearing to be 'Yme Groeneveld', written over a horizontal line.

Yme Groeneveld,  
Professional representative



## Acknowledgement of receipt

We hereby acknowledge receipt of the following subsequently filed document(s):

Submission number	2242017	
Application number	EP10768600.8	
Date of receipt	01 August 2013	
Receiving Office	European Patent Office, The Hague	
Your reference	P30061EP00/AZE	
Applicant	All applicants as on file	
Documents submitted	package-data.xml  epf1038.pdf (1 p.)  CLMS-1.pdfP30061EP00 - amended claims (clean version).pdf (2 p.)	ep-sfd-request.xml  EXRE3-1.pdfP30061EP00 - letter dated August 1, 2013.pdf (4 p.)  CLMS-HWA-1.pdfP30061EP00 - amended claims (marked-up version).pdf (2 p.)
Submitted by	CN=R. Raggars 13051,O=EP&C,C=NL	
Method of submission	Online	
Date and time receipt generated	01 August 2013, 14:10 (CEST)	
Message Digest	DA:E3:D1:A9:56:68:5E:FC:C8:C7:98:91:1C:19:8F:DE:45:12:C5:D7	

### Correction by the EPO of errors in debit instructions filed by eOLF

Errors in debit instructions filed by eOLF that are caused by the editing of Form 1038E entries or the continued use of outdated software (all forms) may be corrected automatically by the EPO, leaving the payment date unchanged (see decision T 152/82, OJ EPO 1984, 301 and point 6.3 ff ADA, Supplement to OJ EPO 10/2007).

P30061EP00

Subsequent to EPO communication of 16.04.2013

AMENDED CLAIMS

1. Method for the preparation of 2,5-furan dicarboxylic acid comprising the step of contacting in a reactor 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~~ oxygen-containing gas being continuously fed and removed to and from the reactor, in the presence of an oxidation catalyst comprising at least one metal selected from Co and Mn, at a temperature between 140 and 200 °C at an oxygen partial pressure of 1 to 10 bar ~~in the presence of~~, wherein a solvent or solvent mixture comprising acetic acid or acetic acid and water mixtures is present.
2. Method according to claim 1, wherein the feed comprises a compound selected from the group consisting of 5-hydroxymethylfurfural ("HMF"), esters of HMF and a mixture thereof.
3. Method according to claim 1 or 2, wherein the oxidation catalyst comprises a source of bromine.
4. Method according to claim 3, wherein the oxidation catalyst contains both Co and Mn.
5. Method according to claim 4, wherein the oxidation catalyst comprises at least one additional metal.
6. Method according to claim 5, wherein the additional metal is Zr and/or Ce.
7. Method according to claims 1-6, wherein the ~~oxidant~~ isoxygen-containing gas selected from oxygen, air or other oxygen-containing gases.
8. Method according to any of the previous claims wherein the temperature is between 160 and 190 °C.

9. Method according to any of the previous claims, wherein the feed comprises an ester of HMF containing an ester moiety of an alkyl carboxylic acid wherein the alkyl group contains up to 6 carbon atoms, preferably from 1 to 5 carbon atoms.

5 10. Process for the preparation of a dialkyl ester of 2,5,-furan dicarboxylic acid, comprising  
| the step of contacting in a reactor 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 oxygen-  
10 | containing gas being continuously fed and removed to and from the reactor, in the presence  
| of an oxidation catalyst comprising at least one metal selected from Co and Mn, at a  
| temperature between 140 and 200 °C at an oxygen partial pressure of 1 to 10 bar ~~in the~~  
| ~~presence of,~~ wherein a solvent or solvent mixture comprising acetic acid or acetic acid and  
| water mixtures, is present, and esterifying the thus obtained product.

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11. Process according to claim 10, wherein the product is esterified with a C<sub>1</sub>-C<sub>5</sub> alkyl alcohol.

12. Process according to claim 11, wherein the C<sub>1</sub>-C<sub>5</sub> alkyl alcohol is methanol and the  
20 dialkyl ester is the dimethylester of 2,5-furan dicarboxylic acid.

P30061EP00

Subsequent to EPO communication of 16.04.2013

AMENDED CLAIMS

1. Method for the preparation of 2,5-furan dicarboxylic acid comprising the step of contacting in a reactor 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  
5 a mixture of two or more of these compounds with an oxygen-containing gas being continuously fed and removed to and from the reactor, in the presence of an oxidation catalyst comprising at least one metal selected from Co and Mn, at a temperature between 140 and 200 °C at an oxygen partial pressure of 1 to 10 bar , wherein a solvent or solvent mixture comprising acetic acid or acetic acid and water mixtures is present.  
10
2. Method according to claim 1, wherein the feed comprises a compound selected from the group consisting of 5-hydroxymethylfurfural ("HMF"), esters of HMF and a mixture thereof.
- 15 3. Method according to claim 1 or 2, wherein the oxidation catalyst comprises a source of bromine.
4. Method according to claim 3, wherein the oxidation catalyst contains both Co and Mn.
- 20 5. Method according to claim 4, wherein the oxidation catalyst comprises at least one additional metal.
6. Method according to claim 5, wherein the additional metal is Zr and/or Ce.
- 25 7. Method according to claims 1-6, wherein the oxygen-containing gas selected from oxygen, air or other oxygen-containing gases.
8. Method according to any of the previous claims wherein the temperature is between 160 and 190 °C.
- 30 9. Method according to any of the previous claims, wherein the feed comprises an ester of HMF containing an ester moiety of an alkyl carboxylic acid wherein the alkyl group

contains up to 6 carbon atoms, preferably from 1 to 5 carbon atoms.

10. Process for the preparation of a dialkyl ester of 2,5-furan dicarboxylic acid, comprising the step of contacting in a reactor a feed comprising a compound selected from the group  
5 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 oxygen-containing gas being continuously fed and removed to and from the reactor, in the presence of an  
10 oxidation catalyst comprising at least one metal selected from Co and Mn, at a temperature between 140 and 200 °C at an oxygen partial pressure of 1 to 10 bar, wherein a solvent or solvent mixture comprising acetic acid or acetic acid and water mixtures, is present, and esterifying the thus obtained product.

11. Process according to claim 10, wherein the product is esterified with a C<sub>1</sub>-C<sub>5</sub> alkyl  
15 alcohol.

12. Process according to claim 11, wherein the C<sub>1</sub>-C<sub>5</sub> alkyl alcohol is methanol and the dialkyl ester is the dimethylester of 2,5-furan dicarboxylic acid.

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## Letter accompanying subsequently filed items

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The document(s) listed below is (are) subsequently filed documents pertaining to the following application:

Application number

10768600.8

Applicant's or representative's reference

P30061EP00/AZE

	Description of document	Original file name	Assigned file name
1	Reply to examination report	P30061EP00 - letter dated August 1, 2013.pdf	EXRE3-1.pdf
2	Amended claims (clean copy)	P30061EP00 - amended claims (clean version).pdf	CLMS-1.pdf
3	Amended claims with annotations	P30061EP00 - amended claims (marked-up version).pdf	CLMS-HWA-1.pdf

### Signatures

Place: **Rijswijk**  
Date: **01 August 2013**  
Signed by: **NL, EP&C, R. Raggars 13051**  
Association: **EP&C**  
Capacity: **(Representative)**

EUROPEAN PATENT OFFICE  
P.O. Box 5818  
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Rijswijk, August 1, 2013

Your ref. : --  
Our ref. : P30061EP00/AZE/bba  
Contact : Tel. 31-70-4145471/ email: Boyle@epc.nl

Application no. : 10768600.8  
Country : Europe  
In the name of : Furanix Technologies B.V.

Dear Madam or Sir,

Reference is made to your communication pursuant to Article 94(3) EPC, dated April 16, 2013.

In the communication objections are raised as to the violation of Art 123(2) EPC and as to alleged lack of inventive step. Priority and novelty of the present claims are acknowledged.

In order to overcome the objection that is raised under Art 123(2) EPC we herewith file a set of amended claims to replace the claims currently in the specification. In accordance with the Examiner's suggestions, amended claim 1 now contains the requirements that the oxidant is an oxygen-containing gas, and that the oxygen-containing gas is continuously fed and removed from the reactor in which the contact of the feedstock with the oxygen-containing gas takes place. Amended claim 1 also covers identical subject matter to the matter that was present in original claim 10. Claims 7 and 11 have been brought into conformity with newly amended claim 1. It is submitted that the amended set of claims overcomes the objections as to added matter.

For your convenience we enclose both a marked-up copy and a clean copy of the amended claims.

Since the priority and novelty of the pending claims are acknowledged, the newly amended claims are also entitled to the priority and are novel.

When assessing the involvement of an inventive step, the problem-solution approach is to be followed. As the first step the "closest prior art", is to be determined.

In general, the closest prior art is that which corresponds to a similar use and requires the minimum of structural and functional modifications to arrive at the claimed invention. Therefore, we consider D8 (WO 01/72732) to represent the closest prior art.

D8 discloses a method for the preparation of 2,5-furan dicarboxylic acid comprising the step of contacting in a reactor 5-hydroxymethylfurfural ("HMF") with a flow of air as oxygen-containing gas that is being continuously fed and removed to and from the reactor, in the presence of a Co and Mn-containing oxidation catalyst, at a temperature between 75 and 150 °C at a pressure of 70 bar in the presence of a solvent comprising acetic acid.

D8 further teaches that the oxidation of 5-hydroxymethylfurfural ("HMF") at lower temperatures (50 to 95 °C) and atmospheric pressure no 2,5-furan dicarboxylic acid is being produced (cf. Examples 1-6 in D8). If the temperature is maintained within this range and the pressure is increased to 70 bar, still no 2,5-furandicarboxylic acid is formed. Instead, the yield of diformylfuran is slightly enhanced.

D8 shows that only at pressures of 70 bar, meaning an oxygen partial pressure of about 14 bar, 2,5-furandicarboxylic acid can be produced if the temperature is above 100 °C. The maximum yield of 2,5-furandicarboxylic acid, at a temperature within the presently claimed range, was 54.6% after two hours at 75 °C and two hours at 150 °C.

In this context reference is made to the examples 7 to 10 and 12 to 15 on the one hand, wherein the oxidation is conducted at a temperature of 50 and 75 °C, respectively, which examples yield diformylfuran, and to examples 16 to 19 and 21 to 24, wherein the same catalyst concentrations and pressures apply, but which are carried out at a temperature of 100 and 125, respectively, and wherein 2,5-furandicarboxylic acid is obtained.

Hence, from D8 the skilled person is taught that the oxidation of 5-hydroxymethylfurfural at low pressure, e.g. 1 bar, and at high pressure, e.g. 70 bar, the use of temperatures of 50 to 95 °C will not yield any 2,5-furandicarboxylic acid. Only at temperatures of at least 100 to 150 °C, 2,5-furandicarboxylic acid can be obtained. Hence, the skilled person is taught that variations in pressure are immaterial.

A main difference between the present invention and the method according to the prior art is constituted by the oxygen partial pressure.

The second step of the problem-and-solution approach is the establishing of the "objective technical problem" to be solved. The problem is to achieve a good yield of 2,5-furandicarboxylic acid from a feedstock that contains certain derivatives of 5-hydroxymethylfurfural and/or 5-hydroxymethylfurfural itself.

The solution has been to conduct such a reaction at an oxygen partial pressure of 1 to 10 bar.

The final question in the problem-solution approach is then to assess whether this solution would have been obvious to the skilled person.



The Examiner seems to believe that the particular partial pressure range is within the common general knowledge of the skilled person. In combination with the teachings of D8, she believes that this combination renders the present invention obvious. We contest this.

It would appear that the Examiner deduces her conclusion from the paragraph on page 4, line 34 to page 5, line 10 of the present application. In this paragraph reference is made to a commercial oxidation process wherein in practice the pressures can be between 5 and 100 bar. It would seem that the underlined phrases gives the Examiner the impression that it is common to have a partial oxygen partial pressure between 1 and 20 bar in any preparation of 2,5-furandicarboxylic acid.

It is respectfully submitted that the Examiner errs in this respect. The paragraph under consideration means that if the skilled person would plan the (future) preparation of 2,5-furandicarboxylic acid on a commercial scale, he is taught to apply a particular oxygen partial pressure when the oxidation is carried out with an oxygen-containing gas that is continuously fed and removed.

The paragraph does not refer to existing commercial processes. Such commercial processes do not exist at the moment. It is therefore, submitted that the feature of an oxygen partial pressure in the range of 1 to 10 bar in the oxidation of 5-hydroxymethylfurfural and derivatives thereof, does not belong to the common general knowledge of the skilled person.

At the risk of labouing the obvious, it is submitted that no reference of a textbook, or something similar has been provided by the Examiner to show that such feature does constitute common general knowledge. It is respectfully submitted that not even a specific publication has been cited that shows the particular pressure range can be used for the presently claimed oxidation..

It is therefore submitted that the present invention is inventive over D8.

The Examiner also refers to D9 (WO 2008/054804). This reference discloses a method for the oxidation of 5-hydroxymethylfurfural with air or oxygen at 50 to 200 °C in the presence of a catalyst that comprises platinum on a carrier. Oxidation products include diformylfuran, formylfuran carboxylic acid and 2,5-furandicarboxylic acid. Pressures that are used in the examples include 150 psig (about 10 barg) air or oxygen. Temperatures in the examples vary from 30 °C to 160 °C, the majority of examples being conducted at 100 °C.

It is evident that the catalyst used in D9 is different from the catalyst employed in the method according to the invention. The platinum on carrier catalyst is a heterogeneous catalyst, and its behaviour cannot be compared with the catalyst according to the present invention, in particular when this catalyst is dissolved (cf. present application page 4, line 10).. D9 also explicitly teaches that "...particular catalysts and sets of reaction conditions and parameters can favour selective production of one or more reaction products or intermediates" (cf. D9, page 8, [0055]).

Hence, D9 teaches that if a particular product is desired, it is not feasible to transfer reaction conditions that are suitable for one catalyst to another catalyst, or that a particular set of reaction conditions are suitable for different catalysts.

It is therefore submitted that the skilled person having the above-mentioned problem and starting from D8, would have no incentive to combine the process of D8 with one particular reaction condition of D9 with the expectation that the problem would be solved. He would certainly not do so, since he would expect from the teachings of D8 that a variation of the pressure would not solve his problem.

Therefore, it is evident that the present application involves an inventive step over D8 alone and over D8 and D9 combined.

Reconsideration and withdrawal of the objection are respectfully requested.

The communication also contains some further comments. The comments regarding claims 1 and 10 have become moot by the amendments as indicated above.

As to the word “preferably” in claim 9 (original claim 11) it is acknowledged that the feature following this word does not create any ambiguity and is entirely optional.

It is suggested to postpone the amendments of the description, including the correction of the compound in example 3, until agreement has been reached about the wording of allowable claims. At the same time, a brief discussion of D7 and D9-D11 will be included in the description.

We trust that the newly presented claims will be found allowable. In case the Examining Division would intend to refuse the application, oral proceedings are requested.

Yours faithfully,  
EP&C



A.W.J. Zeestraten  
Association no. 497

Enclosures: Amended claims (marked-up and clean versions)

The examination is being carried out on the **following application documents**

**Description, Pages**

1-9 as published

**Claims, Numbers**

1-12 filed with entry into the regional phase before the EPO

The present application relates to a process for the preparation of FDCA from HMF with an oxidant, an oxidation catalyst comprising at least one metal selected from Co and Mn, in acetic acid or acetic acid and water mixtures as solvent, at a temperature between 140 and 200 °C and at an oxygen partial pressure of 1 to 10 bar. Further, it relates to the further conversion of FDCA to a dialkyl ester thereof.

Reference is made to the following documents; the numbering will be adhered to in the rest of the procedure.

- D1 WALT PARTENHEIMER ET AL.: "Synthesis of 2,5-diformylfuran and furan-2,5-dicarboxylic acid by catalytic air oxidation of 5-hydroxymethylfurfural. Unexpectedly selective aerobic oxidation of benzyl alcohol to benzaldehyde with metal/bromide catalysts", ADV. SYNTH. CATAL., vol. 343, no. 1, 2001, pages 102-111, XP002584717,
- D2 US 2009/156841 A1 (SANBORN ALEXANDRA J [US] ET AL) 18 June 2009 (2009-06-18)
- D3 JP 2009 242312 A (AIR WATER INC) 22 October 2009 (2009-10-22)
- D4 HAWORTH W N ET AL: "The conversion of sucrose into furan compounds. Part II. Some 2 : 5-disubstituted tetrahydrofurans and their products of ring scission", JOURNAL OF THE CHEMICAL SOCIETY, CHEMICAL SOCIETY, LETCHWORTH; GB, no. 1, 1 January 1945 (1945-01-01), pages 1-4, XP008122626, ISSN: 0368-1769, DOI: DOI:10.1039/JR9450000001

- D5 WO 2006/063220 A2 (ARCHER DANIELS MIDLAND CO [US]; SANBORN ALEXANDRA J [US]) 15 June 2006 (2006-06-15)
- D6 TONG X ET AL: "Biomass into chemicals: Conversion of sugars to furan derivatives by catalytic processes", APPLIED CATALYSIS A: GENERAL, ELSEVIER SCIENCE, AMSTERDAM, NL, vol. 385, no. 1-2, 15 September 2010 (2010-09-15), pages 1-13, XP027230510, ISSN: 0926-860X [retrieved on 2010-07-30]
- D7 BOISEN A ET AL: "Process integration for the conversion of glucose to 2,5-furandicarboxylic acid", CHEMICAL ENGINEERING RESEARCH AND DESIGN, PART A, INSTITUTION OF CHEMICAL ENGINEERS, XX, vol. 87, no. 9, 1 September 2009 (2009-09-01), pages 1318-1327, XP026613647, ISSN: 0263-8762, DOI: DOI:10.1016/J.CHERD.2009.06.010 [retrieved on 2009-07-25]
- D8 WO 01/72732 A2 (DU PONT [US]; GRUSHIN VLADIMIR [US]; PARTENHEIMER WALTER [US]; MANZER) 4 October 2001 (2001-10-04)
- D9 WO 2008/054804 A2 (BATTELLE MEMORIAL INSTITUTE [US]; LILGA MICHAEL A [US]; HALLEN RICHARD) 8 May 2008 (2008-05-08)
- D10 JP 2009 001519 A (CANON KK) 8 January 2009 (2009-01-08)
- D11 SU 636 233 A1 (INST ORGANICHESKOGO SINTEZA AK [SU]; INST KHM FIZ AN SSSR [SU]) 5 December 1978 (1978-12-05)
- D12 WO 2010/132740 A2 (ARCHER DANIELS MIDLAND CO [US]; SANBORN ALEXANDRA [US]) 18 November 2010 (2010-11-18)
- D13 EP 0 356 703 A2 (HOECHST AG [DE]) 7 March 1990 (1990-03-07)
- D14 GRABOWSKI G ET AL: "The electrochemical oxidation of 5-hydroxymethylfurfural with the nickel oxide/hydroxide electrode", ELECTROCHIMICA ACTA, ELSEVIER SCIENCE PUBLISHERS, BARKING, GB,

vol. 36, no. 13, 1 January 1991 (1991-01-01), page 1995, XP026726025,  
ISSN: 0013-4686, DOI: DOI:10.1016/0013-4686(91)85084-K  
[retrieved on 1991-01-01]

1 Article 123(2) EPC

The Applicant filed with entry into the European Phase an amended set of 12 claims.

Claim 1 was amended and features of the dependent claims 3, 9 and 10 as well as of the description were introduced in said claim. The introduction of the features of claims 3, 9 and 10 in claim 1 does not contravene Article 123(2) EPC.

However, the introduction of the feature "at an oxygen partial pressure of 1 to 10 bar" in claim 1 is contrary to the requirements of Article 123(2) EPC:

- first of all, although said passage relates to an oxygen partial pressure, the oxidant is not restricted in claim 1 to oxygen or oxygen-containing gases,
- secondly, the relevant passage on page 5, relates not only to oxygen-containing gases but also to continuous feeding and removing of the oxidant gas (it is stated in lines 4-9 of page 5 that if the gas is supplied all at the start of the reaction the pressure of the system is significantly higher).

According to established jurisprudence of the boards of appeal, if a claim is to be restricted to a preferred embodiment, it is normally not admissible under Article 123(2) EPC to extract isolated features from a set of features which have originally been disclosed in combination for that embodiment. Such kind of amendment would only be justified in the absence of any clearly recognisable functional or structural relationship among said features (see the examples cited in "Case Law of the Boards of Appeal of the European Patent Office, 10th edition 2010", European Patent Office 1999, Section III-A, 2).

Therefore, introduction of the feature "at an oxygen partial pressure of 1 to 10 bar" in claim 1 contravenes Article 123(2) EPC.

2 Article 89 EPC

Close inspection of the priority documents has shown that the priority is validly claimed.

### 3 Article 54 EPC

Although the amendments carried out with entry into the European phase are not allowable under Article 123(2) EPC, short reference is made to the novelty of presently claimed subject-matter.

Compared to the originally filed claim 1 present claim 1 restricts the oxidation catalyst to one comprising at least one metal from Co and Mn, the temperature to 140-200 °C, the solvent to acetic acid or mixtures thereof with water and the oxygen partial pressure to 1 to 10 bar.

As mentioned in the Written Opinion of the International Search Authority in detailed manner, documents D7, D8, D9, D10 and D11 are prejudicial for the novelty of the originally filed claim 1.

Said documents disclose further features:

- D7 (Ribeiro disclosure) discloses  $\text{CO}(\text{acac})_3$  as a catalyst, deionized water as a solvent, a temperature of 160 °C and a pressure of 20 bar of synthetic air, i.e. 4.2 bar partial oxygen pressure,
- D8 discloses Co/Mn/Br/Zr as a catalyst, acetic acid as solvent, a temperature of 150 °C and a pressure of 1000psi (7MPa=70bar) of an oxygen containing gas i.e. 14.7 bar partial oxygen pressure,
- D9 discloses oxygen as oxidant and acetic acid as solvent, a temperature of 150 °C and a pressure of 150psi (=10,34 bar) air i.e. 31.5 psi / 2.17 bar partial oxygen pressure; the catalyst used, however, is a catalyst comprising Pt on a support material, such as  $\text{ZrO}_2$ ,
- D10 discloses a cobalt containing catalyst, water as a solvent, oxygen as oxidant, temperatures between 50-200 °C and a pressure between 1 and 40 MPa (i.e. 10-400 bar),
- D11 discloses  $\text{CuO-Ag}_2\text{O-Ce}_2\text{O}_3$  as catalyst, temperatures between 110-150 °C and a pressure between 25-30 atm (~25-30bar).

Further, it is mentioned that since the priority is validly claimed documents D3 and D6 are not relevant for the examination of novelty. The late published document D12 has entered the European Phase and discloses oxygen as oxidant, acetic acid as solvent, a catalyst containing cobalt and manganese, a temperature of 120° to 140 °C and a pressure of 1000psi (=69bar).

In view of the above, novelty could have been in principle acknowledged, since not all presently claimed features are disclosed in the same document.

4 Article 56 EPC

4.1 With the amendments filed with entry into the European Phase the Applicant attempted to delimit the claimed subject-matter by introducing further features in the independent claim 1. However, as it can be seen in the documents cited in the Search Report, oxygen or an oxygen containing gas is normally used as oxidant in the preparation of FDCA from HMF, further this preparation is normally conducted in acetic acid, the catalyst is normally one comprising at least one metal selected from Co and Mn, there are documents (such as D7-D11) that disclose a high reaction temperature such as 150°C and there are documents that disclose an oxygen partial pressure within or close to the claimed range (D7-D9).

Through the introduction of the features of the solvent, catalyst and pressure in present claim 1 in addition to the feature of temperature existing in the originally filed claim 1, the Applicant rendered the claimed subject-matter novel over the disclosure of the prior art.

However, the reader is left into doubt which is the special technical feature of the claimed process that leads to the claimed effect, .i.e an improved process for the preparation of FDCA.

4.2 The present application discloses that:

"The pressure in a commercial oxidation process may vary within wide ranges. **When a diluent is present, and in particular with acetic acid as diluent, the temperature and the pressure in such a process are not independent.** The pressure is determined by the solvent (e.g., acetic acid) pressure at a certain temperature. The pressure of the reaction mixture is preferably selected such that the solvent is mainly in the liquid phase. In practice this means that pressures between 5 and 100 bar can be used **with a preference for pressures between 10 and 80 bar.** In case the oxidant is an oxygen-containing gas, such as air, the gas can be continuously fed to and removed from the reactor, or the gas can be supplied all at the start of the reaction. In the latter case, the pressure of the system will depend on the headspace volume and the amount of gas required to convert the starting material. It is clear that in the latter case, the pressure of the system may be significantly higher than the pressure in a process wherein an oxygen containing gas is continuously fed and removed. In the case of continuously feeding and removing the oxidant gas to and from the reactor, the oxygen partial pressure will suitably be between 1 and 30 bar or more preferably between 1 and 10 bar."

The cited passage is perceived as relating to the common general knowledge of the person skilled in the art (The pressure in a commercial oxidation process may vary within wide ranges. When a diluent is present, and in particular with acetic acid as diluent, the temperature and the pressure in such a process are not independent). It talks

about the interconnection of solvent, temperature and pressure in the preparation of FDCA and what is more it explicitly states that "*In practice this means that pressures between 5 and 100 bar can be used with a preference for pressures between 10 and 80 bar*" in other words that it is common practice in the preparation of FDCA to have a partial oxygen pressure between 1 and 20 bar, preferably between 2 and 16 (the preference of between 1 and 10 bar relates to a continuous feeding and removing the oxidant gas).

- 4.3 Furthermore, reference is also made to document D9. In figure 31 it is shown that in the experiments carried out there is 100% conversion of HMF and the selectivity to FDCA increases with increased temperature and reduced pressure. In addition, according to example 1 of D9 the process described therein leads to complete oxidation of HMF and testing at chromatography revealed an absence of detectable DFF and FFCA.

The Applicant referred to document D8 in his argumentation relating to inventive step.

D8 discloses the preparation of FDCA from HMF with an oxygen containing gas in acetic acid as a solvent and with a Co/Mn/Br/Zr catalyst. It was found out that increase of the temperature leads to higher yields.

The disclosure of D8 differs, however, from the presently claimed subject-matter in the pressure of the oxidant used.

According to the Applicant the effect of this difference is that the claimed process leads to higher yields of FDCA due to 100% conversion of HMF.

However, the person skilled in the art either by starting from D8 alone and combining it with the common general knowledge as cited in the present application or by combining it with the teaching of D9, in particular with figure 31 and example 1, he would decrease the pressure of the oxygen containing gas and he would thus arrive to the process presently claimed.

Consequently, the claimed subject-matter is not regarded as inventive and the requirements of Article 56 EPC are therefore considered not be fulfilled.

## 5 Further Comments

- 5.1 Claim 10 relating to the further conversion of FDCA to a dialkyl ester, does not include in its wording the limitation with respect to the oxygen partial pressure. The introduction of this feature in claim 1 was found not be allowable under Article 123(2) EPC. However, it should be mentioned that as claim 10



(originally filed claim 12) relates to the further conversion of the FDCA produced according to the claimed process, the features used when defining the process for the preparation of FDCA should be the same used for defining its preparation also in the claim relating to its further conversion (otherwise objections as to Non-unity may arise).

- 5.2 The Applicant introduced features of the dependent claims 3, 9 and 10 into present claim 1. The introduction of these specific features was found not to contravene Article 123(2) EPC; however, the Applicant is advised to use, wording as close as possible to that originally filed. E.g. originally filed claim 10 relates to a solvent or solvent mixture comprising acetic acid or acetic acid and water mixtures. The passage of present claim 1, however, uses only the wording "solvent".
- 5.3 Claim 11 uses the wording "preferably". This wording has no limiting effect on the scope of a claim; that is to say, the feature following any such expression is to be regarded as entirely optional.
- 5.4 In example 3 it is erroneously referred to 2,5-dimethylfurfural. The correct reference is to 2,5-dimethylfuran (DMF).

- 6 When filing amended claims the applicant should at the same time bring the description into conformity with the amended claims. Care should be taken during revision, especially of the introductory portion and any statements of problem or advantage, not to add subject-matter which extends beyond the content of the application as originally filed (Article 123(2) EPC).

In order to facilitate the examination of the conformity of the amended application with the requirements of Article 123(2) EPC, the applicant should clearly identify the amendments made, irrespective of whether they concern amendments by addition, replacement or deletion, and indicate the passages of the application as filed on which these amendments are based.

If the applicant considers it appropriate, these indications could be submitted in handwritten form on a copy of the relevant parts of the application as filed.

In addition to these, any information the applicant may wish to submit concerning the subject - matter of the invention, for example further details of its advantages or of the problem it solves, and for which there is no basis in the application as filed, should be confined to the letter of reply and not be incorporated into the application (Article 123(2) EPC).



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Application No. 10 768 600.8 - 1462	Ref. P30061EP00/AZE	Date 16.04.2013
Applicant Furanix Technologies B.V		

### Communication pursuant to Article 94(3) EPC

The examination of the above-identified application has revealed that it does not meet the requirements of the European Patent Convention for the reasons enclosed herewith. If the deficiencies indicated are not rectified the application may be refused pursuant to Article 97(2) EPC.

You are invited to file your observations and insofar as the deficiencies are such as to be rectifiable, to correct the indicated deficiencies within a period

**of 4 months**

from the notification of this communication, this period being computed in accordance with Rules 126(2) and 131(2) and (4) EPC. One set of amendments to the description, claims and drawings is to be filed within the said period on separate sheets (R. 50(1) EPC).

If filing amendments, you must identify them and indicate the basis for them in the application as filed. Failure to meet either requirement may lead to a communication from the Examining Division requesting that you correct this deficiency (R. 137(4) EPC).

**Failure to comply with this invitation in due time will result in the application being deemed to be withdrawn (Art. 94(4) EPC).**

**The notification of this communication starts the 24-month period according to Rule 36(1)(a) EPC for filing a voluntary divisional application divided from this application or from any sequential application. For further information see Guidelines for Examination, A-IV, 1.1.1.2 and 1.1.1.4.**



Papathoma, Sofia  
Primary Examiner  
**For the Examining Division**

Enclosure(s): 7 page/s reasons (Form 2906)

## Acknowledgement of receipt

We hereby acknowledge receipt of the following subsequently filed document(s):

Submission number	1872188	
Application number	EP10768600.8	
Date of receipt	07 November 2012	
Receiving Office	European Patent Office, The Hague	
Your reference	P30061EP00/AZE	
Applicant	All applicants as on file	
Documents submitted	package-data.xml  epf1038.pdf (1 p.)  CLMS-1.pdfP30061EP00 - amended claims (clean version).pdf (2 p.)	ep-sfd-request.xml  EPLETT-1.pdfP30061EP00 - letter dated November 7, 2012.pdf (3 p.)  CLMS-HWA-1.pdfP30061EP00 - amended claims (marked-up).pdf (2 p.)
Submitted by	CN=A. Zeestraten 22141,O=Exter Polak & Charlouis B.V.,C=NL	
Method of submission	Online	
Date and time receipt generated	07 November 2012, 09:07 (CET)	
Message Digest	F1:C2:0A:C0:63:E3:45:6F:91:B5:13:CC:37:FA:7E:D5:C2:62:D2:12	

### Correction by the EPO of errors in debit instructions filed by eOLF

Errors in debit instructions filed by eOLF that are caused by the editing of Form 1038E entries or the continued use of outdated software (all forms) may be corrected automatically by the EPO, leaving the payment date unchanged (see decision T 152/82, OJ EPO 1984, 301 and point 6.3 ff ADA, Supplement to OJ EPO 10/2007).

P30061EP00

AMENDED CLAIMS (clean version)

1. Method 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  
5 a mixture of two or more of these compounds with an oxidant in the presence of an oxidation catalyst comprising at least one metal selected from Co and Mn, at a temperature between 140 and 200 °C at an oxygen partial pressure of 1 to 10 bar in the presence of a solvent comprising acetic acid or acetic acid and water mixtures.
- 10 2. Method according to claim 1, wherein the feed comprises a compound selected from the group consisting of 5-hydroxymethylfurfural ("HMF"), esters of HMF and a mixture thereof.
3. Method according to claim 1 or 2, wherein the oxidation catalyst comprises a source of  
15 bromine.
4. Method according to claim 3, wherein the oxidation catalyst contains both Co and Mn.
5. Method according to claim 4, wherein the oxidation catalyst comprises at least one  
20 additional metal.
6. Method according to claim 5, wherein the additional metal is Zr and/or Ce.
7. Method according to claims 1-6, wherein the oxidant is selected from oxygen, air or  
25 other oxygen-containing gases.
8. Method according to any of the previous claims wherein the temperature is between 160 and 190 °C.
- 30 9. Method according to any of the previous claims, wherein the feed comprises an ester of HMF containing an ester moiety of an alkyl carboxylic acid wherein the alkyl group contains up to 6 carbon atoms, preferably from 1 to 5 carbon atoms.

10. Process for the preparation of a dialkyl ester 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-hydroxymethyl-furfural, 5-methylfurfural, 5-(chloromethyl)furfural, 5-methylfuroic acid, 5-(chloromethyl)furoic acid, 2,5-dimethylfuran and
- 5 a mixture of two or more of these compounds with an oxidant in the presence of an oxidation catalyst comprising at least one metal selected from Co and Mn, at a temperature between 140 and 200 °C in the presence of a solvent comprising acetic acid or acetic acid and water mixtures, and esterifying the thus obtained product.
- 10 11. Process according to claim 10, wherein the product is esterified with a C<sub>1</sub>-C<sub>5</sub> alkyl alcohol.
12. Process according to claim 11, wherein the C<sub>1</sub>-C<sub>5</sub> alkyl alcohol is methanol and the dialkyl ester is the dimethylester of 2,5-furan dicarboxylic acid.

15

P30061EP00

AMENDED CLAIMS (Marked-up version)

1. Method 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  
5 a mixture of two or more of these compounds with an oxidant in the presence of an oxidation catalyst comprising at least one metal selected from Co and Mn, at a temperature higher than 140 °C between 140 and 200 °C at an oxygen partial pressure of 1 to 10 bar in the presence of a solvent comprising acetic acid or acetic acid and water mixtures.
- 10 2. Method according to claim 1, wherein the feed comprises a compound selected from the group consisting of 5-hydroxymethylfurfural ("HMF"), esters of HMF and a mixture thereof.
- ~~3. Method according to claim 1 or 2, wherein the oxidation catalyst comprises at least one~~  
15 ~~metal selected from the group consisting of Co and Mn.~~
- ~~34. Method according to claim 1 or 2 or 3, wherein the oxidation catalyst comprises a source of bromine.~~
- 20 ~~54. Method according to claim 43, wherein the oxidation catalyst contains both Co and Mn.~~
- ~~65. Method according to claim 54, wherein the oxidation catalyst comprises at least one additional metal.~~
- 25 ~~76. Method according to claim 65, wherein the additional metal is Zr and/or Ce.~~
- ~~87. Method according to claims 1-6, wherein the oxidant is selected from oxygen, air or other oxygen-containing gases.~~
- 30 ~~98. Method according to any of the previous claims wherein the temperature is between 140 and 200 °C, most preferably between 160 and 190 °C.~~

~~10. Method according to any one of the previous claims, wherein a solvent or solvent mixture is present, preferably comprising a solvent containing a monocarboxylic acid functional group, more preferably acetic acid or acetic acid and water mixtures.~~

5 ~~119. Method according to any of the previous claims, wherein the feed comprises an ester of HMF containing an ester moiety of an alkyl carboxylic acid wherein the alkyl group contains up to 6 carbon atoms, preferably from 1 to 5 carbon atoms.~~

~~1210. Process for the preparation of a dialkyl ester 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-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 comprising at least one metal selected from Co and Mn, at a temperature higher than 140 °C between 140 and 200 °C in the presence of a solvent comprising acetic acid or acetic acid and water mixtures, and esterifying the thus obtained product.~~

20 ~~1311. Process according to claim 1210, wherein the product is esterified with a C<sub>1</sub>-C<sub>5</sub> alkyl alcohol.~~

~~1412. Process according to claim 1311, wherein the C<sub>1</sub>-C<sub>5</sub> alkyl alcohol is methanol and the dialkyl ester is the dimethylester of 2,5-furan dicarboxylic acid.~~

25 ~~15. Method for the preparation of 2,5-furandicarboxylic acid wherein a carbohydrate source is converted in the presence of an alkyl carboxylic acid into products comprising an HMF ester and optionally 5-hydroxymethyl furfural, from which is isolated a feed comprising the ester of HMF and optionally 5-hydroxymethyl furfural, and which method comprises further the subsequent step of contacting the feed with an oxidant in the presence of an oxidation catalyst, preferably a cobalt and manganese and bromide-containing catalyst, under appropriate reaction conditions.~~



EUROPEAN PATENT OFFICE  
P.O. Box 5818  
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Rijswijk, November 7, 2012

Our ref. : P30061EP00/AZE/bba  
Contact : Tel. 31-70-4145471/ email: Boyle@epc.nl

Application no. : 10768600.8  
Country : Europe  
In the name of : Furanix Technologies B.V.

Dear Madam or Sir,

Reference is made to the communication pursuant to Rules 161(1) and 162 EPC dated May 31, 2012. The communication contained an invitation to correct any deficiencies that were reported in the written opinion that accompanied the search report of the corresponding international application.

According to the written opinion the Examiner considers that the present claims lack novelty in view of a number of references, viz. D7 (Boisen et al., Chem Eng. Research Design, 87 (2009) 1318-1327), D8 (WO 01/72732), D9 (WO 2008/054804), D10 (JP 2009 001519) and D11 (RU 636233). In order to overcome the novelty objections please find herewith a set of amended claims to replace the claims currently in the specification. For your convenience we enclose a marked-up version of the amended claims wherein the amendments are visible, as well as a clean version.

The amended claim 1 now stipulates that the oxidation catalyst comprises at least one of the metals Co and Mn (cf. original claim 3). It further contains an upper limit for the reaction temperature (cf. original claim 9). It requires the presence of a solvent comprising acetic acid or a mixture of acetic acid and water (cf. original claim 10). Finally, it includes the feature that the oxygen partial pressure is from 1 to 10 bar (cf. page 5, lines 11-12).

Original claims 3 and 10 have been deleted. Also claim 15 has been deleted. New claim 10 has been amended to include i.a. the presence of an acetic acid-containing solvent. Other amendments are of an editorial nature and are clearly visible from the marked-up version of the amended claims.

It is submitted that the amended claims find proper basis in the application as filed.

As to the references cited the following is observed.

D7 refers to an article by Ribeiro and Schuchardt wherein cobalt acetylacetonate encapsulated in silica is used in the production of 2,5-furan dicarboxylic acid ("FDCA") from fructose via the formation of 5-hydroxymethyl furfural ("HMF"). This reaction is different from the presently claimed method.

D7 further refers to an article by Partenheimer and Grushin, that was cited by the Examiner as D1. The Examiner has already concluded that the present claim is novel over D1. In view thereof it is concluded that the present claims are novel over D7.

D8 relates to the oxidation of HMF to various products, including FDCA. The temperatures for the preparation of the diacid are stated to be between 50 and 250 °C. The catalyst is Co/Mn/Br, wherein optionally Zr may be included. Experiments with these catalyst systems were conducted wherein HMF was oxidised with air at 7 MPa at temperatures ranging from 75 to 150 °C. At 105 °C for 12 hours almost 59% FDCA was obtained; in a two stage oxidation at 75 °C in the first stage and 150 °C in the second stage, yields of up to almost 55 % FDCA were obtained.

As indicated above, the pressure at the reaction was 7MPa, i.e. 70 bar. This corresponds to an oxygen partial pressure of about 14 bar.

In accordance with the present claim the oxygen partial pressure in the presently claimed process amounts from 1 to 10 bar. This is lower than according to D8. Therefore, the amended claims are novel over D8.

D9 relates to the oxidation of HMF using air or O<sub>2</sub> as oxidant over a platinum-supported catalyst; the temperature ranges from about 50 to about 200 °C. The catalyst differs from the catalyst of the presently claimed method. Further, there is no mentioning of an acetic acid-containing solvent. Therefore the presently claimed method is novel over D9.

D10 discloses the oxidation of HMF over a catalyst containing Ru, Co and Ce with molecular oxygen in an aqueous solution. The temperature may be from 50 to 200 °C.

D10 is silent about the presence of an acetic acid-containing solvent. Therefore the presently claimed method is novel over D10.

D11 discloses the oxidation of HMF over a catalyst comprising CuO.Ag<sub>2</sub>O.Ce<sub>2</sub>O<sub>3</sub> on alumina. The oxidant is oxygen or air, the pressure is 25 - 30 atm and the temperature is 110 - 150 °C.

The catalyst is different from the one of the presently claimed method. Moreover, the acetic acid-containing solvent has not been mentioned. Therefore, the amended claims are novel over D11.

The claims are also inventive.

The closest prior art is considered to be D8. An important difference between D8 and the presently claimed method resides in a lower oxygen pressure.

This difference is also inventive, since it is surprising that at a higher oxygen pressure, the yield on FDCA reaches a maximum of about 55%, based on HMF (cf. D8, page 16, Experiments 38 - 40).

In the process according to the present invention experiments with HMF and air are conducted at 20 bar, representing about 4 bar oxygen. The HMF conversion was 100% and the yield on FDCA was between about 68 and 78% (cf. present application, page 8, experiments 1a, 1e, 1i and 1m). It is surprising that at lower oxygen pressure, the yield on desired product is increased.

Therefore, we respectfully submit that the present claims contain patentable subject matter.

It is proposed to postpone the amendment to the description, including the correction of the typographical error in example 3, until the Examiner has expressed his agreement to the wording of the allowable claims.

We look forward to receiving your further report on this application in due course.

Yours faithfully,  
EP&C

A handwritten signature in black ink, appearing to read 'A.W.J. Zeestraten', is written over a series of horizontal dotted lines.

A.W.J. Zeestraten

Enclosure: Amended claims (marked-up version and clean version)



## Letter accompanying subsequently filed items

Representative:

**A.W.J. Zeestraten**  
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The document(s) listed below is (are) subsequently filed documents pertaining to the following application:

Application number

10768600.8

Applicant's or representative's reference

P30061EP00/AZE

	Description of document	Original file name	Assigned file name
1	Letter relating to the search and examination procedure	P30061EP00 - letter dated November 7, 2012.pdf	EPLETT-1.pdf
2	Amended claims (clean copy)	P30061EP00 - amended claims (clean version).pdf	CLMS-1.pdf
3	Amended claims with annotations	P30061EP00 - amended claims (marked-up).pdf	CLMS-HWA-1.pdf

### Signatures

Place: **Rijswijk**  
Date: **07 November 2012**  
Signed by: **NL, Exter Polak & Charlouis B.V., A. Zeestraten 22141**  
Capacity: **(Representative)**



Zeestraten, Albertus W. J.  
Exter Polak & Charlouis B.V. (EP&C)  
P.O. Box 3241  
NL-GE Rijswijk  
PAYS-BAS

**For any questions about  
this communication:**

Tel.: +31 (0)70 340 45 00

Date

18.07.12

Reference P30061EP00/AZE	Application No./Patent No. 10768600.8 - 2117 / 2486028
Applicant/Proprietor Furanix Technologies B.V	

**Communication of European publication number and information on the application of Article 67(3) EPC**

The provisional protection under Article 67(1) and (2) EPC in the individual Contracting States becomes effective only when the conditions referred to in Article 67(3) EPC have been fulfilled (for further details, see information brochure of the European Patent Office "National Law relating to the EPC" and additional information in the Official Journal of the European Patent Office).

Pursuant to Article 153(3) EPC the publication under Article 21 PCT of an international application for which the European Patent Office is a designated or elected Office takes the place of the publication of a European patent application.

The bibliographic data of the above-mentioned Euro-PCT application will be published on 15.08.12 in Section I.1 of the European Patent Bulletin. The European publication number is 2486028.

In all future communications to the European Patent Office, please quote the application number plus Directorate number.

**For the Examining Division**





Zeestraten, Albertus W. J.  
Exter Polak & Charlouis B.V. (EP&C)  
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this communication:**

Tel.: +31 (0)70 340 45 00

Date

31.05.12

Reference P30061EP00/AZE	Application No./Patent No. 10768600.8 - 2117 PCT/NL2010050654
Applicant/Proprietor Furanix Technologies B.V	

## Communication pursuant to Rules 161(1) and 162 EPC

### 1. Correction of deficiencies noted in the written opinion and amendment of the application (R. 161(1) EPC)

The above-mentioned international (Euro-PCT) application has entered the European phase.

The EPO as International Searching Authority and, where a demand under Article 31 PCT was filed, also as International Preliminary Examining Authority has drawn up a written opinion on this application or the EPO as Supplementary International Searching Authority has issued explanations pursuant to Rule 45*bis*.7(e) PCT to the supplementary international search report.

You are invited to correct any deficiencies noted in the written opinion of the International Searching Authority or in the International Preliminary Examination Report, or in the explanations to the supplementary international search report and to amend the description, claims and any drawings within a **non-extendable period of six months** after notification of the present invitation.

Should you not comply with or comment on this invitation within the time limit, **the application will be deemed to be withdrawn** in accordance with Rule 161(1) EPC.

### 2. Amendment of application

Under Articles 28, 41 PCT and Rules 52, 78 PCT the application may be amended before a designated or elected Office, and in accordance with Rule 137(2) EPC the applicant may amend the description, claims and drawings of his own volition together with any comments, corrections or amendments made in response to the communication under Rule 161(1) EPC.

Whether or not you have already done so, you now have a further opportunity to file amended claims or other application documents within the above-mentioned period.

If filing amendments, you must identify them and indicate the basis for them in the application as filed. Failure to meet either requirement may lead to a communication from the Examining Division requesting that you correct this deficiency (R. 137(4) EPC).

The claims applicable on expiry of the above period, i.e. those filed on entry into the European phase or in response to the present communication, will form the basis for the calculation of any claims fee to be paid (see page 2).

### 3. Claims fees under Rule 162 EPC

If the application documents on which the European grant procedure is to be based comprise more than fifteen claims, a claims fee shall be payable for the sixteenth and each subsequent claim within the period provided for in Rule 159(1) EPC.

- Based on the application documents currently on file, all necessary claims fees have already been paid (or the documents do not comprise more than 15 claims).
- All necessary fees will be/have been debited automatically according to the automatic debit order.
- The claims fees due for the claims ..... to ..... were not paid within the above-mentioned period.

Any outstanding claims fee, either based on the current set of claims or on any amended claims to be filed pursuant to Rule 161 EPC (see page 1), may still be validly paid within a **non-extendable period of six months** after notification of this communication (R. 162(2) EPC).

If a payment is made for only some of the claims, you must indicate for which claims it is intended. If a claims fee is not paid in due time, the claim concerned is deemed to be abandoned (R. 162(4) EPC).

If claims fees have already been paid, but on expiry of the above-mentioned period there is a new set of claims containing fewer fee-incurring claims than before, the claims fees in excess of those due under Rule 162(2), second sentence EPC will be refunded (R. 162(3) EPC).

#### The claims fee is currently

**EUR 225 for the 16th and each subsequent claim up to the limit of 50  
EUR 555 for the 51st and each subsequent claim**

#### Note to users of the automatic debiting procedure

Unless the EPO receives prior instructions to the contrary, the fees for all claims incurring fees will be debited on the last day of the period for payment. For further details see the Arrangements for the automatic debiting procedure, Supplement to OJ EPO 3/2009.

#### Important information concerning fee amounts

Following any amendment to the Rules relating to Fees, the amount(s) mentioned in this communication may be different from the amount(s) **actually due on the date of payment**. The latest version of the Schedule of fees and expenses, published as a Supplement to the Official Journal of the EPO, is also available on the EPO website ([www.epo.org](http://www.epo.org)) and can be found under [www.epo.org/schedule-of-fees](http://www.epo.org/schedule-of-fees), which allows the viewing, downloading and searching for individual fee amounts, both current and previous.

Payments by cheque delivered or sent direct to the EPO are no longer accepted as from 1 April 2008 (see OJ EPO 2007, 626).

#### For the Examining Division



## Acknowledgement of receipt

We hereby acknowledge receipt of the form for entry into the European phase (EPO as designated or elected Office) as follows:

Submission number	1608007	
PCT application number	PCT/NL2010/050654	
EP application number	10768600.8	
Date of receipt	07 May 2012	
Receiving Office	European Patent Office, The Hague	
Your reference	P30061EP00/AZE	
Applicant		
Country		
Documents submitted	package-data.xml  application-body.xml	ep-euro-pct.xml  epf1200.pdf (4 p.)
Submitted by	CN=A. Zeestraten 22141,O=Exter Polak & Charlouis B.V.,C=NL	
Method of submission	Online	
Date and time receipt generated	07 May 2012, 10:20 (CEST)	
Message Digest	0E:9B:06:02:B2:A7:38:BE:1F:4F:85:DE:6E:28:BF:7A:9E:DE:C9:C9	

### Correction by the EPO of errors in debit instructions filed by eOLF

Errors in debit instructions filed by eOLF that are caused by the editing of Form 1038E entries or the continued use of outdated software (all forms) may be corrected automatically by the EPO, leaving the payment date unchanged (see decision T 152/82, OJ EPO 1984, 301 and point 6.3 ff ADA, Supplement to OJ EPO 10/2007).

/European Patent Office/





## Entry into the European phase (EPO as designated or elected Office)

To the European Patent Office

European application number	EP10768600.8
PCT application number	PCT/NL2010/050654
PCT publication number	WO2011043661
Applicant's or representative's reference	P30061EP00/AZE
International Filing Date	06.10.2010
International Searching Authority (ISA)	EP
International Preliminary Examining Authority (IPEA)	not applicable
<b>1. Applicant</b>	
Indications concerning the applicant(s) are contained in the international publication or were recorded by the International Bureau after the international publication.	<input checked="" type="checkbox"/>
Changes which have not yet been recorded by the International Bureau are set out here:	<input type="checkbox"/>
<b>2. Representative</b>	
This is the representative who will be listed in the Register of European Patents and to whom notifications will be made	
<b>Representative 1</b>	
Name:	Zeestraten A.W.J.
Company:	EP&C
Address of place of business:	P.O. Box 3241 2280 GE RIJSWIJK, Netherlands
<b>3. Authorisation</b>	
An individual authorisation is attached.	<input type="checkbox"/>
A general authorisation has been registered under No:	<input type="checkbox"/>
A general authorisation has been filed, but not yet registered.	<input type="checkbox"/>
The authorisation filed with the EPO as PCT receiving Office expressly includes the European phase.	<input type="checkbox"/>
<b>4. Request for examination</b>	
Examination of the application under Art. 94 EPC is hereby requested. The examination fee is being (has been, will be) paid.	<input checked="" type="checkbox"/>
Request for examination in an admissible non-EPO language:	<input checked="" type="checkbox"/>
	Verzocht wordt om onderzoek van de aanvraag als bedoeld in Art. 94.
The applicant waives his right to be asked under Rule 70(2) EPC whether he wishes to proceed further with the application.	<input type="checkbox"/>
<b>5. Copies</b>	
Additional copies of the documents cited in the supplementary European search report are requested.	<input type="checkbox"/>
Number of additional sets of copies	
<b>6. Documents intended for proceedings before the EPO</b>	
Number of claims on entry into the European phase:	15
6.1 Proceedings before the EPO as designated Office (PCT I) are to be based on the following documents:	
the application documents published by the International Bureau (with all claims, description and drawings), where applicable with amended claims under Art. 19 PCT	<input checked="" type="checkbox"/>
unless replaced by the amendments attached.	<input type="checkbox"/>
<i>Where necessary, clarifications should be attached as 'Other documents'</i>	

6.2 Proceedings before the EPO as elected Office (PCT II) are to be based on the following documents:

the documents on which the international preliminary examination report is based, including any annexes

unless replaced by the amendments attached.

*Where necessary, clarifications should be attached as 'Other documents'*

If the EPO as International Preliminary Examining Authority has been supplied with test reports, these may be used as the basis of proceedings before the EPO.

6.3 A copy of the results of the search carried out by the authority with which the previous application(s) whose priority is claimed was (were) filed is attached (R. 141(1) EPC).

6.4 The applicant waives his right to the communication under Rules 161(1) or (2) and 162 EPC.

## 7. Translations

Translations in one of the official languages of the EPO (English, French, German) are attached as crossed below:

*\* In proceedings before the EPO as designated or elected Office (PCT I + II):*

Translation of the international application (description, claims, any text in the drawings) as originally filed, of the abstract as published and of any indication under Rule 13bis.3 and 13bis.4 PCT regarding biological material

Translation of the priority application(s) (to be filed only at the EPO's request, Rule 53(3) EPC)

It is hereby declared that the international application as originally filed is a complete translation of the previous application (Rule 53(3) EPC)

*\* In addition, in proceedings before the EPO as designated Office (PCT I):*

Translation of amended claims and any statement under Art. 19 PCT, if the claims as amended are to form the basis for the proceedings before the EPO (see Section 6).

*\* In addition, in proceedings before the EPO as elected Office (PCT II):*

Translation of annexes to the international preliminary examination report

## 8. Biological material

The invention uses and/or relates to biological material deposited under Rule 31 EPC.

The particulars referred to in Rule 31(1)(c) EPC (if not yet known, the depositary institution and the identification reference(s)) [number, symbols, etc.] of the depositor) are given in the international publication or in the translation submitted in Section 7 on:

page(s) / line(s)

The receipt(s) of deposit issued by the depositary institution is (are) enclosed.

will be filed later.

Waiver of the right to an undertaking from the requester pursuant to Rule 33(2) EPC attached.

## 9. Nucleotide and amino acid sequences

The international application contains a sequence listing as part of the description

9.1 The sequence listing was filed under Rule 5.2(a) PCT, or furnished to the EPO as ISA under Rule 13ter.1(a) PCT, or is otherwise available to the EPO, in computer-readable format in accordance with WIPO ST.25.

9.2

The sequence listing is attached in computer-readable format in accordance with WIPO Standard ST.25

The sequence listing is attached in PDF format.

The sequence listing does not include matter which goes beyond the content of the application as filed.

## 10. Designation fees

All the contracting states party to the EPC at the time of filing of the international patent application and designated in the international application are deemed to be designated (see Article 79(1) EPC).

The following states, which were contracting states to the EPC at the time of filing of the international application, are designated:

AL AT BE BG CH&LI 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

**11. Extension of the European patent**

This application is deemed to be a request to extend the European patent application and the European patent granted in respect of it to all the non-contracting states to the EPC designated in the international application and with which extension agreements are in force on the date on which the international application is filed. However, the extension only takes effect if the prescribed extension fee is paid.

It is currently intended to pay the extension fee for the following states:

Note: Under the automatic debiting procedure, extension fees will only be debited for states indicated here, unless the EPO is instructed otherwise before expiry of the period for payment.

**12. List of enclosed documents**

Description of document	Original file name	Assigned file name
-------------------------	--------------------	--------------------

**13. Mode of payment: Debit from deposit account**

Currency

EUR

The European Patent Office is hereby authorised, to debit from the deposit account with the EPO any fees and costs indicated on the fees page.

Deposit account number

28090031

Account holder

Exter Polak & Charlouis

**14. Any refunds should be made to the following EPO deposit account:**

Number and account holder

Exter Polak & Charlouis,  
28090031

**15. Fees**

		Factor/reducti on applied	Fee schedule	Amount to be paid
15-1	002 Fee for a European search - Applications filed on/after 01.07.2005	-1165	1 165.00	0.00
15-2	005 Designation fee - For each State designated (max. 7x) for applications filed before 01.04.2009 Designated states: AL, AT, BE, BG, CH&LI, 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	0	95.00	0.00
15-3	005e Designation fee - For all contracting States designated for applications filed on/after 01.04.2009	1	555.00	555.00
15-4	006e Examination fee - For applications filed before 01.07.2005 and for international applications filed on/after 01.07.2005 without supplementary European search report	0.8	1 730.00	1 384.00
15-5	015 Claims fee - For the 16th to the 50th claim	0	225.00	0.00
15-6	020 Filing fee - entry EP phase - online	1	115.00	115.00
15-7	520 Additional filing fee for the 36th and each subsequent page - entry into EP phase	0	14.00	0.00
	<b>Total:</b>		<b>EUR</b>	<b>2 054.00</b>

**16. Annotations**

**17. Signature(s) of applicant(s) or representative**

Place: Rijswijk  
 Date: 07 May 2012  
 Signed by: NL, Exter Polak & Charlouis B.V., A. Zeestraten  
 22141  
 Capacity: (Representative)

## Table for section 6 of Form 1200.3

In accordance with the Notice from the European Patent Office dated 26 January 2009 concerning the 2009 fee structure (OJ EPO 2009, 118, and Guidelines for Examination in the EPO, April 2009, A-III, 13.2), the amount of the additional fee (Art. 2, item 1a, Rules relating to Fees) for the pages of this European patent application is calculated as follows:

**Documents intended for proceedings before the EPO (R. 159 (1) (b) EPC) and for calculating the additional fee (Art. 2, item 1a, RFees):**

	Page(s) from ... to ...	Number of pages
<b>Description:</b> International application as published	1-9	9
<b>Claims:</b> International application as published	10-11	2
<b>Drawings:</b> NONE	-	-
<b>Abstract:</b> Default count: one page		1
<b>Total number of pages</b>		12
<b>Fee-exempt pages (Art. 2, item 1a, RFees)</b>		-35
<b>Number of pages to be paid for</b>		0
(x 14 EUR per page)		
<b>Total amount payable</b>	EUR	0

**PATENT COOPERATION TREATY**

**PCT**

**INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY**

(Chapter I of the Patent Cooperation Treaty)

(PCT Rule 44bis)

Applicant's or agent's file reference P30061PC00	<b>FOR FURTHER ACTION</b>		See item 4 below
International application No. PCT/NL2010/050654	International filing date ( <i>day/month/year</i> ) 06 October 2010 (06.10.2010)	Priority date ( <i>day/month/year</i> ) 07 October 2009 (07.10.2009)	
International Patent Classification (8th edition unless older edition indicated) See relevant information in Form PCT/ISA/237			
Applicant FURANIX TECHNOLOGIES B.V.			

<p>1. This international preliminary report on patentability (Chapter I) is issued by the International Bureau on behalf of the International Searching Authority under Rule 44 bis.1(a).</p> <p>2. This REPORT consists of a total of 10 sheets, including this cover sheet.</p> <p>In the attached sheets, any reference to the written opinion of the International Searching Authority should be read as a reference to the international preliminary report on patentability (Chapter I) instead.</p>																								
<p>3. This report contains indications relating to the following items:</p> <table> <tr> <td><input checked="" type="checkbox"/></td> <td>Box No. I</td> <td>Basis of the report</td> </tr> <tr> <td><input checked="" type="checkbox"/></td> <td>Box No. II</td> <td>Priority</td> </tr> <tr> <td><input type="checkbox"/></td> <td>Box No. III</td> <td>Non-establishment of opinion with regard to novelty, inventive step and industrial applicability</td> </tr> <tr> <td><input type="checkbox"/></td> <td>Box No. IV</td> <td>Lack of unity of invention</td> </tr> <tr> <td><input checked="" type="checkbox"/></td> <td>Box No. V</td> <td>Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement</td> </tr> <tr> <td><input checked="" type="checkbox"/></td> <td>Box No. VI</td> <td>Certain documents cited</td> </tr> <tr> <td><input checked="" type="checkbox"/></td> <td>Box No. VII</td> <td>Certain defects in the international application</td> </tr> <tr> <td><input checked="" type="checkbox"/></td> <td>Box No. VIII</td> <td>Certain observations on the international application</td> </tr> </table> <p>4. The International Bureau will communicate this report to designated Offices in accordance with Rules 44bis.3(c) and 93bis.1 but not, except where the applicant makes an express request under Article 23(2), before the expiration of 30 months from the priority date (Rule 44bis .2).</p>	<input checked="" type="checkbox"/>	Box No. I	Basis of the report	<input checked="" type="checkbox"/>	Box No. II	Priority	<input type="checkbox"/>	Box No. III	Non-establishment of opinion with regard to novelty, inventive step and industrial applicability	<input type="checkbox"/>	Box No. IV	Lack of unity of invention	<input checked="" type="checkbox"/>	Box No. V	Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement	<input checked="" type="checkbox"/>	Box No. VI	Certain documents cited	<input checked="" type="checkbox"/>	Box No. VII	Certain defects in the international application	<input checked="" type="checkbox"/>	Box No. VIII	Certain observations on the international application
<input checked="" type="checkbox"/>	Box No. I	Basis of the report																						
<input checked="" type="checkbox"/>	Box No. II	Priority																						
<input type="checkbox"/>	Box No. III	Non-establishment of opinion with regard to novelty, inventive step and industrial applicability																						
<input type="checkbox"/>	Box No. IV	Lack of unity of invention																						
<input checked="" type="checkbox"/>	Box No. V	Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement																						
<input checked="" type="checkbox"/>	Box No. VI	Certain documents cited																						
<input checked="" type="checkbox"/>	Box No. VII	Certain defects in the international application																						
<input checked="" type="checkbox"/>	Box No. VIII	Certain observations on the international application																						

	Date of issuance of this report 11 April 2012 (11.04.2012)
The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland	Authorized officer  Nora Lindner
Facsimile No. +41 22 338 82 70	e-mail: pt03.pct@wipo.int

# PATENT COOPERATION TREATY

From the  
INTERNATIONAL SEARCHING AUTHORITY

# PCT

To:

see form PCT/ISA/220

**WRITTEN OPINION OF THE  
INTERNATIONAL SEARCHING AUTHORITY  
(PCT Rule 43bis.1)**

Date of mailing  
(day/month/year) see form PCT/ISA/210 (second sheet)

Applicant's or agent's file reference  
see form PCT/ISA/220

**FOR FURTHER ACTION**  
See paragraph 2 below

International application No. PCT/NL2010/050654	International filing date (day/month/year) 06.10.2010	Priority date (day/month/year) 07.10.2009
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International Patent Classification (IPC) or both national classification and IPC  
INV. C07D307/68

Applicant  
FURANIX TECHNOLOGIES B.V.

1. This opinion contains indications relating to the following items:

- Box No. I Basis of the opinion
- Box No. II Priority
- Box No. III Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- Box No. IV Lack of unity of invention
- Box No. V Reasoned statement under Rule 43bis.1(a)(i) with regard to novelty, inventive step and industrial applicability; citations and explanations supporting such statement
- Box No. VI Certain documents cited
- Box No. VII Certain defects in the international application
- Box No. VIII Certain observations on the international application


**2. FURTHER ACTION**

If a demand for international preliminary examination is made, this opinion will usually be considered to be a written opinion of the International Preliminary Examining Authority ("IPEA") except that this does not apply where the applicant chooses an Authority other than this one to be the IPEA and the chosen IPEA has notified the International Bureau under Rule 66.1bis(b) that written opinions of this International Searching Authority will not be so considered.

If this opinion is, as provided above, considered to be a written opinion of the IPEA, the applicant is invited to submit to the IPEA a written reply together, where appropriate, with amendments, before the expiration of 3 months from the date of mailing of Form PCT/ISA/220 or before the expiration of 22 months from the priority date, whichever expires later.

For further options, see Form PCT/ISA/220.

3. For further details, see notes to Form PCT/ISA/220.

<p>Name and mailing address of the ISA:</p> <div style="text-align: center;">  <p><b>European Patent Office</b> D-80298 Munich Tel. +49 89 2399 - 0 Fax: +49 89 2399 - 4465</p> </div>	<p>Date of completion of this opinion</p> <p>see form PCT/ISA/210</p>	<p>Authorized Officer</p> <p>Papathoma, Sofia</p> <p>Telephone No. +49 89 2399-7536</p>
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**WRITTEN OPINION OF THE  
INTERNATIONAL SEARCHING AUTHORITY**

International application No.  
PCT/NL2010/050654

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**Box No. I Basis of the opinion**

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1. With regard to the **language**, this opinion has been established on the basis of:
  - the international application in the language in which it was filed
  - a translation of the international application into , which is the language of a translation furnished for the purposes of international search (Rules 12.3(a) and 23.1 (b)).
2.  This opinion has been established taking into account the **rectification of an obvious mistake** authorized by or notified to this Authority under Rule 91 (Rule 43bis.1(a))
3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, this opinion has been established on the basis of a sequence listing filed or furnished:
  - a. (means)
    - on paper
    - in electronic form
  - b. (time)
    - in the international application as filed
    - together with the international application in electronic form
    - subsequently to this Authority for the purposes of search
4.  In addition, in the case that more than one version or copy of a sequence listing has been filed or furnished, the required statements that the information in the subsequent or additional copies is identical to that in the application as filed or does not go beyond the application as filed, as appropriate, were furnished.
5. Additional comments:

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**Box No. II Priority**

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1.  The validity of the priority claim has not been considered because the International Searching Authority does not have in its possession a copy of the earlier application whose priority has been claimed or, where required, a translation of that earlier application. This opinion has nevertheless been established on the assumption that the relevant date (Rules 43bis.1 and 64.1) is the claimed priority date.
2.  This opinion has been established as if no priority had been claimed due to the fact that the priority claim has been found invalid (Rules 43bis.1 and 64.1). Thus for the purposes of this opinion, the international filing date indicated above is considered to be the relevant date.
3. Additional observations, if necessary:

**WRITTEN OPINION OF THE  
INTERNATIONAL SEARCHING AUTHORITY**

International application No.  
PCT/NL2010/050654

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**Box No. V Reasoned statement under Rule 43bis.1(a)(i) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement**

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1. Statement

Novelty (N)	Yes: Claims	<u>12-14</u>
	No: Claims	<u>1-11, 15</u>
Inventive step (IS)	Yes: Claims	
	No: Claims	<u>1-15</u>
Industrial applicability (IA)	Yes: Claims	<u>1-15</u>
	No: Claims	

2. Citations and explanations

**see separate sheet**

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**Box No. VI Certain documents cited**

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1. Certain published documents (Rules 43bis.1 and 70.10)

and / or

2. Non-written disclosures (Rules 43bis.1 and 70.9)

**see form 210**

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**Box No. VII Certain defects in the international application**

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The following defects in the form or contents of the international application have been noted:

**see separate sheet**

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**Box No. VIII Certain observations on the international application**

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The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:

**see separate sheet**



**Re Item I**

**Basis of the report**

This Written Opinion is based on the following application documents:

**Description, Pages:**

1-9 as originally filed

**Claims, Numbers:**

1-15 as originally filed

The present application relates to a process for the preparation of FDCA from HMF with an oxidant and an oxidation catalyst at a temperature of higher than 140 °C. Further, it relates to the conversion of FDCA to a dialkyl ester and to the preparation of HMF from a carbohydrate source.

**Re Item II**

**Priority**

The validity of the priority claim has not been considered because the ISA does not have in its possession of copy of the priority application. This opinion has nevertheless been established on the assumption that the effective date is the claimed priority date.

**Re Item V**

**Reasoned statement with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement**

Reference is made to the following documents:

- D1 WALT PARTENHEIMER ET AL.: "Synthesis of 2,5-diformylfuran and furan-2,5-dicarboxylic acid by catalytic air oxidation of 5-hydroxymethylfurfural. Unexpectedly selective aerobic oxidation of benzyl alcohol to benzaldehyde with metal/bromide catalysts", ADV. SYNTH. CATAL., vol. 343, no. 1, 2001, pages 102-111, XP002584717, cited in the application
- D2 US 2009/156841 A1 (SANBORN ALEXANDRA J [US] ET AL) 18 June 2009 (2009-06-18)cited in the application

- D4 HAWORTH W N ET AL: "The conversion of sucrose into furan compounds. Part II. Some 2 : 5-disubstituted tetrahydrofurans and their products of ring scission",  
JOURNAL OF THE CHEMICAL SOCIETY, CHEMICAL SOCIETY,  
LETCHEWORTH; GB,  
no. 1, 1 January 1945 (1945-01-01), pages 1-4, XP008122626,  
ISSN: 0368-1769, DOI: DOI:10.1039/JR9450000001
- D5 WO 2006/063220 A2 (ARCHER DANIELS MIDLAND CO [US];  
SANBORN ALEXANDRA J [US]) 15 June 2006 (2006-06-15)
- D7 BOISEN A ET AL: "Process integration for the conversion of glucose to 2,5-furandicarboxylic acid",  
CHEMICAL ENGINEERING RESEARCH AND DESIGN, PART A,  
INSTITUTION OF CHEMICAL ENGINEERS, XX,  
vol. 87, no. 9, 1 September 2009 (2009-09-01), pages 1318-1327,  
XP026613647,  
ISSN: 0263-8762, DOI: DOI:10.1016/J.CHERD.2009.06.010  
[retrieved on 2009-07-25]
- D8 WO 01/72732 A2 (DU PONT [US]; GRUSHIN VLADIMIR [US];  
PARTENHEIMER WALTER [US]; MANZER) 4 October 2001  
(2001-10-04)
- D9 WO 2008/054804 A2 (BATTELLE MEMORIAL INSTITUTE [US]; LILGA  
MICHAEL A [US]; HALLEN RICHARD) 8 May 2008 (2008-05-08)
- D10 JP 2009 001519 A (CANON KK) 8 January 2009 (2009-01-08)
- D11 SU 636 233 A1 (INST ORGANICHESKOGO SINTEZA AK [SU]; INST  
KHIM FIZ AN SSSR [SU]) 5 December 1978 (1978-12-05)
- D13 EP 0 356 703 A2 (HOECHST AG [DE]) 7 March 1990 (1990-03-07)
- D14 GRABOWSKI G ET AL: "The electrochemical oxidation of 5-hydroxymethylfurfural with the nickel oxide/hydroxide electrode",  
ELECTROCHIMICA ACTA, ELSEVIER SCIENCE PUBLISHERS,  
BARKING, GB,  
vol. 36, no. 13, 1 January 1991 (1991-01-01), page 1995, XP026726025,  
ISSN: 0013-4686, DOI: DOI:10.1016/0013-4686(91)85084-K  
[retrieved on 1991-01-01]

- 1 Article 33(2) PCT
- 1.1 Document D1 discloses the preparation of FDCA from HMF with O<sub>2</sub> with a Co/Mn/Br/(Zr) catalyst at temperature of max.125 °C and makes reference to the preparation of HMF from carbohydrates.  
D1 is thus not prejudicial for the novelty of the claimed subject-matter.
- 1.2 Document D2 relates to a process for the synthesis and recovery of HMF from hexose carbohydrate feedstocks. Further, D2 discloses the preparation of FDCA from HMF with O<sub>2</sub> with a Co/Mn/Br catalyst at a temperature of max. 110 °C (example 7 is carried out at 100 °C).  
D2 is thus not prejudicial for the novelty of the claimed subject-matter.
- 1.3 Document D4 relates to the preparation of HMF from sucrose (see page 1, first paragraph) as well as to the preparation of FDCA and the methyl furan-2,5-dicarboxylate (see page 3, last before paragraph). As in this document FDCA is prepared by boiling potassium hydrogen saccharate and no explicit reference is made to the temperature used, D4 is not prejudicial for the novelty of the claimed subject-matter.
- 1.4 Document D5 relates to the preparation of HMF from a fructose source and is therefore not prejudicial for the novelty of the process of claim 1.
- 1.5 Document D7 relates to the conversion of glucose to HMF and discloses in paragraph 4.2.2 a process for the preparation of FDCA from fructose via HMF at 160 °C. The disclosure of this document is therefore prejudicial for the novelty of claims 1-3, 9, 11 and 15.
- 1.6 Document D8 discloses the preparation of FDCA from HMF with O<sub>2</sub> with a Co/Mn/Br/(Zr) catalyst at temperature of 75 °C, which was further staged to 150 °C (see examples 38-40). In addition, the description states that for the preparation of the diacid the temperature should be between 50 and 250 °C, preferably between 50 and 160 °C (page 7, lines 2-7). The disclosure of this document is therefore prejudicial for the novelty of claims 1-10 and 15.
- 1.7 Document D9 discloses in figure 31 an experiment where the temperature was 100-160 °C. In addition the description states that for the preparation of the diacid the temperature should be between 50 and 200 °C, preferably between 100 and 160 °C. The disclosure of this document is therefore prejudicial for the novelty of claims 1, 2, 8-11 and 15.

- 1.8 Document D10 discloses the preparation of FDCA from HMF with O<sub>2</sub> with a catalyst comprising Co at temperature between 50-200 °C (see paragraph 25). The disclosure of this document is therefore prejudicial for the novelty of claims 1-3, 8 and 9.
- 1.9 Document D11 discloses the preparation of FDCA from HMF with O<sub>2</sub> on supported copper-silver-cerium oxide catalyst at temperature between 110-150 °C. The disclosure of this document is therefore prejudicial for the novelty of claims 1, 2, 8 and 9.
- 1.10 Document D13 discloses the preparation of FDCA from HMF with O<sub>2</sub> with a catalyst comprising platinum at a temperature between 60 and 90 °C. This document is therefore not prejudicial for the novelty of the claimed subject-matter.
- 1.11 Document D14 refers to the preparation of FDCA from HMF with O<sub>2</sub> catalysed by palladium or platinum in a basic solution. No reference is made to the temperature used. This document is therefore not prejudicial for the novelty of the claimed subject-matter.

Summarizing, claims 1-11 and 15 do not fulfil the requirements of Article 33(2) PCT. Only claims 12-14 can be acknowledged to be novel in view of the cited prior art.

**2 Article 33(3) PCT**

- 2.1 The present application relates to a process for the preparation of FDCA from HMF. The wording of claim 1 is broad without any restriction as to the oxidant and catalyst used and only restricts the reaction-temperature which has to be higher than 140 °C.

As mentioned under point 1, the process as defined on claim 1 is not novel as there is a plurality of documents disclosing the preparation of FDCA from HMF at a temperature of higher than 140 °C (see documents D7-D11).

- 2.2 Even when "restricting" claim 1 to a process where the oxidant is oxygen and the catalyst is a Co/Mn/Br, the claimed process is not novel. Document D8 also discloses the preparation of FDCA from HMF with O<sub>2</sub> with a Co/Mn/Br(/Zr) catalyst in acetic acid at temperatures between 50 and 250 °C, preferably

between 50 and 160 °C (page 7, lines 2-7). In particular, examples 38-40 disclose for said reaction a temperature of 75 °C, which was further staged to 150 °C.

Thus, even if the staging of the temperature were to be regarded as a difference, this difference is so minor that it does not involve an inventive step.

- 2.3 Furthermore, as it can be seen from example 3 of the present application, at 180 °C and for 5MF and DMF as starting materials the "improvement" of higher yields is not achieved.
- 2.4 What is more, claim 1 does not define an upper limit for the claimed process nor the oxidant and the catalyst. There are therefore reasonable doubts whether the reaction can "work" at any high temperature and/or with any oxidant and catalyst at a temperature above 140 °C (see in this respect documents D13 and D14).
- 2.5 In view of the above, the requirements of Article 33(3) PCT are not fulfilled.

### **Re Item VI**

#### **Certain documents cited**

##### Documents:

- D3 JP 2009 242312 A (AIR WATER INC) 22 October 2009 (2009-10-22)
- D6 TONG X ET AL: "Biomass into chemicals: Conversion of sugars to furan derivatives by catalytic processes",  
APPLIED CATALYSIS A: GENERAL, ELSEVIER SCIENCE,  
AMSTERDAM, NL,  
vol. 385, no. 1-2, 15 September 2010 (2010-09-15), pages 1-13,  
XP027230510,  
ISSN: 0926-860X  
[retrieved on 2010-07-30]
- D12 WO 2010/132740 A2 (ARCHER DANIELS MIDLAND CO [US];  
SANBORN ALEXANDRA [US]) 18 November 2010 (2010-11-18)

can not be considered as prior art documents according to the Article 33(2) PCT, because D3 and D6 are published after the priority day and before the filing day of the application and D12 after the filing day of the present application. However care

should be taken by the applicant when entering the regional phase and in case that the priority is not validly claimed, because these documents will be relevant for the examination, as :

- D3 discloses the preparation of FDCA from HMF with O<sub>2</sub> with a Co/Mn/Br catalyst at a temperature of 90-150 °C (see paragraph 31); in particular the working example is carried out at a temperature of 120 °C which is further increased to 150 °C,
- D6 discloses a temperature of 160 °C in a process for the preparation of FDCA from HMF, and
- D12 discloses in example 8 a temperature between 120-140 °C for the preparation of FDCA from HMF with O<sub>2</sub> and with a Co/Mn catalyst.

### **Re Item VII**

#### **Certain defects in the international application**

In example 3 it is erroneously referred to 2,5-dimethylfurfural. The correct reference is to 2,5-dimethylfuran (DMF).

### **Re Item VIII**

#### **Certain observations on the international application**

- 1 In claim 1 the open-end definition "at a temperature higher than 140 °C" is objected under Article 6 PCT. The upper limit of the temperature has to be given in the claim.
- 2 Claims 9-11 use the wording "preferably". This wording has no limiting effect on the scope of a claim; that is to say, the feature following any such expression is to be regarded as entirely optional.
- 3 Further, the term "carbohydrate source" has to be more precisely defined in the claim in order the requirements of Article 6 PCT to be fulfilled.



VOLMER, J.C.  
Exter Polak&Charlouis B.V.  
P.O. Box 3241  
NL-2280 G  
E Rijswijk  
PAYS-BAS

**For any questions about this communication:**  
Tel.:+31 (0)70 340 45 00

Date

17.02.12

Reference	Application No./Patent No. 10768600.8 - 2117 PCT/NL2010050654
Applicant/Proprietor Furanix Technologies B.V	

### Entry into the European phase before the European Patent Office

The following information describes the procedural steps required for entry into the European phase before the European Patent Office (EPO). You are advised to read it carefully because failure to take the necessary action in due time can lead to a loss of rights.

1. The above mentioned international patent application has been given the **European application No. 10768600.8**.
2. Applicants **without a residence or their principal place of business** in an EPC Contracting State may themselves initiate European processing of their international applications, provided they do so before expiry of the 31st month from the priority date.

During the European phase before the EPO as designated or elected Office, however, such applicants **must** be represented by a professional representative (Art. 133(2) and Art. 134(1) and (8) EPC).

Where, at the expiry of the time period laid down in Rule 163(5) EPC, the requirements of Article 133(2) EPC have not been complied with, the European patent application will be **refused**, pursuant to Rule 163(6) EPC.

Please note that a professional representative authorised to act before the EPO and who acted for the applicant during the international phase does not automatically become the representative for the European phase. Applicants are therefore strongly advised to appoint in good time any representative they wish to initiate the European phase for them; otherwise the EPO has to send all communications directly to the applicant.

3. Applicants **with a residence or their principal place of business** in an EPC Contracting State are not obliged to appoint for the European phase a professional representative authorised to act before the EPO. However, in view of the complexity of the procedure it is recommended that they do so.
4. Applicants and professional representatives are also strongly advised to initiate the European phase using **EPO Form 1200**. It is available free of charge from the EPO or via the EPO website at **www.epo.org**. Similarly, it can be or generated with the Online Filing software, obtainable free of charge from the EPO (**www.epoline.org**) The use of the form is not compulsory.

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5. Where the EPO acts as designated or elected Office (Art. 22(1) and (3) and 39(1) PCT), to enter the European phase before the EPO, the **following acts** must be performed by the applicant within **31 months** from the date of filing of the international application or (where applicable) the earliest priority date:
- a) Supply a translation of the international application into an EPO official language, if the International Bureau did not publish the application in such language (Art. 22(1) PCT and R. 159(1)(a) EPC);
  - b) Specify the application documents, as originally filed or as amended, on which the European grant procedure is to be based (R. 159(1)(b) EPC);
  - c) Pay the filing fee and, where applicable, the additional fee for a European patent application comprising more than 35 pages (R. 159(1)(c) EPC, Art. 2, items 1, 1a Rules relating to Fees);
  - d) Pay the search fee where a supplementary European search report has to be drawn up (R. 159(1)(e) EPC);
  - e) Pay the designation fee if the time limit laid down in Rule 39(1) EPC (i.e. six months after publication of the international search report) has expired before the 31-month period pursuant to Rule 159(1) EPC (R. 159(1)(d) EPC);
  - f) File the written request for examination and pay the examination fee if the time limit laid down in Rule 70(1) EPC has expired before the 31-month period pursuant to Rule 159(1) EPC (R. 159(1)(f) EPC);
  - g) Pay the renewal fee in respect of the third year, if the fee has fallen due (see Rule 51(1) EPC) before expiry of the 31-month period pursuant to Rule 159(1) EPC (R. 159(1)(g) EPC);
  - h) File, where applicable, the certificate of exhibition referred to in Article 55(2) and Rule 25 EPC (R. 159(1)(h) EPC);
  - i) Pay the claims fees for the sixteenth and each subsequent claim when the application documents on which the European grant procedure is to be based comprise more than fifteen claims (R. 162(1) EPC). For applications entering the European phase on or after 1 April 2009, a higher amount is payable for the 51st and each subsequent claim (Decision of the Administrative Council of 14 December 2007 amending the Rules relating to Fees, OJ EPO 2008, 10).

If either the translation of the international application or the request for examination is not filed in time, or if the filing fee, the additional fee, the search fee, the designation fee or the examination fee is not paid in due time, the application shall be deemed to be withdrawn (R. 160(1) EPC).

## 6. Payment of fees

An up-to-date guidance for the payment of fees, expenses and prices and a list of the euro accounts of the European Patent Organisation are published in each issue of the Official Journal of the EPO. The guidance includes inter alia a reference to the latest version of the Schedule of fees and expenses where the amounts of fees are set out.

The Schedule of fees and expenses, published as a Supplement to the Official Journal of the EPO, is also available on the EPO website ([www.epo.org](http://www.epo.org)) and can be found under **[www.epo.org/schedule-of-fees](http://www.epo.org/schedule-of-fees)**, which allows the viewing, downloading and searching for individual fee amounts, both current and previous.

Applicants should always check the fee amounts applying at the time of payment.



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For information on the calculation of the additional fee for applications comprising more than 35 pages, see Notice from the European Patent Office dated 26 January 2009 concerning the 2009 fee structure (OJ EPO 2009, 118), Notice supplementing the notice from the European Patent Office dated 26 January 2009 concerning the 2009 fee structure (OJ EPO 2009, 338) and Guidelines for Examination in the EPO, April 2010, A-III, 13.2.

For an overview of search and examination fees, see Notice from the European Patent Office dated 8 February 2010 (OJ EPO 2010, 133). Fee information is also published on the EPO website under [www.epo.org/fees](http://www.epo.org/fees).

#### 7. Restoration of priority right

Where the international application contains a priority claim to an earlier application and it has been filed within two months from the expiration of the 12-month priority period, a request for restoration before the EPO as designated Office (R. 49ter.2 PCT) applies under the following circumstances:

- a) No request for restoration filed before the receiving Office (RO) during the international phase (R. 26bis.3 PCT)
- b) Negative decision by the RO irrespective of the criterion applied (due care/ unintentionality)
- c) Positive decision by the RO based on the unintentionality criterion.

For a request to be admissible, it must be filed and the requisite fee must be paid (R. 49ter.2(b)(iii) and R. 49ter.2(d) PCT) within one month from the applicable time limit under Article 22 PCT for entering the regional phase (R. 49ter.2(b)(i) PCT). The request for restoration also needs to state the reasons for the failure to file the international application within the priority period (Rule 49ter.2(b)(ii) PCT).

8. If the applicant had appointed a representative during the application's international phase, the present Form will be sent to the representative, asking him to inform the applicant accordingly. All subsequent communications will be sent to the applicant, or - if the EPO is informed of his appointment in time - to the applicant's European representative.
9. For more details about time limits and procedural acts before the EPO as designated or elected Office, see the EPO brochure "How to get a European patent", Guide for applicants - Part 2, PCT procedure before the EPO - "Euro-PCT". This brochure, the list of professional representatives before the EPO as well as Form 1200 are available on the Internet under [www.epo.org](http://www.epo.org).

#### Receiving Section



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Hierbij wordt verklaard, dat in Nederland op 7 oktober 2009 onder nummer 2003606,  
ten name van:

**FURANIX TECHNOLOGIES B.V.**

te Amsterdam

een aanvraag om octrooi werd ingediend voor:

"Method for preparation of 2,5-furandicarboxylic acid from 5-hydroxymethylfurfural and/or derivatives thereof, and the use thereof",

en dat de hieraan gehechte stukken overeenstemmen met de oorspronkelijk ingediende stukken.

Rijswijk, 15 oktober 2010

De Directeur van NL Octrooicentrum,  
voor deze,

M.W.C.M.A. Steng

### Abstract

The application describes a method for the preparation of 2,5-furandicarboxylic acid comprising the step of contacting a feed comprising 5-hydroxymethylfurfural (HMF), one or more derivatives of HMF or a mixture of HMF with one or more derivatives of HMF as starting material, with an oxidant in the presence of an oxidation catalyst at a temperature higher than 140°C.

P30061NL00/MKO

Title: Method for the preparation of 2,5-furandicarboxylic acid from 5-hydroxymethylfurfural and/or derivatives thereof, and the use thereof

The present invention relates to a method for the preparation of 2,5-furandicarboxylic acid ("FDCA") from 5-hydroxymethylfurfural ("HMF") and/or derivatives thereof, in particular from esters of HMF such as for example 5-acetoxymethylfurfural (AMF), from 5-(chloromethyl)furfural, 5-(chloromethyl)furoic acid, 5-methylfurfural, 5-methylfuroic acid or 5 2,5-dimethylfuran, or from a mixture of two or more of these HMF derivatives or a mixture of one or more of these derivatives with HMF, such as for example from a mixture of AMF + HMF.

2,5-Furandicarboxylic acid, also known as dehydromucic acid is a furan derivative. This organic compound was first obtained by Fittig and Heinzelmann in 1876. The first 10 review, by Henry Hill was published in 1901 (Am. Chem. Journ. 25, 439). FDCA was more than 125 years later identified by the US Department of Energy as one of 12 priority chemicals for establishing the "green" chemistry industry of the future. However, to date, no commercial process exists for its production. On the laboratory scale it is often synthesized from 5-hydroxymethylfurfural (HMF), which in turn can be obtained from carbohydrate 15 containing sources such as glucose, fructose, sucrose and starch. From fructose and glucose HMF is obtained by acidic elimination of three mols of water.

The derivatives of HMF are identified as potential and versatile fuel components and precursors for the production of plastics. The polyester from FDCA dimethyl diester and ethylene glycol was first reported in 1946 (GB 621,971).

20 WO0172732 describes the oxidation of HMF to FDCA. The maximum FDCA yield reported is 59%, obtained at 105 °C. The oxidation of HMF in an aqueous medium with oxygen using a catalyst from the Pt-group is described in US4977283. Taarning et al. described the oxidation of HMF over gold based catalysts (ChemSusChem, 2008, 1, 1-4).

Partenheimer et al describes the synthesis of furan-2,5-dicarboxylic acid by catalytic 25 air-oxidation of 5-hydroxymethylfurfural with metal/bromide catalysts such as Co/Mn/Br in Adv. Synth. Catal. **2001**, 343, pp 102-11. With the Co/Mn/Br catalyst the highest FDCA yield obtained is 35.2% (Table 3, experiment 4). On page 103 of the same paper, under the header "products formed" it is stated: "A side reaction is the esterification of the alcohols [HMF and 5-(hydroxymethyl)furan-2-carboxylic acid] to form the more oxidatively stable acetate [respectively 5-(acetoxymethyl)furfural (from HMF) and 5-(acetoxymethyl)furan-2- 30 carboxylic acid from the intermediate 5-(hydroxymethyl)-2-furan carboxylic acid]." And further

on page 106 under the header "general considerations" it is stated: "Although acetoxylation of the alcohols with the acetic acid solvent does occur, this side reaction results in only a 5-8% yield loss". Also, in the reaction scheme given in Figure 1 on page 103, it is indicated that 5-(acetoxymethyl)furfural is an end-point. There is no further reaction of this compound  
5 indicated to FDCA (in contrast to the ester of the intermediate product 5-(acetoxymethyl)furan-2-carboxylic acid). In other words, the 5-(acetoxymethyl)furfural (AMF) formed through reaction of HMF with acetic acid solvent, is not oxidized to FDCA and its formation leads therefore to yield loss.

Unknowningly to the authors, this result was confirmed recently in US2009/0156841  
10 (ADM). On page 6, in paragraph [0060] it is stated:

*"A mixture of HMF ester such as ...5-acetoxymethylfurfural (AcHMF), ...acetic acid, along with cobalt acetate, manganese acetate and sodium bromide is placed in a reactor and subjected to between about 400 to about 1000 psi oxygen.....at between about 85 °C to about 110 °C, ....for between about 100 to about 150 minutes. The solution is filtered and  
15 the solvent evaporated to obtain 2,5-Furandicarboxylic acid (FDCA)."*

This general recipe is illustrated in Example 7 on page 10 of this reference:

*"A reaction mixture containing AcHMF (5.0 g), acetic acid (50 mL), cobalt acetate (0.132 g), manganese acetate (0.135 g), and sodium bromide (0.114 g) is placed in a 100 mL reactor and subjected to 500-800 psi oxygen at 100 °C for 2 hours. Upon filtration and  
20 evaporation of the solvent, 2.53 g of tan solid is isolated. <sup>1</sup>H NMR indicates substantially pure FDCA. The overall yield of FDCA from AcHMF is 54%.."*

Although the intention of the authors was to obtain FDCA, the product they isolated and erroneously characterized as being FDCA was in fact the starting material AcHMF. Under the low temperature conditions deployed (100 °C), AcHMF is quite stable, as was  
25 already reported by Partenheimer (see above). FDCA has an extremely low solubility in acetic acid, even at 100 °C. Taking into account that water is formed during the oxidation we can note the following two observations by Partenheimer in Adv. Synth. Catal. 2001, 343:

On page 105, right column we can read that FDCA precipitates during the reaction, even at 100-125 °C.

30 On page 110 (right column) it is stated: *"The solubility of 2,5-Furandicarboxylic acid is  $6.6 \times 10^{-4}$  g/g in 3% H<sub>2</sub>O/HOAc at room temperature. Hence 99% of the 2,5-furandicarboxylic acid precipitates."*

The authors wrote that the FDCA product was obtained from the solution after filtration and evaporation. Thus, taking into account the Partenheimer statements, which  
35 were independently confirmed by us, this isolated product cannot be FDCA.

The authors showed an <sup>1</sup>H NMR spectrum of their product in Figure 8 and concluded that it is FDCA. However, this is not the case. The <sup>1</sup>H NMR spectrum of the product shown in Figure 8 is without doubt the starting material AcHMF. Finally, the authors refer to the product as a tan solid. In our experience, AcHMF is a tan solid, while FDCA is a white solid.

5 We have repeated the results of experiments executed under the US2009/0156841 conditions. These comparative experiments confirm the low reactivity of AMF under conditions given in US2009/0156841 (cf. the results reported in the experimental section). Thus, a person skilled in the art would therefore have concluded that FDCA cannot be obtained in interesting yields from AMF (AcHMF) using the conditions reported in  
10 US2009/0156841 using a Co/Mn/Br catalyst in acetic acid at between 85 and 110 °C within a time frame of from 100 and 150 minutes. In Example 7 of this prior art reference, 2.53 g or slightly more than 50% of the starting material was the only product isolated from the reaction.

The present inventors have now surprisingly found that when using a catalyst based  
15 on both Cobalt and Manganese and containing a bromide, at temperatures higher than 140 °C the derivatives of HMF, and in particular esters of HMF optionally in combination with HMF, such as for example 5-(acetoxymethyl)furfural (AMF) can be oxidized within 1 hour to FDCA in high yields.

Thus, in a first aspect the invention relates to a method for the preparation of 2,5-  
20 furandicarboxylic acid comprising the step of contacting a feed comprising 5-hydroxymethylfurfural (HMF), one or more derivatives of HMF or a mixture of HMF with one or more derivatives of HMF, e.g., 5-acetoxymethylfurfural (AMF) or 5-hydroxymethylfurfural (HMF) or mixtures thereof (AMF+HMF) as starting material with an oxidant in the presence of a catalyst based on both Cobalt and Manganese and containing a bromide at a  
25 temperature higher than 140 °C.

The invention is described hereinafter with 5-acetoxymethylfurfural as the preferred feedstock, by itself or in combination with HMF. 5-(Chloromethyl)furfural, or 5-(chloromethyl)furoic acid, or 5-methylfurfural, or 5-methylfuroic acid, or 2,5-dimethylfuran, or an ester of 5-(hydroxymethyl)furfural may be used instead, as well as combinations of two or  
30 more of these HMF derivatives, or combinations of one or more of these HMF derivatives together with 5-(hydroxymethyl)furfural.

In WO2007104515 and WO2009030512, the synthesis of esters of HMF such as 5-acetoxymethylfurfural (AMF) from biomass sources is described. Given the higher stability of the HMF esters than HMF and hence improved production pathways and given the fact that  
35 upon oxidation in acetic acid the acetoxy functionality that was obtained from acetic acid is now liberated as acetic acid and given the green reputation of these esters, they were considered by the present inventors as interesting starting point in the preparation of furan-

based monomers that could be used for the production of furandicarboxylic acid -based polyesters, for instance as an alternative for PET or FDCA-based polyamids (nylons). The most important conventional, oil-based, polyester monomer to produce PET is Purified Terephthalic acid (PTA) and its dialkyl ester dimethyl Terephthalate (DMT).

5 AMF can be obtained from biomass sources as described in WO2007104515 and WO2009030512. Depending on the process conditions the product obtained in accordance with the process of these references may also contain HMF.

The alkyl of the ester functionality of the HMF ester can be C1-C5 alkyl, i.e. methyl, ethyl, propyl, isopropyl, butyl, 2-butyl, tert-butyl, pentyl, 2-pentyl, neopentyl and 3-pentyl.

10 There is a preference for methyl, giving (5-acetylmethyl)furfural

FDCA, the product of the reaction can be used in the preparation of a polyester, by reaction of FDCA or its dialkyl ester with a suitable diol. Such polyester preparations are preferably performed by transesterification, whereby the di-methyl ester or di-ethyl ester of FDCA is used and wherein the methyl or ethyl groups are exchanged in the form of a volatile  
15 alcohol during the transesterification with the diol.

The bromine source can be any compound that produces bromide ions in the reaction mixture. These compounds include hydrogen bromide, sodium bromide, elemental bromine, benzyl bromide, tetrabromoethane. Also other bromine salts, such as an alkali or earth alkali metal bromide or another metal bromide such as  $ZnBr_2$  can be used. There is a preference  
20 for hydrobromic acid or sodium bromide. The amount of bromine mentioned in here relates to the amount measured as Br relative to cobalt.

Metal bromide catalysts employed in all of the processes of this invention comprise a preferably soluble cobalt compound and a preferably soluble manganese compound and a preferably soluble bromine-containing compound.

25 The metal and bromide catalyst contains next to bromide Co and Mn and optionally can contain Zr and/or Ce or other metals. Alternative and suitable catalysts are described in W. Partenheimer, *Catalysis Today* 23(2), 69-158 (1995) in particular on pages 89-99, included herein by reference.

Each of the metal components can be provided in any of their known ionic forms.  
30 Preferably the metal or metals are in a form that is soluble in the reaction solvent. Examples of suitable counterions for cobalt and manganese include, but are not limited to, carbonate, acetate, acetate tetrahydrate and halide with bromide being the preferred halide.

As described in Partenheimer, *ibid*, pages 86-88, suitable solvents for use in the processes of the present invention, described above, preferably have at least one  
35 component that contains a monocarboxylic acid functional group. The solvent may also function as one of the reagents. The processes may be run in a solvent or solvent mixture that does not contain an acid group. In that case, preferably one of the reagents does



contain a monocarboxylic acid functional group. Suitable solvents can also be aromatic acids such as benzoic acid and derivatives thereof. A preferred solvent is an aliphatic C<sub>2</sub>-C<sub>6</sub> monocarboxylic acid, such as but not limited to acetic acid, propionic acid, n-butyric acid, isobutyric acid, n-valeric acid, trimethylacetic acid, and caproic acid and mixtures thereof.

- 5 Components of said mixtures can include benzene, acetonitrile, heptane, acetic anhydride, chlorobenzene, o-dichlorobenzene, and water. Most preferred as solvent is acetic acid ("AcOH").

The oxidant in the processes of the present invention is preferably an oxygen-containing gas or gas mixture, such as, but not limited to air. Oxygen by itself is also a  
10 preferred oxidant.

The processes of the instant invention described above can be conducted in the batch, semi-continuous or continuous mode. Especially for the manufacture of FDCA, 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  
15 reaction, and variation of the catalyst composition during the reaction is desirable. For example, variation of the catalyst composition during reaction can be accomplished by addition of cobalt and/or manganese and/or zirconium, and/or cerium, and/or bromide at specified times.

The temperature and pressure in a commercial oxidation process with acetic acid as  
20 diluent are not independent. The pressure is determined by the solvent (e.g., acetic acid) pressure at a certain temperature. The pressure of the reaction mixture is preferably selected such that the solvent is mainly in the liquid phase. In practice this means that pressures between 5 and 100 bar can be used with a preference for pressures between 10 and 80 bars. In case the oxidant is an oxygen containing gas, such as air, the gas can be  
25 continuously fed to and removed from the reactor, or the gas can be supplied all at the start of the reaction. In the latter case, the pressure of the system will depend on the headspace volume and the amount of gas required to convert the starting material. It is clear that in the latter case, the pressure of the system will be significantly higher than when continuously feeding and removing an oxygen containing gas. In the case of continuously adding and  
30 removing the oxidant gas to and from the reactor, the oxygen partial pressure will be between 1 and 30 bars or more preferably between 1 and 10 bars.

The temperature of the reaction mixture is between 140 and 200 degrees Celsius, most preferably between 160 and 190 degrees Celsius. Temperatures higher than 180 degrees Celsius tend to lead to decarboxylation and to other degradation products. Good  
35 results to FDCA have been achieved at a temperature of about 180 °C.

Ratio's of Cobalt to Manganese (Co/Mn) are typically 1/1000 - 100/1, preferably 1/100 - 10/1 and more preferably 1/10 - 4/1.

Ratio's of bromine to metals (e.g.  $\text{Br}/(\text{Co}+\text{Mn})$ ) are typically 0.001-5.00, preferably 0.01 - 2.00 and more preferably 0.1 - 0.9.

Catalyst concentration (Co + Mn) is typically between 0.1 - 10 mol % relative to the substrate, with a preference for loads between 2 and 6 mol %. Good results were obtained  
5 in general with catalyst loads of around 4 mol %.

In another aspect of the invention, we have also investigated the oxidation of other furan-based substrates under the process conditions according to the current invention. We have been able to convert 5-(chloromethyl)furfural, 5-(chloromethyl)furoic acid, 5-methylfurfural, 5-methylfuroic acid and 2,5-dimethylfuran all to FDCA in very interesting  
10 yields.

In another aspect, the FDCA obtained according to the process of the present invention can be transformed using common esterification reactions to a diester by contacting the starting material under appropriate conditions with the relevant alcohol. Thus, in one aspect, the invention also relates to the use of FDCA obtained according to the  
15 process of the current invention in the preparation of a dialkylester of 2,5-dicarboxylic acid by reaction of the FDCA with a  $\text{C}_1\text{-C}_5$  alkyl alcohol, preferably methanol to prepare the dimethyl ester of FDCA.

In a further aspect of the invention, the di-methylester can be used in the preparation of polyester polymers by reaction with a diol. Reacting the di-methylester with a diol will  
20 result in the formation of methanol that quickly vaporises. In 1946 the polymerization of FDCA dimethyl ester with ethylene glycol was described as a first example of such a polymerization (GB 621,971).

Indeed, polyesters are generally made by a combined esterification/polycondensation reaction between monomer units of a diol (e.g., ethylene glycol (EG)) and a dicarboxylic  
25 acid. Additives such as catalysts and stabilizers may be added to facilitate the process and stabilize the polyester towards degradation.

#### Description of the figures:

Figure 1 shows the yield of FDCA in the oxidation of HMF, of a HMF/AMF 3/2 mixture,  
30 of a HMF/AMF 2/3 mixture and of AMF, respectively with 2.7 mol% Co catalyst (relative to substrate), 0.26 M substrate concentration in acetic acid and Co/Mn ratio of 1/1 and  $\text{Br}/(\text{Co}+\text{Mn})$ : 1.0; 0.7; 0.4 and 0.1 at 180 °C for 1 hr with 20 bar air. Under these conditions, higher Br amounts give higher yields but when  $\text{Br}/(\text{Co}+\text{Mn}) > 1$ , corrosion will be a problem on commercial scale. HMF gives slightly higher yields than AMF at one hour reaction time.  
35 The data of these experiments is also given in Table 1.

Figure 2 shows the selectivity to FDCA for the AMF oxidation of Figure 1 together with the comparative examples based on the experimental conditions described in

US/20090156841; according to the text 10 wt/wt% AMF was oxidized with 1.75 and 2.65 mol % Co catalyst and a fixed Br/(Co/Mn) of 1.0 and a Co/Mn of 1.0 at 100 °C and 30 bar for 2 hours Under these conditions, the yield of FDCA was lower than the result described in US/20090156841 and than the results obtained at high temperature. The data of these  
5 experiments is also given in Table 2.

Figure 3 shows the yield of FDCA in the oxidation of 5-methylfurfural (5MF) and 2,5-dimethylfurfural (DMF) at 180 °C with 2.7 mol% Co catalyst (relative to substrate), 0.26 M substrate concentration in acetic acid and Co/Mn ratio of 1/1 and a Br/(Co+Mn) of 1.0, 0.7, 0.4 and 0.1 at 180 °C for 2 hrs with 50 bars air. Under these conditions, higher Br amounts  
10 give higher yields but when Br/(Co+Mn) > 1, corrosion will be a problem on commercial scale. Reactions with 5MF give higher yields than reactions with DMF. The data of these experiments is also given in Table 3.

#### Examples:

15 Experiments were carried out in parallel 8 mL magnetically stirred stainless steel batch reactors. The reactors are grouped in blocks containing 12 batch reactors. The standard procedure for all the reactions was as follows:

0.5 ML of starting material stock solution in acetic acid (0.78 mmol/ml) were added into a reactor lined with a Teflon insert. 1 ML of a catalyst stock solution in acetic acid was  
20 subsequently added to the reactor. In a typical experiment, a catalyst composition Co/Mn/Br with a relative 1-x-y ratio, the concentration of Co(OAc)<sub>2</sub>\*4H<sub>2</sub>O was varied. As a Mn source, Mn(OAc)<sub>2</sub>\*4H<sub>2</sub>O was used and as a bromine source NaBr was used. The reactors were closed with a rubber septum, after which the reactors were sealed and pressurized to the desired air pressure, ranging from 20-60 bars. After pressurization, the block with 12  
25 reactors was placed in the test unit which was preheated at the desired temperature, ranging from 100 to 220 °C. After the desired reaction time, ranging from 0.5 hr to 24 hrs, the block is placed into an ice bath for 20 minutes. When the block had cooled down, it was depressurized. After opening, HPLC samples were prepared. First 5 ml of a saccharine solution in DMSO (11.04 mg/mL) was added to the each reactor and the mixture was stirred  
30 for 5 minutes. Then 10 µL of this mixture was diluted to 1000 µL with water in a HPLC vial. The samples were analyzed using HPLC.

Illustrative but not limiting results are presented in the figures 1-3 and Tables 1-3.



Table 2

Substrate	Temp [° C]	Reaction time [Hours]	Catalyst concentration [(Co + Mn) mol %]	Mn/Co	Br/ (Co+Mn)	O <sub>2</sub> /Subs [mol/mol]	Substrate concentration [wt %]	Conversion [%]	s FDCA [%]
AMF	180	1	5.4	1	1	2.69	3.3	100.00	64.82
AMF	180	1	5.4	1	1	2.69	3.3	100.00	63.76
AMF	180	1	5.4	1	0.7	2.69	3.8	100.00	60.64
AMF	180	1	5.4	1	0.7	2.69	3.8	100.00	59.83
AMF	180	1	5.4	1	0.4	2.69	4.0	100.00	57.11
AMF	180	1	5.4	1	0.4	2.69	4.0	100.00	57.36
AMF	180	1	5.4	1	0.1	2.69	4.4	100.00	46.85
AMF	180	1	5.4	1	0.1	2.69	4.4	100.00	46.53
AMF	100	2	3.5	1	1	2.88	10.0	100.00	23.48
AMF	100	2	3.5	1	1	2.88	10.0	100.00	23.96
AMF	100	2	5.25	1	1	2.88	10.0	100.00	29.05
AMF	100	2	5.25	1	1	2.88	10.0	100.00	29.87

Table 3

Substrate	Temp [° C]	Reaction time [Hours]	Catalyst concentration [(Co + Mn) mol %]	Mn/Co	Br/ (Co+Mn)	O <sub>2</sub> /Subs [mol/mol]	Substrate concentration [wt %]	Conversion [%]	s FDCA [%]
5-MF	180	1	5.4	1	1	6.7	2.9	100.00	42.62
5-MF	180	1	5.4	1	1	6.7	2.9	100.00	42.04
5-MF	180	1	5.4	1	0.7	6.7	2.9	100.00	39.47
5-MF	180	1	5.4	1	0.7	6.7	2.9	100.00	39.94
DMF	180	1	5.4	1	1	6.7	2.5	100.00	16.13
DMF	180	1	5.4	1	1	6.7	2.5	100.00	16.17
DMF	180	1	5.4	1	0.7	6.7	2.5	100.00	13.68
DMF	180	1	5.4	1	0.7	6.7	2.5	100.00	14.09
DMF	180	1	5.4	1	0.4	6.7	2.5	100.00	11.30
DMF	180	1	5.4	1	0.4	6.7	2.5	100.00	10.89
DMF	180	1	5.4	1	0.1	6.7	2.5	100.00	7.19
AMF	180	1	5.4	1	0.1	6.7	2.5	100.00	7.12

Claims

1. Method for the preparation of 2,5-furandicarboxylic acid comprising the step of contacting a feed comprising 5-hydroxymethylfurfural (HMF), one or more derivatives of HMF or a mixture of HMF with one or more derivatives of HMF as starting material, with an oxidant in the presence of an oxidation catalyst at a temperature higher than 140°C.
- 5 2. Method according to claim 1 comprising the step of contacting an ester of 5-(hydroxymethyl)furfural or 5-(hydroxymethyl)furfural or a mixture of these components with an oxidant in the presence of an oxidation catalyst at a temperature higher than 140 °C.
- 3 Method according to claim 1 or 2, wherein the oxidation catalyst comprises at least one metal selected from the group consisting of Co and Mn.
- 10 4 Method according to claim 1 or 2 or 3, wherein the oxidation catalyst comprises a source of bromine.
- 5 Method according to claim 4, wherein the oxidation catalyst contains both Co and Mn.
- 6 Method according to claim 5, wherein the oxidation catalyst comprises at least one additional metal.
- 15 7. Method according to claim 6, wherein the additional metal is Zr and or Ce.
8. Method according to claims 1-6, wherein the oxidant is selected from oxygen, air or other oxygen-containing gases.
9. Method according to any of the previous claims wherein the temperature is between 140 and 200 degrees Celsius, most preferably between 160 and 190 degrees Celsius.
- 20 10. Method according to any one of the previous claims, wherein a solvent or solvent mixture is present, preferably comprising a solvent containing a monocarboxylic acid functional group, more preferably acetic acid or acetic acid and water mixtures.
11. Method according to any of the previous claims wherein the alkyl of the ester group of the HMF ester is C<sub>1</sub>-C<sub>5</sub> alkyl, preferably methyl.
- 25 12 Use of the reaction product obtained via the method of any of the claims 1-11 in the preparation of a dialkylester of 2,5-furan dicarboxylic acid via an esterification reaction with a C<sub>1</sub>-C<sub>5</sub> alkyl alcohol.
13. Use according to claim 12 wherein the C<sub>1</sub>-C<sub>5</sub> alkylalcohol is methanol and the diester is the dimethylester of 2,5-furan dicarboxylic acid.
- 30 14. Method for the preparation of 2,5-furandicarboxylic acid wherein a carbohydrate source is converted in the presence of an alkyl carboxylic acid into products comprising an HMF ester and optionally 5-hydroxymethyl furfural, from which is isolated a feed comprising the ester of HMF and optionally 5-hydroxymethyl furfural, comprising the subsequent step of contacting the feed with an oxidant in the presence of a cobalt and manganese and bromide  
35 containing catalyst under appropriate reaction conditions.

**Fig 1**

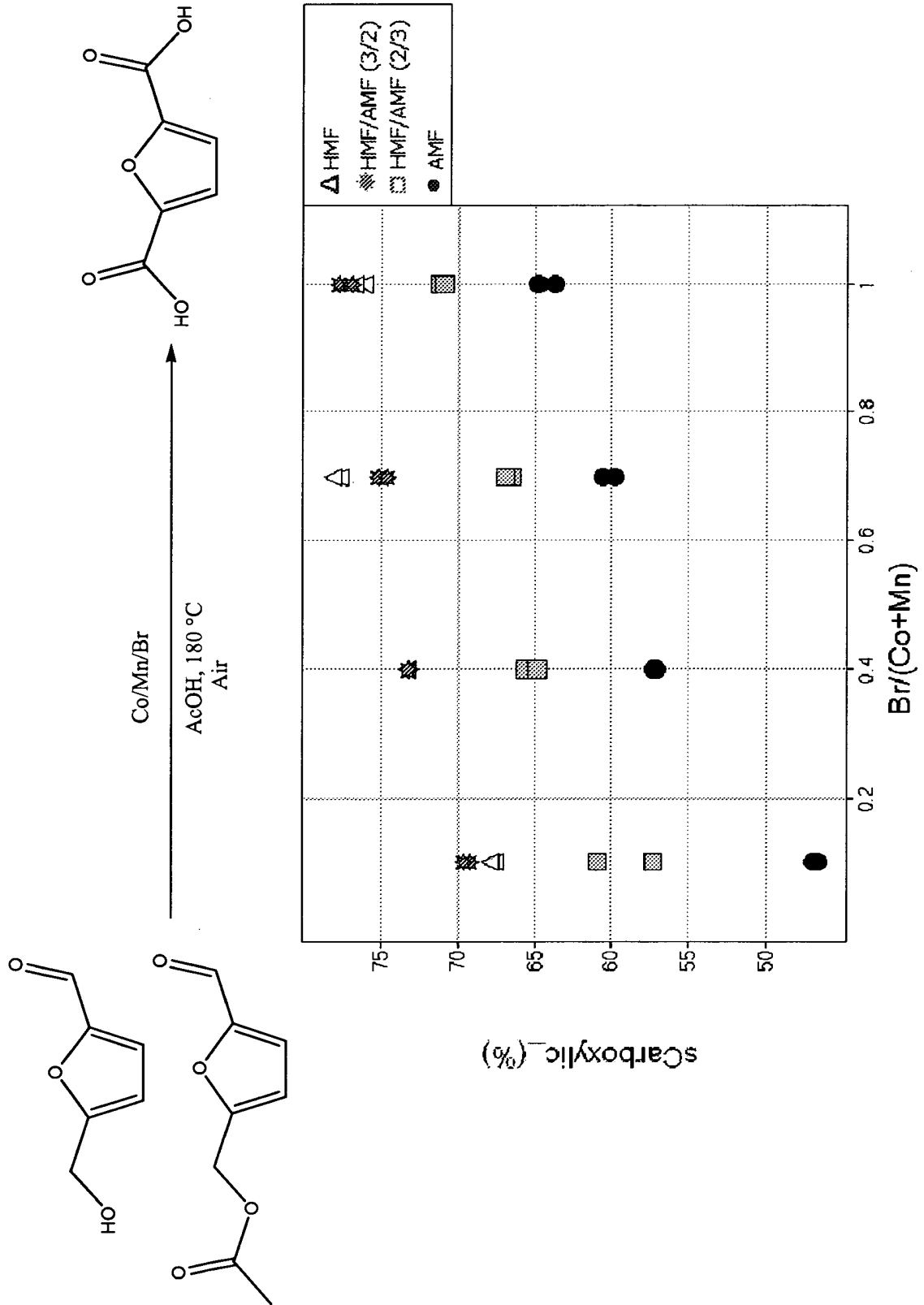
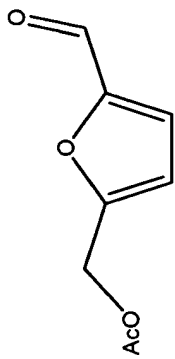
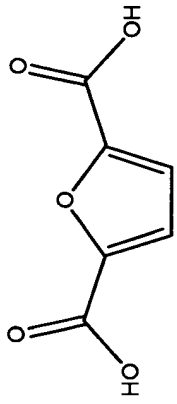
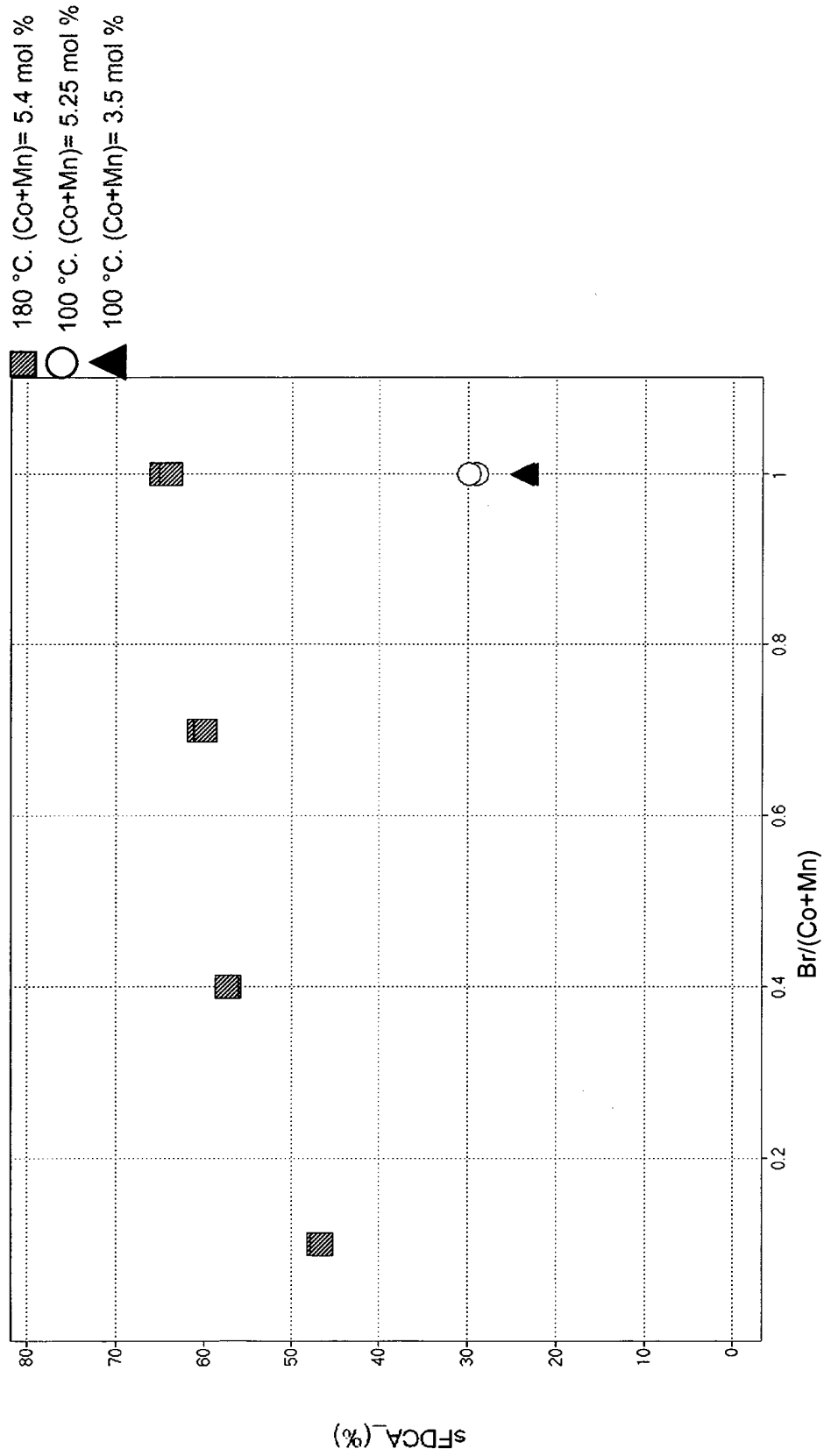




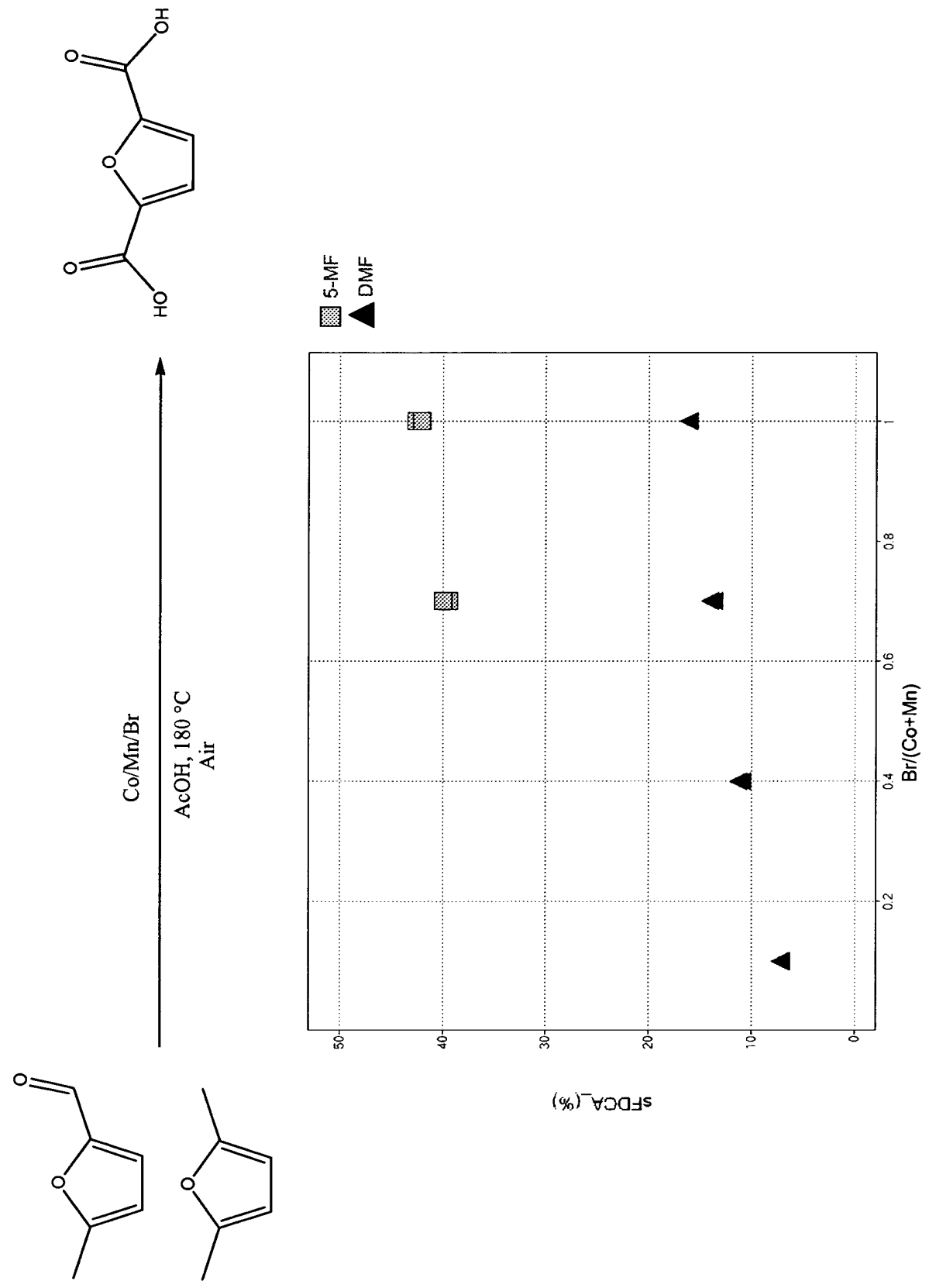
Fig 2



Co/Mn/Br  
AcOH, 100/180 °C  
Air



**Fig 3**



# Document made available under the Patent Cooperation Treaty (PCT)

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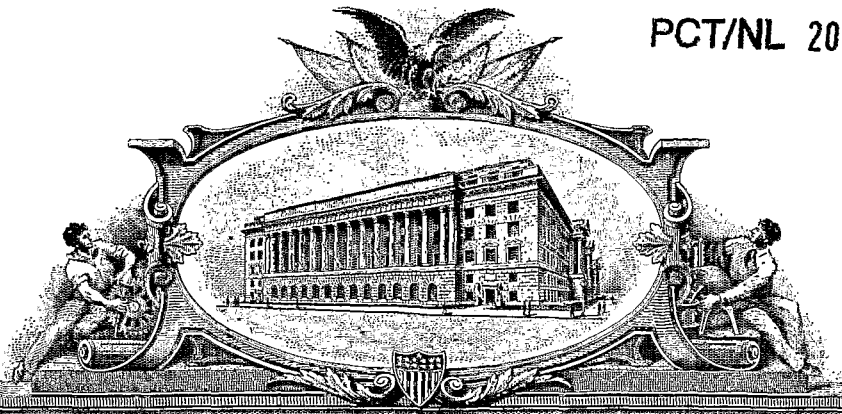
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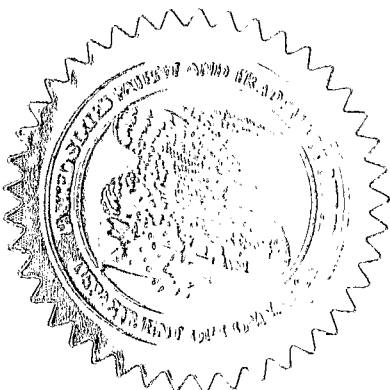
**APPLICATION NUMBER: 61/249,395**

**FILING DATE: October 07, 2009**

**THE COUNTRY CODE AND NUMBER OF YOUR PRIORITY APPLICATION, TO BE USED FOR FILING ABROAD UNDER THE PARIS CONVENTION, IS US61/249,395**

**By Authority of the  
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**W. MONTGOMERY**  
Certifying Officer



## Electronic Acknowledgement Receipt

<b>EFS ID:</b>	6219460
<b>Application Number:</b>	61249395
<b>International Application Number:</b>	
<b>Confirmation Number:</b>	9251
<b>Title of Invention:</b>	METHOD FOR THE PREPARATION OF 2,5-FURANDICARBOXYLIC ACID FROM 5-HYDROXYMETHYLFURFURAL AND/OR DERIVATIVES THEREOF, AND THE USE THEREOF
<b>First Named Inventor/Applicant Name:</b>	Cesar MUNOZ DE DIEGO
<b>Customer Number:</b>	01444
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		Petitioners' Exhibit 1010			Page 1 of 231

1	Provisional Cover Sheet (SB16)	2009-10-07transmittal.pdf	42445	no	1
			cb9f12528b9515c247daab86371014aac425b20		

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Document Description	Start	End
Specification	1	10
Claims	11	11
Abstract	12	12
Drawings-only black and white line drawings	13	15

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If a new application is being filed and the application includes the necessary components for a filing date (see 37 CFR 1.53(b)-(d) and MPEP 506), a Filing Receipt (37 CFR 1.54) will be issued in due course and the date shown on this Acknowledgement Receipt will establish the filing date of the application.

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If a timely submission to enter the national stage of an international application is compliant with the conditions of 35 U.S.C. 371 and other applicable requirements a Form PCT/DO/EO/903 indicating acceptance of the application as a national stage submission under 35 U.S.C. 371 will be issued in addition to the Filing Receipt, in due course.

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If a new international application is being filed and the international application includes the necessary components for an international filing date (see PCT Article 11 and MPEP 1810), a Notification of the International Application Number and of the International Filing Date (Form PCT/RO/105) will be issued in due course, subject to prescriptions concerning national security, and the date shown on this Acknowledgement Receipt will establish the international filing date of the application.

**U.S. PATENT AND TRADEMARK OFFICE  
PROVISIONAL APPLICATION FOR PATENT COVER SHEET**

This is a request for filing a PROVISIONAL APPLICATION FOR PATENT  
under 37 C.F.R. §1.53(b)(2)

Atty. Docket: MUNOZ=1

INVENTOR(S)/APPLICANT(S)				
LAST NAME	GIVEN NAME	RESIDENCE (CITY AND EITHER STATE OR FOREIGN COUNTRY)		
MUÑOZ DE DIEGO	Cesar	Amsterdam, Netherlands		
<input type="checkbox"/> Additional inventors are being named on separately numbered sheets attached hereto				
TITLE OF THE INVENTION (500 characters max)				
METHOD FOR THE PREPARATION OF 2,5-FURANDICARBOXYLIC ACID FROM 5-HYDROXYMETHYLFURFURAL AND/OR DERIVATIVES THEREOF, AND THE USE THEREOF				
CORRESPONDENCE ADDRESS				
Direct all correspondence to the address associated with <b>Customer Number 001444</b> , which is presently:				
BROWDY AND NEIMARK, P.L.L.C. 624 Ninth Street, N.W., Suite 300 Washington, D.C. 20001-5303				
ENCLOSED APPLICATION PARTS (check all that apply)				
<input checked="" type="checkbox"/> Specification	Number of Pages <u>12</u>		<input type="checkbox"/> Other _____	
<input checked="" type="checkbox"/> Drawings	Number of Pages <u>3</u>			
FEES AND METHOD OF PAYMENT OF FILING FEES (check all that apply)				
<input checked="" type="checkbox"/> Basic Filing fee				\$ 220.00
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15- 100 =	/ 50 =		× 260.00	\$
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<b>TOTAL FILING FEES</b>				\$220.00
<input checked="" type="checkbox"/> Credit Card Payment authorization submitted herewith to cover the total filing fees.				
<input checked="" type="checkbox"/> The Commissioner is hereby authorized to charge any underpayment of filing fees and credit any overpayments to Deposit Account Number 02-4035.				
The invention was made by an agency of the United States Government or under a contract with an agency of the United States Government.				
<input checked="" type="checkbox"/> No <input type="checkbox"/> Yes, the name of the U.S. Government agency and the Government contract number are: _____				

Respectfully submitted,  
BROWDY AND NEIMARK, P.L.L.C.

Date: October 7, 2009

RSJ:klb

By: /Ronni S. Jillions/  
Ronni Jillions  
Registration No.: 31,979

Petitioners' Exhibit 1010, Page 199 of 231

P30061US00/MKO

Title: Method for the preparation of 2,5-furandicarboxylic acid from 5-hydroxymethylfurfural and/or derivatives thereof, and the use thereof

The present invention relates to a method for the preparation of 2,5-furandicarboxylic acid ("FDCA") from 5-hydroxymethylfurfural ("HMF") and/or derivatives thereof, in particular from esters of HMF such as for example 5-acetoxymethylfurfural (AMF), from 5-(chloromethyl)furfural, 5-(chloromethyl)furoic acid, 5-methylfurfural, 5-methylfuroic acid or 2,5-dimethylfuran, or from a mixture of two or more of these HMF derivatives or a mixture of one or more of these derivatives with HMF, such as for example from a mixture of AMF + HMF.

2,5-Furandicarboxylic acid, also known as dehydromucic acid is a furan derivative. This organic compound was first obtained by Fittig and Heinzelmann in 1876. The first review, by Henry Hill was published in 1901 (Am. Chem. Journ. 25, 439). FDCA was more than 125 years later identified by the US Department of Energy as one of 12 priority chemicals for establishing the "green" chemistry industry of the future. However, to date, no commercial process exists for its production. On the laboratory scale it is often synthesized from 5-hydroxymethylfurfural (HMF), which in turn can be obtained from carbohydrate containing sources such as glucose, fructose, sucrose and starch. From fructose and glucose HMF is obtained by acidic elimination of three mols of water.

The derivatives of HMF are identified as potential and versatile fuel components and precursors for the production of plastics. The polyester from FDCA dimethyl diester and ethylene glycol was first reported in 1946 (GB 621,971).

WO172732 describes the oxidation of HMF to FDCA. The maximum FDCA yield reported is 59%, obtained at 105 °C. The oxidation of HMF in an aqueous medium with oxygen using a catalyst from the Pt-group is described in US4977283. Taarning et al. described the oxidation of HMF over gold based catalysts (ChemSusChem, 2008, 1, 1-4).

Partenheimer et al describes the synthesis of furan-2,5-dicarboxylic acid by catalytic air-oxidation of 5-hydroxymethylfurfural with metal/bromide catalysts such as Co/Mn/Br in Adv. Synth. Catal. 2001, 343, pp 102-11. With the Co/Mn/Br catalyst the highest FDCA yield obtained is 35.2% (Table 3, experiment 4). On page 103 of the same paper, under the header "products formed" it is stated: "A side reaction is the esterification of the alcohols [HMF and 5-(hydroxymethyl)furan-2-carboxylic acid] to form the more oxidatively stable acetate [respectively 5-(acetoxymethyl)furfural (from HMF) and 5-(acetoxymethyl)furan-2-carboxylic acid from the intermediate 5-(hydroxymethyl)-2-furan carboxylic acid]." And further on page 106 under the header "general considerations" it is stated: "Although acetoxylation of the



alcohols with the acetic acid solvent does occur, this side reaction results in only a 5-8% yield loss". Also, in the reaction scheme given in Figure 1 on page 103, it is indicated that 5-(acetoxymethyl)furfural is an end-point. There is no further reaction of this compound indicated to FDCA (in contrast to the ester of the intermediate product 5-(acetoxymethyl)furan-2-carboxylic acid). In other words, the 5-(acetoxymethyl)furfural (AMF) formed through reaction of HMF with acetic acid solvent, is not oxidized to FDCA and its formation leads therefore to yield loss.

Unknowingly to the authors, this result was confirmed recently in US2009/0156841 (ADM). On page 6, in paragraph [0060] it is stated:

10        *"A mixture of HMF ester such as ...5-acetoxymethylfurfural (AcHMF), ...acetic acid, along with cobalt acetate, manganese acetate and sodium bromide is placed in a reactor and subjected to between about 400 to about 1000 psi oxygen.....at between about 85 °C to about 110 °C,....for between about 100 to about 150 minutes. The solution is filtered and the solvent evaporated to obtain 2,5-Furandicarboxylic acid (FDCA)."*

15        This general recipe is illustrated in Example 7 on page 10 of this reference:

*"A reaction mixture containing AcHMF (5.0 g), acetic acid (50 mL), cobalt acetate (0.132 g), manganese acetate (0.135 g), and sodium bromide (0.114 g) is placed in a 100 mL reactor and subjected to 500-800 psi oxygen at 100 °C for 2 hours. Upon filtration and evaporation of the solvent, 2.53 g of tan solid is isolated. <sup>1</sup>H NMR indicates substantially pure*  
20 *FDCA. The overall yield of FDCA from AcHMF is 54%.."*

      Although the intention of the authors was to obtain FDCA, the product they isolated and erroneously characterized as being FDCA was in fact the starting material AcHMF. Under the low temperature conditions deployed (100 °C), AcHMF is quite stable, as was already reported by Partenheimer (see above). FDCA has an extremely low solubility in acetic acid,  
25 even at 100 °C. Taking into account that water is formed during the oxidation we can note the following two observations by Partenheimer in Adv. Synth. Catal. 2001, 343:

      On page 105, right column we can read that FDCA precipitates during the reaction, even at 100-125 °C.

      On page 110 (right column) it is stated: *"The solubility of 2,5-Furandicarboxylic acid is*  
30 *6.6 x 10<sup>-4</sup> g/g in 3% H<sub>2</sub>O/HOAc at room temperature. Hence 99% of the 2,5-furandicarboxylic acid precipitates."*

      The authors wrote that the FDCA product was obtained from the solution after filtration and evaporation. Thus, taking into account the Partenheimer statements, which were independently confirmed by us, this isolated product cannot be FDCA.

35        The authors showed an <sup>1</sup>H NMR spectrum of their product in Figure 8 and concluded that it is FDCA. However, this is not the case. The <sup>1</sup>H NMR spectrum of the product shown in

Figure 8 is without doubt the starting material AcHMF. Finally, the authors refer to the product as a tan solid. In our experience, AcHMF is a tan solid, while FDCA is a white solid.

We have repeated the results of experiments executed under the US2009/0156841 conditions. These comparative experiments confirm the low reactivity of AMF under  
5 conditions given in US2009/0156841 (cf. the results reported in the experimental section). Thus, a person skilled in the art would therefore have concluded that FDCA cannot be obtained in interesting yields from AMF (AcHMF) using the conditions reported in US2009/0156841 using a Co/Mn/Br catalyst in acetic acid at between 85 and 110 °C within a time frame of from 100 and 150 minutes. In Example 7 of this prior art reference, 2.53 g or  
10 slightly more than 50% of the starting material was the only product isolated from the reaction.

The present inventors have now surprisingly found that when using a catalyst based on both Cobalt and Manganese and containing a bromide, at temperatures higher than 140 °C the derivatives of HMF, and in particular esters of HMF optionally in combination with HMF,  
15 such as for example 5-(acetoxymethyl)furfural (AMF) can be oxidized within 1 hour to FDCA in high yields.

Thus, in a first aspect the invention relates to a method for the preparation of 2,5-furandicarboxylic acid comprising the step of contacting a feed comprising 5-hydroxymethylfurfural (HMF), one or more derivatives of HMF or a mixture of HMF with one  
20 or more derivatives of HMF, e.g., 5-acetoxymethylfurfural (AMF) or 5-hydroxymethylfurfural (HMF) or mixtures thereof (AMF+HMF) as starting material with an oxidant in the presence of a catalyst based on both Cobalt and Manganese and containing a bromide at a temperature higher than 140 °C.

The invention is described hereinafter with 5-acetoxymethylfurfural as the preferred  
25 feedstock, by itself or in combination with HMF. 5-(Chloromethyl)furfural, or 5-(chloromethyl)furoic acid, or 5-methylfurfural, or 5-methylfuroic acid, or 2,5-dimethylfuran, or an ester of 5-(hydroxymethyl)furfural may be used instead, as well as combinations of two or more of these HMF derivatives, or combinations of one or more of these HMF derivatives together with 5-(hydroxymethyl)furfural.

30 In WO2007104515 and WO2009030512, the synthesis of esters of HMF such as 5-acetoxymethylfurfural (AMF) from biomass sources is described. Given the higher stability of the HMF esters than HMF and hence improved production pathways and given the fact that upon oxidation in acetic acid the acetoxy functionality that was obtained from acetic acid is now liberated as acetic acid and given the green reputation of these esters, they were  
35 considered by the present inventors as interesting starting point in the preparation of furan-based monomers that could be used for the production of furandicarboxylic acid-based polyesters, for instance as an alternative for PET or FDCA-based polyamids (nylons). The

most important conventional, oil-based, polyester monomer to produce PET is Purified Terephthalic acid (PTA) and its dialkyl ester dimethyl Terephthalate (DMT).

AMF can be obtained from biomass sources as described in WO2007104515 and WO2009030512. Depending on the process conditions the product obtained in accordance  
5 with the process of these references may also contain HMF.

The alkyl of the ester functionality of the HMF ester can be C1-C5 alkyl, i.e. methyl, ethyl, propyl, isopropyl, butyl, 2-butyl, tert-butyl, pentyl, 2-pentyl, neopentyl and 3-pentyl. There is a preference for methyl, giving (5-acetylmethyl)furfural

FDCA, the product of the reaction can be used in the preparation of a polyester, by  
10 reaction of FDCA or its dialkyl ester with a suitable diol. Such polyester preparations are preferably performed by transesterification, whereby the di-methyl ester or di-ethyl ester of FDCA is used and wherein the methyl or ethyl groups are exchanged in the form of a volatile alcohol during the transesterification with the diol.

The bromine source can be any compound that produces bromide ions in the reaction  
15 mixture. These compounds include hydrogen bromide, sodium bromide, elemental bromine, benzyl bromide, tetrabromoethane. Also other bromine salts, such as an alkali or earth alkali metal bromine or another metal bromide such as  $ZnBr_2$  can be used. There is a preference for hydrobromic acid or sodium bromide. The amount of bromine mentioned in here relates to the amount measured as Br relative to cobalt.

20 Metal bromide catalysts employed in all of the processes of this invention comprise a preferably soluble cobalt compound and a preferably soluble manganese compound and a preferably soluble bromine-containing compound.

The metal and bromide catalyst contains next to bromide Co and Mn and optionally can contain Zr and/or Ce or other metals. Alternative and suitable catalysts are described in W.  
25 Partenheimer, Catalysis Today 23(2), 69-158 (1995) in particular on pages 89-99, included herein by reference.

Each of the metal components can be provided in any of their known ionic forms. Preferably the metal or metals are in a form that is soluble in the reaction solvent. Examples of suitable counterions for cobalt and manganese include, but are not limited to, carbonate,  
30 acetate, acetate tetrahydrate and halide with bromide being the preferred halide.

As described in Partenheimer, *ibid*, pages 86-88, suitable solvents for use in the processes of the present invention, described above, preferably have at least one component that contains a monocarboxylic acid functional group. The solvent may also function as one of the reagents. The processes may be run in a solvent or solvent mixture that does not  
35 contain an acid group. In that case, preferably one of the reagents does contain a monocarboxylic acid functional group. Suitable solvents can also be aromatic acids such as benzoic acid and derivatives thereof. A preferred solvent is an aliphatic  $C_2$ - $C_6$  monocarboxylic

acid, such as but not limited to acetic acid, propionic acid, n-butyric acid, isobutyric acid, n-valeric acid, trimethylacetic acid, and caproic acid and mixtures thereof. Components of said mixtures can include benzene, acetonitrile, heptane, acetic anhydride, chlorobenzene, o-dichlorobenzene, and water. Most preferred as solvent is acetic acid ("AcOH").

5 The oxidant in the processes of the present invention is preferably an oxygen-containing gas or gas mixture, such as, but not limited to air. Oxygen by itself is also a preferred oxidant.

The processes of the instant invention described above can be conducted in the batch, semi-continuous or continuous mode. Especially for the manufacture of FDCA, operation in  
10 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 desirable. For example, variation of the catalyst composition during reaction can be accomplished by addition of cobalt and/or manganese and/or zirconium, and/or cerium, and/or bromide at specified times.

15 The temperature and pressure in a commercial oxidation process with acetic acid as diluent are not independent. The pressure is determined by the solvent (e.g., acetic acid) pressure at a certain temperature. The pressure of the reaction mixture is preferably selected such that the solvent is mainly in the liquid phase. In practice this means that pressures between 5 and 100 bar can be used with a preference for pressures between 10 and 80 bars.  
20 In case the oxidant is an oxygen containing gas, such as air, the gas can be continuously fed to and removed from the reactor, or the gas can be supplied all at the start of the reaction. In the latter case, the pressure of the system will depend on the headspace volume and the amount of gas required to convert the starting material. It is clear that in the latter case, the pressure of the system will be significantly higher than when continuously feeding and  
25 removing an oxygen containing gas. In the case of continuously adding and removing the oxidant gas to and from the reactor, the oxygen partial pressure will be between 1 and 30 bars or more preferably between 1 and 10 bars.

The temperature of the reaction mixture is between 140 and 200 degrees Celsius, most preferably between 160 and 190 degrees Celsius. Temperatures higher than 180  
30 degrees Celsius tend to lead to decarboxylation and to other degradation products. Good results to FDCA have been achieved at a temperature of about 180 °C.

Ratio's of Cobalt to Manganese (Co/Mn) are typically 1/1000 - 100/1, preferably 1/100 - 10/1 and more preferably 1/10 - 4/1.

Ratio's of bromine to metals (e.g. Br/(Co+Mn)) are typically 0.001-5.00, preferably 0.01  
35 - 2.00 and more preferably 0.1 - 0.9.

Catalyst concentration (Co + Mn) is typically between 0.1 - 10 mol % relative to the substrate, with a preference for loads between 2 and 6 mol %. Good results were obtained in general with catalyst loads of around 4 mol %.

5 In another aspect of the invention, we have also investigated the oxidation of other furan-based substrates under the process conditions according to the current invention. We have been able to convert 5-(chloromethyl)furfural, 5-(chloromethyl)furoic acid, 5-methylfurfural, 5-methylfuroic acid and 2,5-dimethylfuran all to FDCA in very interesting yields.

10 In another aspect, the FDCA obtained according to the process of the present invention can be transformed using common esterification reactions to a diester by contacting the starting material under appropriate conditions with the relevant alcohol. Thus, in one aspect, the invention also relates to the use of FDCA obtained according to the process of the current invention in the preparation of a dialkylester of 2,5-dicarboxylic acid by reaction of the FDCA with a C<sub>1</sub>-C<sub>5</sub> alkyl alcohol, preferably methanol to prepare the dimethyl ester of FDCA.

15 In a further aspect of the invention, the di-methylester can be used in the preparation of polyester polymers by reaction with a diol. Reacting the di-methylester with a diol will result in the formation of methanol that quickly vaporises. In 1946 the polymerization of FDCA dimethyl ester with ethylene glycol was described as a first example of such a polymerization (GB 621,971).

20 Indeed, polyesters are generally made by a combined esterification/polycondensation reaction between monomer units of a diol (e.g., ethylene glycol (EG)) and a dicarboxylic acid. Additives such as catalysts and stabilizers may be added to facilitate the process and stabilize the polyester towards degradation.

25 Description of the figures:

Figure 1 shows the yield of FDCA in the oxidation of HMF, of a HMF/AMF 3/2 mixture, of a HMF/AMF 2/3 mixture and of AMF, respectively with 2.7 mol% Co catalyst (relative to substrate), 0.26 M substrate concentration in acetic acid and Co/Mn ratio of 1/1 and Br/(Co+Mn): 1.0; 0.7; 0.4 and 0.1 at 180 °C for 1 hr with 20 bar air. Under these conditions, 30 higher Br amounts give higher yields but when Br/(Co+Mn) > 1, corrosion will be a problem on commercial scale. HMF gives slightly higher yields than AMF at one hour reaction time. The data of these experiments is also given in Table 1.

Figure 2 shows the selectivity to FDCA for the AMF oxidation of Figure 1 together with the comparative examples based on the experimental conditions described in 35 US/2009015684; according to the text 10 wt/wt% AMF was oxidized with 1.75 and 2.65 mol % Co catalyst and a fixed Br/(Co/Mn) of 1.0 and a Co/Mn of 1.0 at 100 °C and 30 bar for 2 hours Under these conditions, the yield of FDCA was lower than the result described in

US/20090156841 and than the results obtained at high temperature. The data of these experiments is also given in Table 2.

Figure 3 shows the yield of FDCA in the oxidation of 5-methylfurfural (5MF) and 2,5-dimethylfurfural (DMF) at 180 °C with 2.7 mol% Co catalyst (relative to substrate), 0.26 M substrate concentration in acetic acid and Co/Mn ratio of 1/1 and a Br/(Co+Mn) of 1.0, 0.7, 0.4 and 0.1 at 180 °C for 2 hrs with 50 bars air. Under these conditions, higher Br amounts give higher yields but when Br/(Co+Mn) > 1, corrosion will be a problem on commercial scale. Reactions with 5MF give higher yields than reactions with DMF. The data of these experiments is also given in Table 3.

10

Examples:

Experiments were carried out in parallel 8 mL magnetically stirred stainless steel batch reactors. The reactors are grouped in blocks containing 12 batch reactors. The standard procedure for all the reactions was as follows:

15 0.5 ML of starting material stock solution in acetic acid (0.78 mmol/ml) were added into a reactor lined with a Teflon insert. 1 ML of a catalyst stock solution in acetic acid was subsequently added to the reactor. In a typical experiment, a catalyst composition Co/Mn/Br with a relative 1-x-y ratio, the concentration of  $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$  was varied. As a Mn source,  $\text{Mn}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$  was used and as a bromine source NaBr was used. The reactors were  
20 closed with a rubber septum, after which the reactors were sealed and pressurized to the desired air pressure, ranging from 20-60 bars. After pressurization, the block with 12 reactors was placed in the test unit which was preheated at the desired temperature, ranging from 100 to 220 °C. After the desired reaction time, ranging from 0.5 hr to 24 hrs, the block is placed into an ice bath for 20 minutes. When the block had cooled down, it was depressurized. After  
25 opening, HPLC samples were prepared. First 5 ml of a saccharine solution in DMSO (11.04 mg/mL) was added to the each reactor and the mixture was stirred for 5 minutes. Then 10  $\mu\text{L}$  of this mixture was diluted to 1000  $\mu\text{L}$  with water in a HPLC vial. The samples were analyzed using HPLC.

Illustrative but not limiting results are presented in the figures 1-3 and Tables 1-3.

Table 1

Substrate HMF/AMF molar ratio		Temp [°C]	Reaction time [Hours]	Catalyst concentration [(Co + Mn) mol %]	Mn/Co	Br/ (Co+Mn)	O <sub>2</sub> /Subs [mol/mol]	Substrate concentration [wt %]	Conversion [%]	s FDCA [%]
HMF	AMF									
1	0	180	1	5.4	1	1	2.69	3.3	100.00	76.11
1	0	180	1	5.4	1	1	2.69	3.3	100.00	76.66
3	2	180	1	5.4	1	1	2.69	3.8	100.00	71.19
3	2	180	1	5.4	1	1	2.69	3.8	100.00	70.91
2	3	180	1	5.4	1	1	2.69	4.0	100.00	77.66
2	3	180	1	5.4	1	1	2.69	4.0	100.00	76.84
0	1	180	1	5.4	1	1	2.69	4.4	100.00	64.82
0	1	180	1	5.4	1	1	2.69	4.4	100.00	63.76
1	0	180	1	5.4	1	0.7	2.69	3.3	100.00	77.69
1	0	180	1	5.4	1	0.7	2.69	3.3	100.00	78.08
3	2	180	1	5.4	1	0.7	2.69	3.8	100.00	66.53
3	2	180	1	5.4	1	0.7	2.69	3.8	100.00	66.96
2	3	180	1	5.4	1	0.7	2.69	4.0	100.00	75.14
2	3	180	1	5.4	1	0.7	2.69	4.0	100.00	74.55
0	1	180	1	5.4	1	0.7	2.69	4.4	100.00	60.64
0	1	180	1	5.4	1	0.7	2.69	4.4	100.00	59.83
1	0	180	1	5.4	1	0.4	2.69	3.3	100.00	73.27
1	0	180	1	5.4	1	0.4	2.69	3.3	100.00	73.23
3	2	180	1	5.4	1	0.4	2.69	3.8	100.00	65.67
3	2	180	1	5.4	1	0.4	2.69	3.8	100.00	64.89
2	3	180	1	5.4	1	0.4	2.69	4.0	100.00	73.15
2	3	180	1	5.4	1	0.4	2.69	4.0	100.00	73.21
0	1	180	1	5.4	1	0.4	2.69	4.4	100.00	57.11
0	1	180	1	5.4	1	0.4	2.69	4.4	100.00	57.36
1	0	180	1	5.4	1	0.1	2.69	3.3	100.00	67.57
1	0	180	1	5.4	1	0.1	2.69	3.3	100.00	67.92
3	2	180	1	5.4	1	0.1	2.69	3.8	100.00	60.92
3	2	180	1	5.4	1	0.1	2.69	3.8	100.00	57.38
2	3	180	1	5.4	1	0.1	2.69	4.0	100.00	69.18
2	3	180	1	5.4	1	0.1	2.69	4.0	100.00	69.64

Table 2

Substrate	Temp [°C]	Reaction time [Hours]	Catalyst concentration [(Co + Mn) mol %]	Mn/Co	Br/ (Co+Mn)	O <sub>2</sub> /Subs [mol/mol]	Substrate concentration [wt %]	Conversion [%]	s FDCA [%]
AMF	180	1	5.4	1	1	2.69	3.3	100.00	64.82
AMF	180	1	5.4	1	1	2.69	3.3	100.00	63.76
AMF	180	1	5.4	1	0.7	2.69	3.8	100.00	60.64
AMF	180	1	5.4	1	0.7	2.69	3.8	100.00	59.83
AMF	180	1	5.4	1	0.4	2.69	4.0	100.00	57.11
AMF	180	1	5.4	1	0.4	2.69	4.0	100.00	57.36
AMF	180	1	5.4	1	0.1	2.69	4.4	100.00	46.85
AMF	180	1	5.4	1	0.1	2.69	4.4	100.00	46.53
AMF	100	2	3.5	1	1	2.88	10.0	100.00	23.48
AMF	100	2	3.5	1	1	2.88	10.0	100.00	23.96
AMF	100	2	5.25	1	1	2.88	10.0	100.00	29.05
AMF	100	2	5.25	1	1	2.88	10.0	100.00	29.87



Table 3

Substrate	Temp [°C]	Reaction time [Hours]	Catalyst concentration [(Co + Mn) mol %]	Mn/Co	Br/ (Co+Mn)	O <sub>2</sub> /Subs [mol/mol]	Substrate concentration [wt %]	Conversion [%]	s FDCA [%]
5-MF	180	1	5.4	1	1	6.7	2.9	100.00	42.62
5-MF	180	1	5.4	1	1	6.7	2.9	100.00	42.04
5-MF	180	1	5.4	1	0.7	6.7	2.9	100.00	39.47
5-MF	180	1	5.4	1	0.7	6.7	2.9	100.00	39.94
DMF	180	1	5.4	1	1	6.7	2.5	100.00	16.13
DMF	180	1	5.4	1	1	6.7	2.5	100.00	16.17
DMF	180	1	5.4	1	0.7	6.7	2.5	100.00	13.68
DMF	180	1	5.4	1	0.7	6.7	2.5	100.00	14.09
DMF	180	1	5.4	1	0.4	6.7	2.5	100.00	11.30
DMF	180	1	5.4	1	0.4	6.7	2.5	100.00	10.89
DMF	180	1	5.4	1	0.1	6.7	2.5	100.00	7.19
AMF	180	1	5.4	1	0.1	6.7	2.5	100.00	7.12

Claims

1. Method for the preparation of 2,5-furandicarboxylic acid comprising the step of contacting a feed comprising 5-hydroxymethylfurfural (HMF), one or more derivatives of HMF or a mixture of HMF with one or more derivatives of HMF as starting material, with an oxidant in the presence of an oxidation catalyst at a temperature higher than 140°C.
- 5 2. Method according to claim 1 comprising the step of contacting an ester of 5-(hydroxymethyl)furfural or 5-(hydroxymethyl)furfural or a mixture of these components with an oxidant in the presence of an oxidation catalyst at a temperature higher than 140 °C.
- 3 Method according to claim 1, wherein the oxidation catalyst comprises at least one metal selected from the group consisting of Co and Mn.
- 10 4 Method according to claim 1, wherein the oxidation catalyst comprises a source of bromine.
- 5 Method according to claim 4, wherein the oxidation catalyst contains both Co and Mn.
- 6 Method according to claim 5, wherein the oxidation catalyst comprises at least one additional metal.
- 15 7. Method according to claim 6, wherein the additional metal is Zr and or Ce.
8. Method according to claims 1, wherein the oxidant is selected from oxygen, air or other oxygen-containing gases.
9. Method according to claim 1, wherein the temperature is between 140 and 200 degrees Celsius, most preferably between 160 and 190 degrees Celsius.
- 20 10. Method according to claim 1, wherein a solvent or solvent mixture is present, preferably comprising a solvent containing a monocarboxylic acid functional group, more preferably acetic acid or acetic acid and water mixtures.
11. Method according to claim 1 wherein the alkyl of the ester group of the HMF ester is C<sub>1</sub>-C<sub>5</sub> alkyl, preferably methyl.
- 25 12 Use of the reaction product obtained via the method claim 1 in the preparation of a dialkylester of 2,5-furan dicarboxylic acid via an esterification reaction with a C<sub>1</sub>-C<sub>5</sub> alkyl alcohol.
13. Use according to claim 12 wherein the C<sub>1</sub>-C<sub>5</sub> alkylalcohol is methanol and the diester is the dimethylester of 2,5-furan dicarboxylic acid.
- 30 14. Method for the preparation of 2,5-furandicarboxylic acid wherein a carbohydrate source is converted in the presence of an alkyl carboxylic acid into products comprising an HMF ester and optionally 5-hydroxymethyl furfural, from which is isolated a feed comprising the ester of HMF and optionally 5-hydroxymethyl furfural, comprising the subsequent step of contacting the feed with an oxidant in the presence of a cobalt and manganese and bromide  
35 containing catalyst under appropriate reaction conditions.

## Abstract

The application describes a method for the preparation of 2,5-furandicarboxylic acid comprising the step of contacting a feed comprising 5-hydroxymethylfurfural (HMF), one or more derivatives of HMF or a mixture of HMF with one or more derivatives of HMF as starting material, with an oxidant in the presence of an oxidation catalyst at a temperature higher than 140°C.

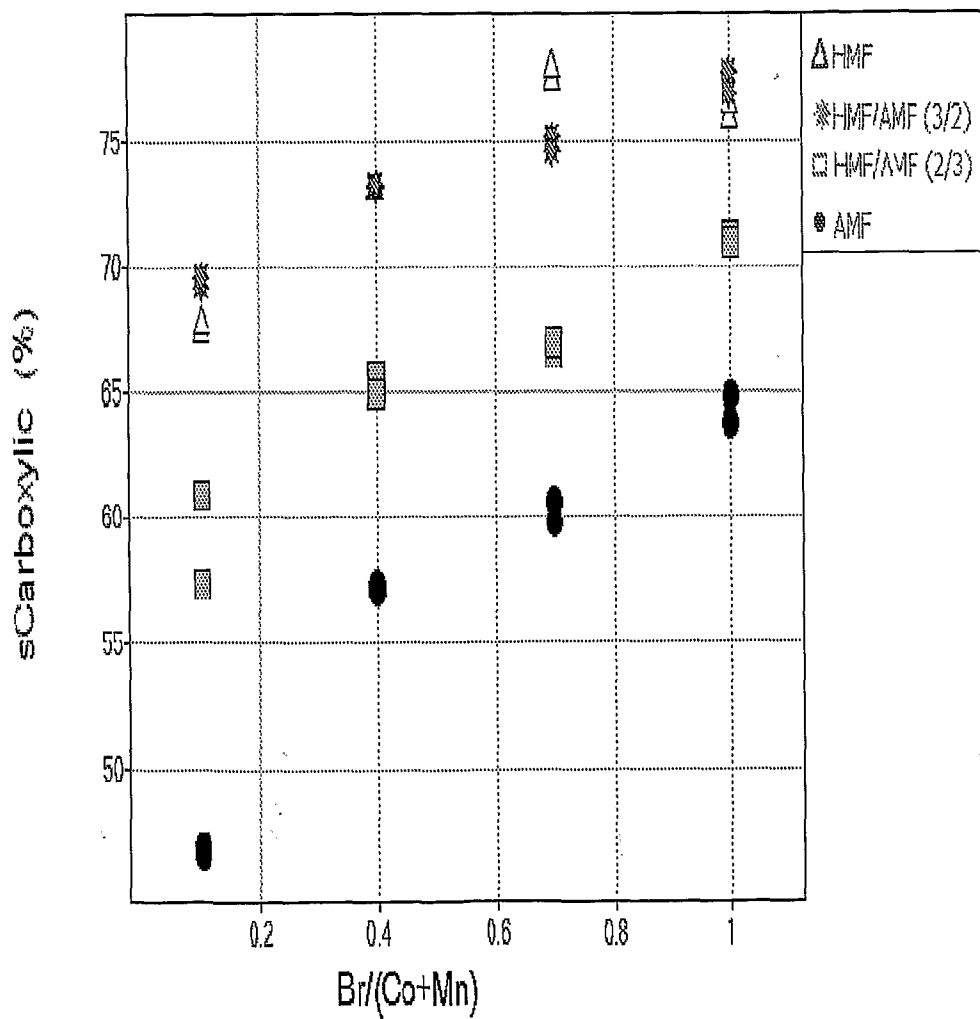
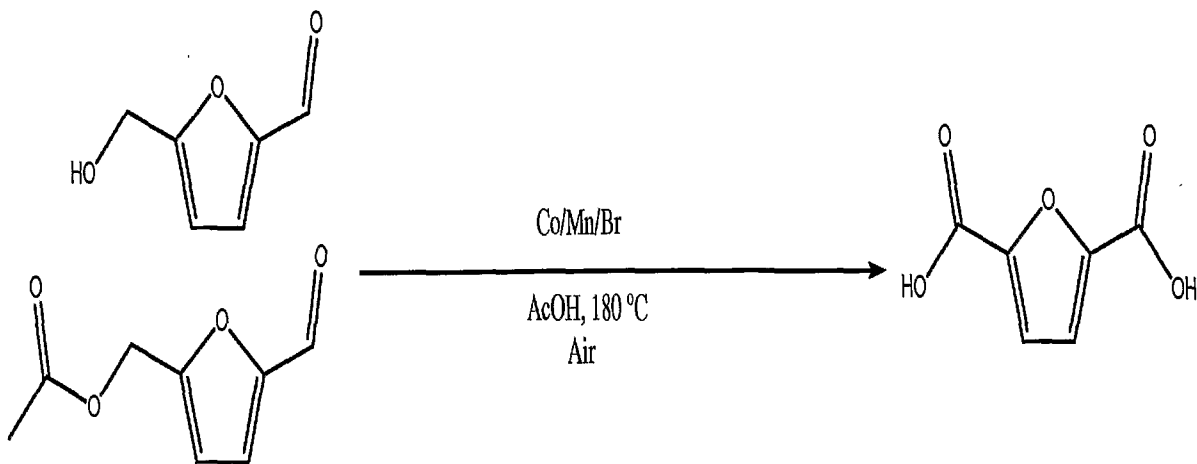


FIG 1

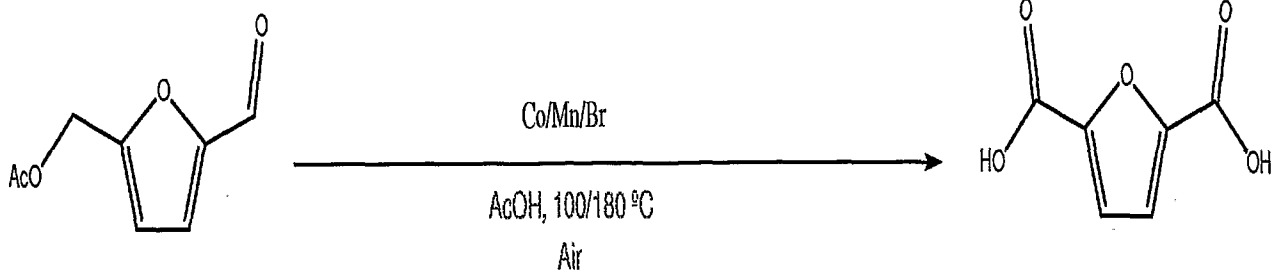
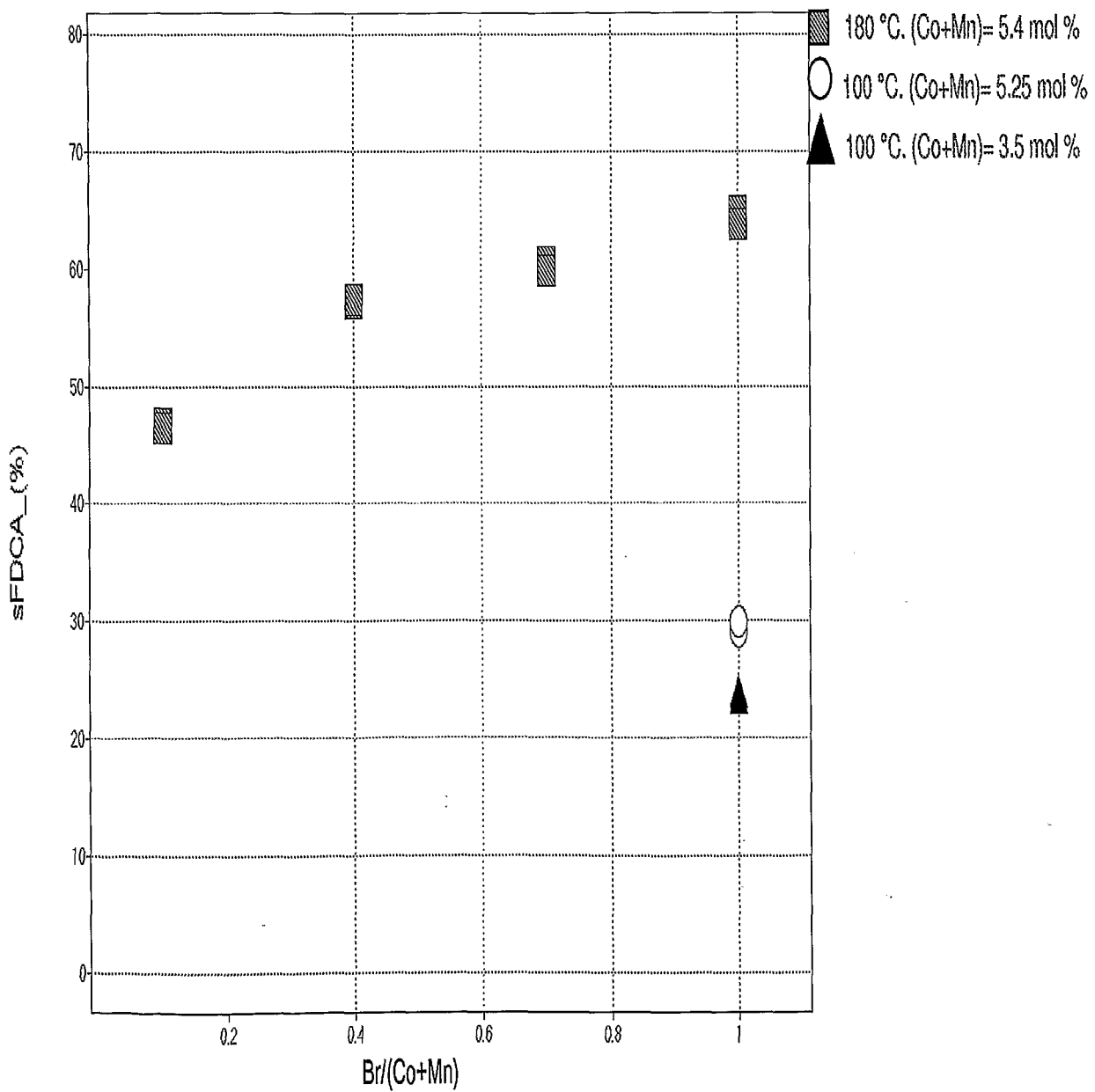


FIG 2



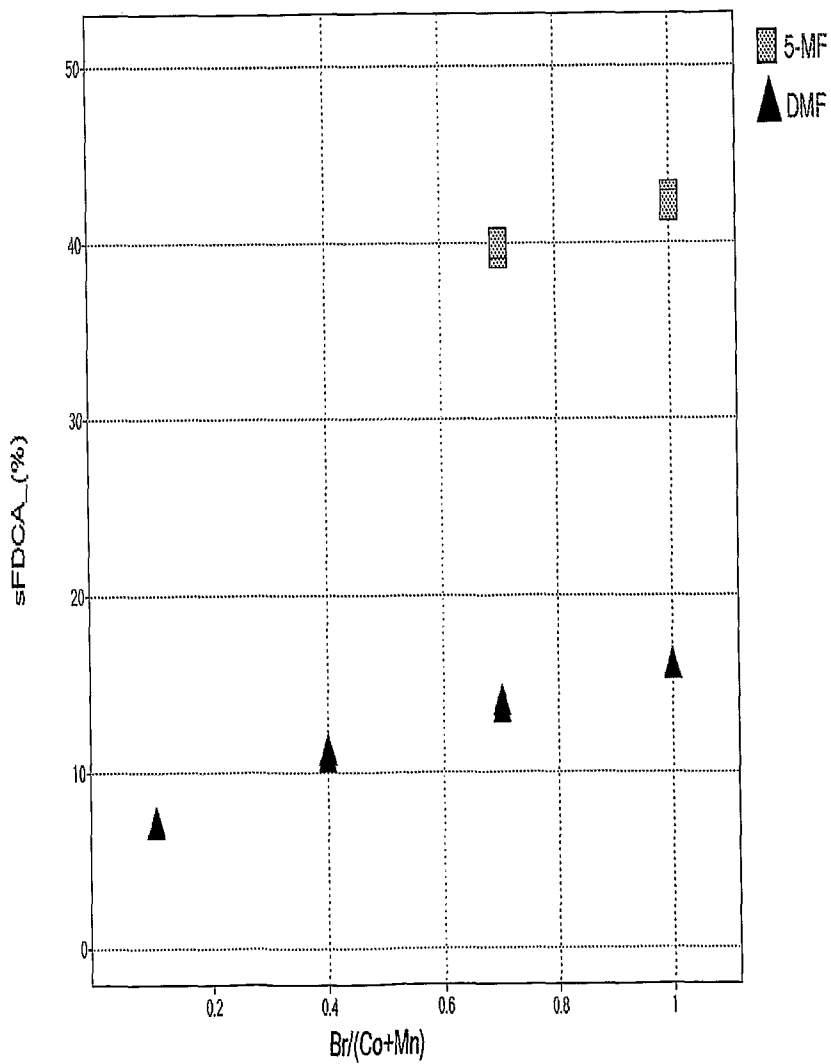
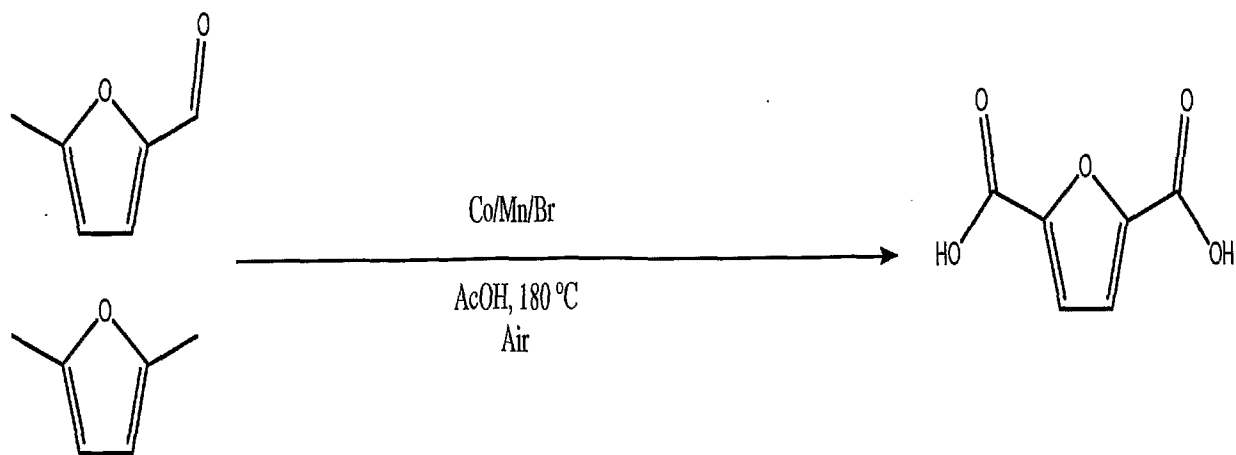


Fig 3

3/3

# INTERNATIONAL SEARCH REPORT

International application No  
PCT/NL2010/050654

**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 practical, search terms used)

EPO-Internal, WPI Data, BIOSIS, EMBASE, CHEM ABS Data

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>WALT PARTENHEIMER ET AL.: "Synthesis of 2,5-diformylfuran and furan-2,5-dicarboxylic acid by catalytic air oxidation of 5-hydroxymethylfurfural. Unexpectedly selective aerobic oxidation of benzyl alcohol to benzaldehyde with metal/bromide catalysts", ADV. SYNTH. CATAL., vol. 343, no. 1, 2001, pages 102-111, XP002584717, cited in the application the whole document in particular figure 1, tables 1 and 3.</p> <p style="text-align: center;">----- -/--</p>	1-11,15

Further documents are listed in the continuation of Box C.

See patent family annex.

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Petitioners' Exhibit 1010, Page 215 of 231

## INTERNATIONAL SEARCH REPORT

International application No

PCT/NL2010/050654

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## INTERNATIONAL SEARCH REPORT

International application No

PCT/NL2010/050654

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Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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International application No  
PCT/NL2010/050654

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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Information on patent family members

International application No

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(74) Agent: **VOLMER, J.C.**; Exter Polak & Charlois B.V., P.O. Box 3241, NL-2280 GE Rijswijk (NL).

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(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, 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, ML, MR, NE, SN, TD, TG).

Published:

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



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(54) Title: METHOD FOR THE PREPARATION OF 2,5-FURANDICARBOXYLIC ACID AND FOR THE PREPARATION OF THE DIALKYL ESTER OF 2,5-FURANDICARBOXYLIC ACID

(57) Abstract: The application describes a method 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-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.

Title: Method for the preparation of 2,5-furandicarboxylic acid and for the preparation of the dialkyl ester of 2,5-furandicarboxylic acid

The present invention relates to a method for the preparation of 2,5-furandicarboxylic acid ("FDCA") from 5-hydroxymethylfurfural ("HMF") and/or derivatives thereof. FDCA can be produced in particular from esters of HMF, such as for example 5-acetoxymethylfurfural (AMF) or a mixture of one or more of these compounds with HMF, such as for example from  
5 a mixture of AMF and HMF. The invention further relates to a process for the preparation of the dialkyl ester of 2,5-furandicarboxylic acid.

2,5-Furandicarboxylic acid, also known as dehydromucic acid is a furan derivative. This organic compound was first obtained by Fittig and Heinzelmann in 1876. The first review, by Henry Hill was published in 1901 (Am. Chem. Journ. 25, 439). FDCA was more than 125  
10 years later identified by the US Department of Energy as one of 12 priority chemicals for establishing the "green" chemistry industry of the future. However, to date, no commercial process exists for its production. On laboratory scale it is often synthesized from 5-hydroxymethylfurfural (HMF), which in turn can be obtained from carbohydrate containing sources such as glucose, fructose, sucrose and starch. From fructose and glucose HMF is  
15 obtained by acidic elimination of three moles of water.

The derivatives of HMF are identified as potential and versatile fuel components and precursors for the production of plastics. The polyester from FDCA dimethyl diester and ethylene glycol was first reported in 1946 (GB 621,971).

WO 01/72732 describes the oxidation of HMF to FDCA. The maximum FDCA yield  
20 reported is 59%, obtained at 105 °C. The oxidation of HMF in an aqueous medium with oxygen using a catalyst from the Pt-group is described in US 4977283. Taarning et al. described the oxidation of HMF over gold based catalysts (ChemSusChem, 2008, 1, 1-4).

Partenheimer et al (Adv. Synth. Catal. **2001**, 343, pp 102-11) describe the synthesis of 2,5-furandicarboxylic acid by catalytic air-oxidation of 5-hydroxymethylfurfural with  
25 metal/bromide catalysts such as Co/Mn/Br in acetic acid at temperatures ranging from 50 to 125 °C. With the Co/Mn/Br catalyst the highest FDCA yield obtained is 35.2% (Table 3, experiment 4). On page 103 of the same paper, under the header "products formed" it is stated: "A side reaction is the esterification of the alcohols to form the more oxidatively stable acetate ...." As apparently 5-hydroxymethylfurfural reacts with acetic acid a loss of the  
30 starting material takes place. Further, in the reaction scheme given in Figure 1 on page 103, it is indicated that 5-(acetoxymethyl)furfural is an end-point. There is no further reaction of this compound indicated to FDCA (in contrast to the ester of the intermediate product 5-

(acetoxymethyl)furan-2-carboxylic acid). In other words, the 5-(acetoxymethyl)furfural (AMF) formed through reaction of HMF with acetic acid solvent, is not oxidized to FDCA and its formation leads therefore to yield loss.

This result was confirmed in US 2009/0156841. Although the intention of the process according to US 2009/0156841 was to obtain FDCA, the product isolated and erroneously characterized as being FDCA was in fact the starting material acetoxymethyl furfural (AMF). Under the low temperature conditions deployed (100 °C), AMF is quite stable, as was already reported by Partenheimer (see above).

In US 2009/0156841 a <sup>1</sup>H NMR spectrum is shown in Figure 8 and suggested that it is the spectrum of the product that was identified as FDCA. However, this is not the case. The <sup>1</sup>H NMR spectrum of the product shown in Figure 8 is the same as that in Figure 6 and represents the starting material AMF. The 1H NMR spectrum of FDCA shows a singlet at a shift of about 7.26 ppm. Moreover, the product is described as a tan solid. In the experience of the present inventors, AMF is a tan solid, while FDCA is a white solid. It would seem that no FDCA was obtained in the experiments according to US 2009/0156841.

The experiments executed under the conditions of US 2009/0156841 were repeated. These comparative experiments confirm the low reactivity of AMF under conditions given in US 2009/0156841. Thus, a person skilled in the art would therefore have concluded that FDCA cannot be obtained in interesting yields from AMF using the conditions that are reported in US 2009/0156841, i.e., using a Co/Mn/Br catalyst in acetic acid at between 85 and 110 °C within a time frame of from 100 and 150 minutes. In Example 7 of US 2009/0156841, slightly more than 50% of the starting material was the only product isolated from the reaction.

The present inventors have now surprisingly found that when using an oxidation catalyst, e.g., based on both cobalt and manganese and containing a bromide, at temperatures higher than 140 °C, derivatives of HMF, and in particular esters of HMF optionally in combination with HMF, such as for example 5-(acetoxymethyl)furfural (AMF) can be oxidized to FDCA in high yields.

Thus, in a first aspect the invention provides a method 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. The feed may optionally comprise 5-hydroxymethylfurfural as a further compound.

The invention described hereinafter may use any of the compounds described above in the feed. A preferred ester of HMF contains an ester moiety of an alkyl carboxylic acid

wherein the alkyl group contains up to 6 carbon atoms, preferably from 1 to 5 carbon atoms, i.e. methyl, ethyl, propyl, isopropyl, butyl, 2-butyl, tert-butyl, pentyl, 2-pentyl, neopentyl and 3-pentyl. Particularly preferred are alkyl groups with 1 to 4 carbon atoms. There is a preference for methyl, giving (5-acetoxymethyl)furfural. Hence, 5-acetoxymethylfurfural is the preferred  
5 feedstock, by itself or in combination with HMF.

In another aspect of the invention, we have also investigated the oxidation of other furan-based substrates under the process conditions according to the current invention. We have been able to convert 5-(chloromethyl)furfural, 5-(chloromethyl)furoic acid, 5-methylfurfural, 5-methylfuroic acid and 2,5-dimethylfuran all to FDCA in very interesting  
10 yields.

In WO 2007/104515 and WO 2009/030512, the synthesis of esters of HMF such as 5-acetoxymethylfurfural (AMF) from biomass sources is described. Given the higher stability of the HMF esters than HMF and hence improved production pathways and given the fact that upon oxidation in acetic acid the acetoxy functionality that was obtained from acetic acid is  
15 now liberated as acetic acid and given the green reputation of these esters, they were considered by the present inventors as interesting starting point in the preparation of furan-based monomers that could be used for the production of furandicarboxylic acid-based polyesters, for instance as an alternative for PET or FDCA-based polyamids (nylons). The most important conventional, oil-based, polyester monomer to produce PET is Purified  
20 Terephthalic acid (PTA) and its dialkyl ester DiMethyl Terephthalate (DMT).

AMF can be obtained from biomass sources as described in WO 2007/104515 and WO 2009/030512. Depending on the process conditions the product obtained in accordance with the process of these references may also contain HMF.

FDCA, the product of the reaction can be used in the preparation of a polyester, by  
25 reaction of FDCA or its dialkyl ester with a suitable diol. Such polyester preparations are preferably performed by transesterification, whereby the di-methyl ester or di-ethyl ester of FDCA is used and wherein the methyl or ethyl groups are exchanged in the form of a volatile alcohol during the transesterification with the diol.

The oxidation catalyst can be selected from a variety of oxidation catalysts, but is  
30 preferably a catalyst based on both cobalt and manganese and suitably containing a source of bromine, preferably a bromide.

The bromine source can be any compound that produces bromide ions in the reaction mixture. These compounds include hydrogen bromide, sodium bromide, elemental bromine, benzyl bromide and tetrabromoethane. Also other bromine salts, such as an alkali or alkaline  
35 earth metal bromide or another metal bromide such as  $ZnBr_2$  can be used. There is a preference for hydrobromic acid or sodium bromide. The amount of bromine mentioned in here relates to the amount measured as Br relative to cobalt.

Suitable metal bromide catalysts employed in all of the processes of this invention comprise a cobalt compound and a manganese compound and a bromine-containing compound. Preferably these compounds are soluble in the reaction mixture.

Preferably, the catalyst comprises both Co and Mn. The metal and bromide catalyst  
5 contains, in addition to bromide, Co and Mn and optionally may contain one or more additional metals, in particular Zr and/or Ce. Alternative and suitable catalysts are described in W. Partenheimer, *Catalysis Today* 23(2), 69-158 (1995) in particular on pages 89-99, included herein by reference.

Each of the metal components can be provided in any of their known ionic forms.  
10 Preferably the metal or metals are in a form that is soluble in the reaction solvent. Examples of suitable counterions for cobalt and manganese include, but are not limited to, carbonate, acetate, acetate tetrahydrate and halide, with bromide being the preferred halide.

As described in Partenheimer, *ibid*, pages 86-88, suitable solvents for use in the processes of the present invention, described above, preferably have at least one  
15 component that contains a monocarboxylic acid functional group. The solvent may also function as one of the reagents. The processes may be run in a solvent or solvent mixture that does not contain an acid group. In that case, preferably one of the reagents does contain a monocarboxylic acid functional group. Suitable solvents can also be aromatic acids such as benzoic acid and derivatives thereof. A preferred solvent is an aliphatic C<sub>2</sub>-C<sub>6</sub>  
20 monocarboxylic acid, such as but not limited to acetic acid, propionic acid, n-butyric acid, isobutyric acid, n-valeric acid, trimethylacetic acid, and caproic acid and mixtures thereof. Said mixtures may also include benzene, acetonitrile, heptane, acetic anhydride, chlorobenzene, o-dichlorobenzene, and water. The most preferred solvent is acetic acid ("AcOH").

25 The oxidant in the processes of the present invention is preferably an oxygen-containing gas or gas mixture, such as, but not limited to air and oxygen-enriched air. Oxygen by itself is also a preferred oxidant.

The processes of the instant invention described above can be conducted in a batch, semi-continuous or continuous mode. Especially for the manufacture of FDCA, operation in  
30 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 desirable. For example, variation of the catalyst composition during the reaction can be accomplished by addition of cobalt and/or manganese and/or zirconium, and/or cerium, and/or bromide at specified times.

35 The pressure in a commercial oxidation process may vary within wide ranges. When a diluent is present, and in particular with acetic acid as diluent, the temperature and the pressure in such a process are not independent. The pressure is determined by the solvent



(e.g., acetic acid) pressure at a certain temperature. The pressure of the reaction mixture is preferably selected such that the solvent is mainly in the liquid phase. In practice this means that pressures between 5 and 100 bar can be used with a preference for pressures between 10 and 80 bar. In case the oxidant is an oxygen-containing gas, such as air, the gas can be continuously fed to and removed from the reactor, or the gas can be supplied all at the start of the reaction. In the latter case, the pressure of the system will depend on the headspace volume and the amount of gas required to convert the starting material. It is clear that in the latter case, the pressure of the system may be significantly higher than the pressure in a process wherein an oxygen containing gas is continuously fed and removed. In the case of continuously feeding and removing the oxidant gas to and from the reactor, the oxygen partial pressure will suitably be between 1 and 30 bar or more preferably between 1 and 10 bar.

The temperature of the reaction mixture is at least 140 °C, preferably from 140 and 200 °C, most preferably between 160 and 190 °C. Temperatures higher than 180 °C may lead to decarboxylation and to other degradation products. Good results to FDCA have been achieved at a temperature of about 180 °C.

Molar ratios of cobalt to manganese (Co/Mn) are typically 1/1000 - 100/1, preferably 1/100 - 10/1 and more preferably 1/10 - 4/1.

Molar ratios of bromine to metals (e.g. Br/(Co+Mn)) are typically 0.001-5.00, preferably 0.01 - 2.00 and more preferably 0.1 - 0.9.

Catalyst concentration (Co + Mn) is typically from 0.1 to 10 mol %, relative to the substrate, with a preference for concentrations from 2 to 6 mol %. Good results were obtained in general with catalyst concentrations of around 4 mol %.

The starting materials for the production of FDCA may originate from a carbohydrate source as described above. Examples of such disclosures are WO 2007/104515 and WO 2009/030512. Accordingly, the invention also provides a method for the preparation of 2,5-furandicarboxylic acid wherein a carbohydrate source is converted in the presence of an alkyl carboxylic acid into products comprising an HMF ester and optionally 5-hydroxymethyl furfural, from which is isolated a feed comprising the ester of HMF and optionally 5-hydroxymethyl furfural, and which method further comprises the subsequent step of contacting the feed with an oxidant in the presence of an oxidation catalyst, in particular a cobalt and manganese and bromide-containing catalyst, under appropriate reaction conditions, in particular at temperatures higher than 140 °C

In another aspect, the FDCA obtained according to the process of the present invention can be transformed using common esterification reactions to a diester by contacting the starting material under appropriate conditions with the relevant alcohol. Thus, in one aspect, the invention also relates to the use of FDCA obtained according to the

process of the current invention in the preparation of a dialkylester of 2,5-dicarboxylic acid by reaction of the FDCA with a C<sub>1</sub>-C<sub>5</sub> alkyl alcohol, preferably methanol to prepare the dimethyl ester of FDCA.

Accordingly, the present invention also provides a process for the preparation of a  
5 dialkyl ester 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-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  
10 temperature higher than 140 °C, and esterifying the thus obtained product. Preferably, the product is esterified with an alkyl alcohol, suitably having 1 to 5 carbon atoms.

The esterification of 2,5-furan dicarboxylic acid is known. As a specific example for the manufacture of these esters, reference is made to US 2673860 wherein the diester is obtained by transesterification of another dicarboxylic acid ester in the presence of sulphuric  
15 acid. A more general description for the esterification of dicarboxylic acids is presented in US 2628249.

In a further aspect of the invention, the di-methylester can be used in the preparation of polyester polymers by reaction with a diol. Reacting the di-methylester with a diol will result in the formation of methanol that quickly vaporises. In 1946 the polymerization of FDCA  
20 dimethyl ester with ethylene glycol was described as a first example of such a polymerization in GB 621,971.

Indeed, polyesters are generally made by a combined esterification/polycondensation reaction between monomer units of a diol (e.g., ethylene glycol (EG)) and a dicarboxylic acid. Additives such as catalysts and stabilizers may be added to facilitate the process and  
25 stabilize the polyester towards degradation.

Examples:

Experiments were carried out in parallel 8 ml magnetically stirred stainless steel batch reactors. The reactors are grouped in blocks containing 12 batch reactors. The standard procedure for all the reactions was as follows:

30 0.5 ml of starting material stock solution in acetic acid (0.78 mmol/ml) were added into a reactor lined with a Teflon insert. To the reactor 1 ml of a catalyst stock solution in acetic acid was subsequently added. In a typical experiment, a catalyst composition Co/Mn/Br with a relative 1-x-y ratio, the concentration of Co(OAc)<sub>2</sub>\*4H<sub>2</sub>O was varied. As a Mn source, Mn(OAc)<sub>2</sub>\*4H<sub>2</sub>O was used and as a bromine source NaBr was used. The reactors were  
35 closed with a rubber septum, after which the reactors were sealed and pressurized to the desired air pressure, ranging from 20-60 bars. After pressurization, the block with 12 reactors was placed in the test unit which was preheated at the desired temperature, ranging from

ranging from 100 to 220 °C. After the desired reaction time, ranging from 0.5 hr to 24 hrs, the block is placed into an ice bath for 20 minutes. When the block had cooled down, it was depressurized. After opening, HPLC samples were prepared. First 5 ml of a saccharine solution in DMSO (11.04 mg/ml) was added to each reactor and the mixture was stirred for 5 minutes. Then 10 µl of this mixture was diluted to 1000 µl with water in a HPLC vial. The samples were analyzed using HPLC.

#### Example 1

Example 1 shows the selectivity of FDCA in the oxidation of HMF, of a HMF/AMF 3/2 mixture, of a HMF/AMF 2/3 mixture and of AMF, respectively, with 2.7 mol% Co catalyst (relative to substrate), and Co/Mn molar ratio of 1/1, so that the catalyst concentration (Co + Mn) amounted to 5.4 mol%. The Br/(Co+Mn) molar ratio was 1.0; 0.7; 0.4 and 0.1 at 0.26 M substrate concentration in acetic acid at 180 °C for 1 hr with 20 bar air. The amount of oxygen was 2.69 mol oxygen per mol substrate. Under these conditions, higher Br amounts give higher yields but when Br/(Co+Mn) > 1, corrosion will be a problem on commercial scale. HMF gives slightly higher yields than AMF at one hour reaction time. The results of these experiments are given in Table 1.

#### Example 2

Example 2 shows the selectivity to FDCA for the AMF oxidation of Example 1, together with the comparative examples based on the experimental conditions described in US 2009/0156841. In those comparative experiments (2a and 2b) 10 wt/wt% AMF in acetic acid was oxidized with 1.75 and 2.65 mol % Co catalyst and a fixed Br/(Co + Mn) molar ratio of 1.0 and a Co/Mn molar ratio of 1.0 at 100 °C and 30 bar for 2 hours. The amount of oxygen was 2.88 mol oxygen per mol substrate. Under these conditions, the yield of FDCA was lower than the result suggested in US 2009/0156841 and also lower than the results obtained at higher temperature. The results of these experiments are given in Table 2.

#### Example 3

Example 3 shows the yield of FDCA in the oxidation of 5-methylfurfural (5MF) and 2,5-dimethylfurfural (DMF) at 180 °C with 2.7 mol% Co catalyst (relative to substrate), and Co/Mn ratio of 1/1, so that the catalyst concentration (Co + Mn) amounted to 5.4 mol%. The Br/(Co+Mn) molar ratio was 1.0, 0.7, 0.4 and 0.1. The substrate concentration was 0.26 M in acetic acid. The reaction temperature was at 180 °C and the reaction was conducted with 50 bars air. The amount of oxygen was 6.7 mol oxygen per mol substrate. Under these conditions, higher Br amounts give higher yields but when Br/(Co+Mn) > 1, corrosion will be a problem on commercial scale. Reactions with 5-MF give higher yields than reactions with DMF. The results of these experiments are also given in Table 3.

Table 1

Experiment No.	Substrate HMF/AMF molar ratio		Br/ (Co+Mn)	Substrate concentration [wt %]	Conversion [%]	s FDCA [%]
	HMF	AMF				
1a	1	0	1	3.3	100.00	76.66
1b	3	2	1	3.8	100.00	71.19
1c	2	3	1	4.0	100.00	77.66
1d	0	1	1	4.4	100.00	64.82
1e	1	0	0.7	3.3	100.00	78.08
1f	3	2	0.7	3.8	100.00	66.96
1g	2	3	0.7	4.0	100.00	75.14
1h	0	1	0.7	4.4	100.00	60.64
1i	1	0	0.4	3.3	100.00	73.27
1j	3	2	0.4	3.8	100.00	65.67
1k	2	3	0.4	4.0	100.00	73.21
1l	0	1	0.4	4.4	100.00	57.36
1m	1	0	0.1	3.3	100.00	67.92
1n	3	2	0.1	3.8	100.00	60.92
1o	2	3	0.1	4.0	100.00	69.64
1p	0	1	0.1	4.4	100.00	46.85

Table 2

Experiment No.	Temp [° C]	Reaction time [Hours]	Catalyst concentration [(Co + Mn) mol %]	Mn/Co	Br/ (Co+Mn)	O <sub>2</sub> /Subs [mol/mol]	Substrate concentration [wt %]	Conversion [%]	s FDCA [%]
1d	180	1	5.4	1	1	2.69	4.4	100.00	64.82
1h	180	1	5.4	1	0.7	2.69	4.4	100.00	60.64
1l	180	1	5.4	1	0.4	2.69	4.4	100.00	57.36
1p	180	1	5.4	1	0.1	2.69	4.4	100.00	46.85
2a	100	2	3.5	1	1	2.88	10.0	100.00	23.48
2b	100	2	5.3	1	1	2.88	10.0	100.00	29.05

Table 3

Experiment No.	Substrate	Reaction time [Hours]	Br/ (Co+Mn)	O <sub>2</sub> /Subs [mol/mol]	Substrate concentration [wt %]	Conversion [%]	s FDCA [%]
3a	5-MF	1	1	6.7	2.9	100.00	42.62
3b	5-MF	1	0.7	6.7	2.9	100.00	39.94
3c	DMF	1	1	6.7	2.5	100.00	16.17
3d	DMF	1	0.7	6.7	2.5	100.00	14.09
3e	DMF	1	0.4	6.7	2.5	100.00	11.30
3f	DMF	1	0.1	6.7	2.5	100.00	7.19

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Claims

1. Method 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  
5 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.
2. Method according to claim 1, wherein the feed comprises a compound selected from the group consisting of 5-hydroxymethylfurfural ("HMF"), esters of HMF and a mixture thereof.
- 10 3. Method according to claim 1 or 2, wherein the oxidation catalyst comprises at least one metal selected from the group consisting of Co and Mn.
4. Method according to claim 1 or 2 or 3, wherein the oxidation catalyst comprises a source of bromine.
5. Method according to claim 4, wherein the oxidation catalyst contains both Co and Mn.
- 15 6. Method according to claim 5, wherein the oxidation catalyst comprises at least one additional metal.
7. Method according to claim 6, wherein the additional metal is Zr and/or Ce.
8. Method according to claims 1-6, wherein the oxidant is selected from oxygen, air or other oxygen-containing gases.
- 20 9. Method according to any of the previous claims wherein the temperature is between 140 and 200 °C, most preferably between 160 and 190 °C.
10. Method according to any one of the previous claims, wherein a solvent or solvent mixture is present, preferably comprising a solvent containing a monocarboxylic acid functional group, more preferably acetic acid or acetic acid and water mixtures.
- 25 11. Method according to any of the previous claims, wherein the feed comprises an ester of HMF containing an ester moiety of an alkyl carboxylic acid wherein the alkyl group contains up to 6 carbon atoms, preferably from 1 to 5 carbon atoms.
12. Process for the preparation of a dialkyl ester of 2,5-furan dicarboxylic acid, comprising the step of contacting a feed comprising a compound selected from the group consisting of  
30 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, and esterifying the thus obtained product.

13. Process according to claim 12, wherein the product is esterified with a C<sub>1</sub>-C<sub>5</sub> alkyl alcohol.
14. Process according to claim 13, wherein the C<sub>1</sub>-C<sub>5</sub> alkyl alcohol is methanol and the dialkyl ester is the dimethylester of 2,5-furan dicarboxylic acid.
- 5 15. Method for the preparation of 2,5-furandicarboxylic acid wherein a carbohydrate source is converted in the presence of an alkyl carboxylic acid into products comprising an HMF ester and optionally 5-hydroxymethyl furfural, from which is isolated a feed comprising the ester of HMF and optionally 5-hydroxymethyl furfural, and which method comprises further the subsequent step of contacting the feed with an oxidant in the presence of an oxidation
- 10 catalyst, preferably a cobalt and manganese and bromide-containing catalyst, under appropriate reaction conditions.