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(54) Title: METHOD FOR PRODUCING DICARBOXYLIC ACID USING CERIUM CO-CATALYST

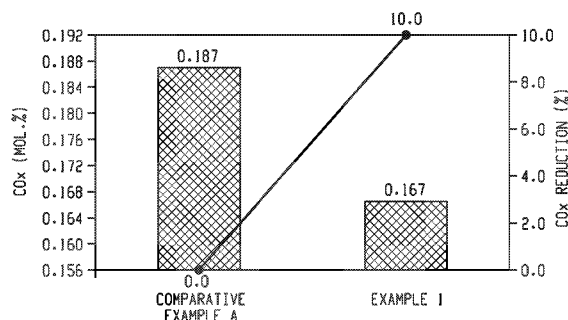


Fig. 2A

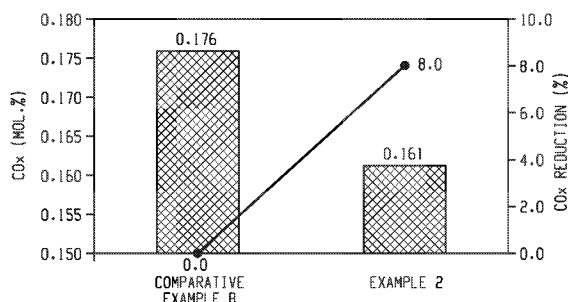


Fig. 2B

(57) Abstract: A method for oxidizing a dimethyl aromatic compound includes reacting the dimethyl aromatic compound and an oxidant in the presence of a catalyst and a co-catalyst in a solvent to produce a reaction product comprising an aromatic dicarboxylic acid. The catalyst comprises cobalt, manganese, and bromine. A weight ratio of cobalt to manganese is equal to or greater than 1:1. The co-catalyst comprises at least one of cerium or iron. The co-catalyst is present in an amount in a range of 10 ppm to 200 ppm, based on a total weight of the dimethyl aromatic compound and the solvent. The aromatic dicarboxylic acid is present in the reaction product in an amount equal to or greater than 70 wt.%, or equal to or greater than 90 wt.%, based on a total weight of solids in the reaction product.



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METHOD FOR PRODUCING DICARBOXYLIC ACID USING CERIUM CO-CATALYST

CROSS-REFERENCE TO RELATED APPLICATION

[0001] This International Application claims priority to US Provisional Application No. 62/789,583, filed January 8, 2019, which is incorporated herein by reference.

BACKGROUND

[0002] Aromatic dicarboxylic acids (e.g., terephthalic acid) can be produced by oxidation of dimethyl aromatic compounds (e.g., *para*-xylene) in the presence of a catalyst. The reaction is normally carried out in the presence of solvent, e.g., acetic acid. The oxidation of dimethyl aromatics to the corresponding dicarboxylic acids proceeds through a number of intermediate steps. Inefficient catalyst and/or oxidation process leads to formation of intermediates as impurities in the product. Moreover, the oxidation process carried out at high pressures and temperatures leads to the formation CO_x through over oxidation of final products (i.e., aromatic dicarboxylic acid) and also burning of solvent, e.g., acetic acid. As a result of by-product formation and/or over oxidation, consumption of the dimethyl aromatic compounds and solvent is undesirably increased.

[0003] U.S. Patent Number 5,453,538 discloses a process for the manufacture of aromatic dicarboxylic acids that uses a low bromine to metals ratio facilitated by the use of cerium along with the cobalt and manganese catalyst.

BRIEF DESCRIPTION OF THE DRAWINGS

[0004] The following figures are exemplary embodiments wherein the like elements are numbered alike.

[0005] FIG. 1 is a process flow diagram of an embodiment of a method for oxidation of *para*-xylene to obtain terephthalic acid.

[0006] FIG. 2A is a graphical illustration of the mole percent of carbon monoxide and carbon dioxide (collectively "CO_x") formed as by-products, based on the total moles of reaction product, in Comparative Example A and Example 1; and the percent reduction in the moles of CO_x in Example 1 as compared to Comparative Example A.

[0007] FIG. 2B is a graphical illustration of the mole percent of CO_x formed as by-products, based on the total moles of reaction product, in Comparative Example B and Example

2; and the percent reduction in the moles of CO_x in Example 2 as compared to Comparative Example B.

[0008] FIG. 3 is a graphical illustration of the weight percent of C₁₀₊ hydrocarbons formed as by-products, based on the total weight of reaction product, in Comparative Examples A-B and Examples 1-2; and the percent reduction in the amount of C₁₀₊ hydrocarbons in Comparative Examples B and Examples 1-2 as compared to Comparative Example A.

[0009] The above described and other features are exemplified by the following detailed description, examples, and claims.

DETAILED DESCRIPTION

[0010] It would be desirable to provide improved methods for oxidizing dimethyl aromatic compounds to selectively produce aromatic dicarboxylic acids, particularly methods that mitigate the aforementioned disadvantages. Accordingly, disclosed herein are methods for oxidizing dimethyl aromatic compounds to obtain aromatic dicarboxylic acids. Desirably, the methods reduce the undesirable side reactions that consume the dimethyl aromatic compounds and solvent to form by-products by oxidizing dimethyl aromatic compounds in the presence of a catalyst including cobalt and manganese in a weight ratio equal to or greater than 1:1 and a co-catalyst including cerium. Previous methods for oxidizing dimethyl aromatic compounds suffered from side reactions, such as oxidation of solvents or over oxidation of the dimethyl aromatic compounds to form by-products such as carbon monoxide, carbon dioxide, or C₁₀₊ hydrocarbons (e.g., intermediates or “heavies”). These side reactions resulted in increased consumption of the dimethyl aromatic compounds and the solvent. For example, approximately 0.010 mole % more dimethyl aromatic compounds and approximately 0.016 mole % more solvent can be consumed by previous methods as compared to the methods of the present disclosure.

[0011] As used herein, the phrase “over oxidation” refers to oxidation of terephthalic acid and acetic acid to CO_x.

[0012] In the methods of the present disclosure dimethyl aromatic compounds are oxidized in the presence of a catalyst including cobalt and manganese in a weight ratio equal to or greater than 1:1, or equal to or greater than 2:1, preferably equal to or greater than 3:1, and a co-catalyst including cerium. Surprisingly, it was found that such a catalyst and co-catalyst reduces the loss of reactant and solvent, increases the selectivity for the aromatic dicarboxylic acids, reduces the amount of at least one of carbon monoxide, carbon dioxide, and C₁₀₊ hydrocarbons in the reaction product, and increases the purity of the aromatic dicarboxylic acids

as compared to previous methods for oxidizing dimethyl aromatic compounds outside the presence of such a catalyst and co-catalyst (e.g., including a weight ratio of cobalt to manganese less than 1:1 and no cerium co-catalyst).

[0013] For instance, the methods of the present disclosure can achieve at least one of: (i) a reduction in the total moles of carbon dioxide and carbon monoxide formed equal to or greater than 5 mole %, or equal to or greater than 10 mole %, preferably equal to or greater than 15 mole %, as compared to the total moles of carbon monoxide and carbon dioxide present in a reaction product obtained from a method for oxidizing a dimethyl aromatic compound outside the presence of such a catalyst and co-catalyst; (ii) a reduction in the amount of C₁₀₊ hydrocarbons formed equal to or greater than 10 weight percent (wt.%), or equal to or greater than 20 wt.%, preferably equal to or greater than 30 wt.%, as compared to the total amount of C₁₀₊ hydrocarbons present in a reaction product obtained from a method for oxidizing a dimethyl aromatic compound outside the presence of such a catalyst and co-catalyst; and (iii) an increase in the moles of aromatic dicarboxylic acid produced equal to or greater than 0.5 mole %, or equal to or greater than 1.0 mole %, preferably equal to or greater than 1.5 mole %, as compared to the moles of aromatic dicarboxylic acid present in a reaction product obtained from previous methods for oxidizing dimethyl aromatic compounds outside the presence of such a catalyst and co-catalyst.

[0014] Moreover, it was surprisingly found that the amount of catalyst could be reduced as compared to previous methods that do not use the catalyst and co-catalyst as described in the present disclosure. For instance, the present methods allow for use of lower amounts of at least one of manganese and bromine in the catalyst, while maintaining the moles of aromatic dicarboxylic acid produced per milligram of catalyst. A reduction in the amount of manganese present can be equal to or greater than 25 wt.%, or equal to or greater than 50 wt.%, or equal to or greater than 75 wt.%, as compared to the moles of manganese present in previous methods for oxidizing dimethyl aromatic compounds outside the presence of such a catalyst and co-catalyst. Desirably, a reduction in the amount of bromine present can reduce, mitigate, or avoid corrosion of the equipment used for the oxidation or allow for use of different materials of construction for the equipment. A reduction in the amount of bromine present can be equal to or greater than 25 wt.%, or equal to or greater than 50 wt.%, or equal to or greater than 75 wt.%, as compared to the moles of bromine present in previous methods for oxidizing dimethyl aromatic compounds outside the presence of such a catalyst and co-catalyst.

[0015] As noted above, a method for oxidizing a dimethyl aromatic compound can include reacting the dimethyl aromatic compound and an oxidant in the presence of a catalyst

and a co-catalyst in a solvent to produce a reaction product comprising an aromatic dicarboxylic acid.

[0016] The dimethyl aromatic compound can include at least one of xylene (e.g., least one of *para*-xylene, *meta*-xylene, and *ortho*-xylene), and 2,6-dimethylnaphthalene; preferably *para*-xylene.

[0017] To catalyze the oxidation of the dimethyl aromatic compound, a catalyst is used. The catalyst can include cobalt, manganese, and bromine. The catalyst can be unsupported and sources of cobalt, manganese, and bromine can be combined to form the catalyst as a catalyst mixture. Sources of cobalt and manganese used for the catalyst can include salts of cobalt (e.g., cobalt (II) acetate tetrahydrate) and manganese (e.g., manganese (II) acetate tetrahydrate), respectively. A bromine source can be hydrobromic acid, sodium bromide, ammonium bromide, tetrabromoethane, or a combination comprising at least one of the foregoing. Other catalyst sources can include metal bromides (e.g., MnBr_2 , CoBr_2 , etc.) and metal nitrate salts. Desirably, the bromine can be at least one of a solid or dissolved in the solvent.

[0018] Desirably, the catalyst can include a weight ratio of cobalt to manganese equal to or greater than 1:1, or equal to or greater than 2:1, preferably equal to or greater than 3:1. A total amount of cobalt and manganese can be equal to or less than 1,000 parts per million by weight (ppm), or equal to or less than 900 ppm, preferably equal to or less than 800 ppm, based on a total weight of reactant mixture including dimethyl aromatics, acetic acid and water.

[0019] Bromine can be present in an amount equal to or less than 800 ppm, or equal to or less than 400 ppm, preferably equal to or less than 200 ppm, based on a total weight of reactant mixture including dimethyl aromatics, acetic acid and water. The catalyst can include a molar ratio of bromine to (cobalt and manganese) in a range of 0.3:1 to 3:1, or 0.3:1 to 2:1, preferably 0.3:1 to 1:1.

[0020] Desirably, in various embodiments, during the reacting, a reaction mixture (e.g., comprising the dimethyl aromatic compound, the oxidant, the catalyst, the co-catalyst, and the solvent) is substantially free of ammonium acetate, *meta*-xylene, and ionic liquid comprising at least one of a bromide anion or an iodide anion; substantially free of ammonium acetate, *meta*-xylene, and ionic liquid comprising a bromide anion. As used herein, the phrase “substantially free of” allows for the presence of impurities in the dimethyl aromatic compound, the oxidant, the catalyst, the co-catalyst, and the solvent. In other words, during the reacting, no ammonium acetate, *meta*-xylene, and ionic liquid including at least one of a bromide anion and an iodide anion, is present besides trace impurities. They are not intentionally added compounds.

[0021] In addition to the catalyst, the method uses a co-catalyst. Desirably, the co-catalyst includes cerium. The cerium can be present in an amount in a range of 10 ppm to 200 ppm, or 20 ppm to 190 ppm, preferably 30 ppm to 180 ppm, based on a total weight of the dimethyl aromatic compound and the solvent.

[0022] The solvent can include at least one of: water, a C₁-C₇ aliphatic carboxylic acid, an aromatic acid, and supercritical CO₂, preferably acetic acid. The solvent can be an aqueous solution. Desirably, a weight ratio of solvent to dimethyl aromatic compound can be in a range of 15:1 to 1:1, or 10:1 to 1:1, preferably 5:1 to 1:1.

[0023] To oxidize the dimethyl aromatic compound, the method uses an oxidant. The oxidant can include hydrogen peroxide, dioxygen, ozone, an anthraquinone, a C₂₋₃₂ alkyl peroxide, a C₂₋₃₂ alkyl hydroperoxide, a C₂₋₃₂ ketone peroxide, a C₂₋₃₂ diacyl peroxide, a C₃₋₂₂ diperoxy, a ketal, a C₂₋₃₂ peroxyester, a C₂₋₃₂ peroxydicarbonate, a C₂₋₃₂ peroxy acid, a C₆₋₃₂ perbenzoic acid, a C₂₋₃₂ peracid, a periodinane, a periodate, or a combination comprising at least one of the foregoing, preferably dioxygen (e.g., in air).

[0024] Desirably, the reaction of the dimethyl aromatic compound and the oxidant can be at a temperature in a range of 170°C to 200°C, or 180°C to 200°C, or 190°C to 200°C.

[0025] The reaction of the dimethyl aromatic compound and the oxidant can be at a pressure in a range of 1 MegaPascals (mPa) to 1.8 mPa, or 1 mPa to 1.7 mPa, preferably 1 mPa to 1.6 mPa.

[0026] A residence time of the reaction of the dimethyl aromatic compound and the oxidant in a reactor can be in a range of 20 minutes to 200 minutes, or 40 minutes to 150 minutes, preferably 60 minutes to 100 minutes.

[0027] The reaction of the dimethyl aromatic compound can be carried out in any reactor capable of operating under the conditions described in the present disclosure, such as a batch reactor, a continuous, or semi-continuous reactor. The reactor can include an inlet for feeding at least one of the dimethyl aromatic compound, the solvent, the catalyst, and the co-catalyst continuously for a period of time and an outlet for removing the reaction product continuously for a period of time or at specific time(s). Desirably, the reacting of the dimethyl aromatic compound and the oxidant can be in a continuous stirred-tank reactor.

[0028] The aromatic dicarboxylic acid can be present in the reaction product in an amount equal to or greater than 70 wt.%, or equal to or greater than 90 wt.%, preferably equal to or greater than 92 wt.%, more preferably equal to or greater than 94 wt.%, based on a total weight of solids in the reaction product, for example, measured by High Pressure Liquid Chromatography (HPLC) at ambient temperature.

[0029] Desirably, the present methods result in C₁₀₊ hydrocarbons being present in the reaction product in an amount equal to or less than 1.5 wt.%, or equal to or less than 1.0 wt.%, preferably equal to or less than 0.5 wt.%, based on a total weight of solids in the reaction product, for example, measured by HPLC at ambient temperature. The catalyst and co-catalyst as described in the present disclosure can contribute to preventing formation of C₁₀₊ hydrocarbons. As used herein “C₁₀₊ hydrocarbon” refers to a hydrocarbon including 10 or more carbon atoms. Any number of C₁₀₊ hydrocarbons can be present in a reaction product, such as at least five different C₁₀₊ hydrocarbons, or at least fifteen different C₁₀₊ hydrocarbons, or at least twenty different C₁₀₊ hydrocarbons.

[0030] The method can further include separating the solvent, the catalyst, and the co-catalyst from the reaction product, and recycling the solvent, the catalyst, and the co-catalyst to the step of reacting the dimethyl aromatic compound. For example, the step of separating can include crystallizing the aromatic dicarboxylic acid to obtain an aromatic dicarboxylic acid crystal. The aromatic dicarboxylic acid crystal can then be separated from the solvent, the catalyst, and the co-catalyst. For instance, the catalyst and the co-catalyst can be in solution in the solvent and the separating can be via filtration or any other solid-liquid separation method. The step of crystallizing the aromatic dicarboxylic acid can be in at least one stage, or at least two stages, preferably at least three stages.

[0031] The method can further include reacting the reaction product and hydrogen in the presence of a hydrogenation catalyst. For example, the method can include reacting the aromatic dicarboxylic acid crystals and hydrogen in the presence of a hydrogenation catalyst to purify the aromatic dicarboxylic acid crystals. The hydrogenation catalyst can include palladium, ruthenium, rhodium, osmium, iridium, platinum, or a combination comprising at least one of the foregoing. The hydrogenation catalyst can be on a support such as silicon dioxide, diatomaceous earth, titanium dioxide, carbon, thorium oxide, zirconium oxide, silicic carbide, aluminum oxides, or a combination comprising at least one of the foregoing. Desirably, the hydrogenation catalyst can be palladium on a carbon support. Thus, the purity of the aromatic dicarboxylic acid crystals and the yield of the aromatic dicarboxylic acid can be improved.

[0032] A reaction mixture for the oxidation of a dimethyl aromatic compound by the above-described methods can include the dimethyl aromatic compound, the oxidant, the catalyst, the co-catalyst, water, and the solvent.

[0033] A reaction product can be produced by the above-described methods, or using the above-described reaction mixture.

[0034] A more complete understanding of the components, processes, and apparatuses disclosed herein can be obtained by reference to the accompanying drawings. These figures (also referred to herein as “FIG.”) are merely schematic representations based on convenience and the ease of demonstrating the present disclosure, and are, therefore, not intended to indicate relative size and dimensions of the devices or components thereof and/or to define or limit the scope of the exemplary embodiments. Although specific terms are used in the following description for the sake of clarity, these terms are intended to refer only to the particular structure of the embodiments selected for illustration in the drawings, and are not intended to define or limit the scope of the disclosure. In the drawings and the following description below, it is to be understood that like numeric designations refer to components of like function.

[0035] As illustrated in FIG. 1, a terephthalic acid production facility can include reactor 10. Reaction mixture 6 including *para*-xylene, solvent, catalyst, and co-catalyst can be fed into reactor 10. An oxidant 8 also can be fed into reactor 10. Upon reaction of the *para*-xylene and oxidant 8, reaction product 12 including terephthalic acid can be removed from reactor 10. Reaction product 12 can be fed into first crystallizer 20 to produce first crystallized stream 22. First crystallized stream 22 can be fed into second crystallizer 30 to produce second crystallized stream 32. Second crystallized stream 32 can be fed into third crystallizer 40 to produce third crystallized stream 42 including crystallized terephthalic acid. Solvent, catalyst, and co-catalyst stream 44 can be separated from third crystallized stream 42 and recycled to reaction mixture 6.

[0036] This disclosure is further illustrated by the follow examples, which are non-limiting.

EXAMPLES

[0037] The following components listed in Table 1 were used in the examples. Unless specifically indicated otherwise, the amount of each component is in weight percent in the following examples, based on the total weight of the composition.

Table 1	
Acronym	Description
Co	Cobalt (II) acetate tetrahydrate
Mn	Manganese (II) acetate tetrahydrate
Br	Hydrobromic acid (48 wt.% aqueous solution)
Cerium	Cerium nitrate
PX	<i>para</i> -xylene
AcOH	Acetic acid including 8 wt.% water

Examples 1-2 and Comparative Examples A-B

[0038] In Examples 1-2 and Comparative Examples A-B, *para*-xylene was oxidized in the presence of different compositions of catalyst and co-catalyst in acetic acid. The oxidation reactions were carried out in a semi continuous flow stirred-tank reactor in the presence of air. In Examples 1-2 cerium was used in an amount of 50 ppm, based on the total weight of the *para*-xylene, water and the acetic acid. In Comparative Examples A-B, cerium co-catalyst was not used. In Example 2 and Comparative Example B, a smaller amount of catalyst was included than in Example 1 and Comparative Example A. The amounts of catalyst, co-catalyst, and solvent used, the weight ratio of solvent to *para*-xylene, and the reaction conditions in the Examples and Comparative Examples are summarized in Table 2.

Table 2								
	Co (ppm)	Mn (ppm)	Ce (ppm)	Br (ppm)	AcOH (grams)	AcOH/PX	Temperature (°C)	Pressure (mPa)
Comp. Ex. A	400	400	0	730	600	5	170	1.3
Ex. 1	400	400	50	730	600	5	170	1.3
Comp. Ex. B	300	100	0	166	600	5	190	1.3
Ex. 2	300	100	50	166	600	5	190	1.3

[0039] As shown in FIG. 2A, a reduction in the total amount of carbon monoxide and carbon dioxide (CO_x) produced of about 10 mole % was seen in Example 1 as compared to Comparative Example A. As shown in FIG. 2B, a reduction in the total amount of carbon monoxide and carbon dioxide (CO_x) produced of about 8 mole % was seen in Example 2 as compared to Comparative Example B. Thus, the catalyst and cerium reduced the oxidation of the solvent and the product terephthalic acid into carbon monoxide and carbon dioxide. Also, the presence of the catalyst and cerium during the oxidation reaction did not significantly affect the terephthalic acid selectivity, which can be measured by High Pressure Liquid Chromatography (HPLC) and calculated based only on solid products, i.e., not gaseous products. For example, the methods of the present disclosure can achieve a purity of terephthalic acid of approximately 96.5 wt. %.

[0040] As seen in FIG. 3, a reduction in the amount of catalyst and use of the co-catalyst reduced the formation of C₁₀₊ hydrocarbons. This decrease in the production of C₁₀₊ hydrocarbons reduces the *para*-xylene specific consumption.

[0041] In Examples 3-27, *para*-xylene was oxidized in the presence of different compositions of catalyst and co-catalyst in acetic acid. The oxidation reactions were carried out in a semi continuous flow stirred-tank reactor in the presence of air. The amounts of the metals in the catalyst based on the total weight of the *para*-xylene, water and the acetic acid. The reaction for Examples 3-10 were carried out at a temperature of 170°C, and for Examples 11-26 were carried out at 190°C. All of the examples were carried out at a pressure of 1.3 mPa.

[0042] The composition of the Co and Mn tested at two levels Co:Mn of 400:400 and Co:Mn of 300:100, but Br was varied from 166 to 730 ppm. The results show the performance of the co-catalyst compared with the performance of the reaction without a co-catalyst (Nil).

[0043] Initial experiments are carried out at temperature 170°C using 50 ppm of each Zr, Pd, Mo, Ce, or Ag as co-catalyst on the p-xylene oxidation process. The results exhibited a decrease in the amount of CO_x formation with the use of Ce as co-catalyst. Among the all metals Zr presented lesser amount of 4-CBA, but it has presented higher amount of CO_x. 4-CBA, which is an unwanted impurity, is around 4 wt.% for the reactions carried at 170°C. It was found that a lower amount of 4-CBA was produced for the reactions carried at 190°C. Therefore, higher reaction temperatures are beneficial in reducing 4-CBA production.

[0044] As reported in Table 3, 50 ppm of Fe, Ag, Ce and Cu tested as co-metals along with the Co-Mn-Br at 190°C. Among the different metals studied, the experiment conducted using copper as a co-catalyst showed incomplete oxidation, i.e., the product distribution analysis proves more intermediate products such as p-toluic acid and 4-CBA than the desired final product, terephthalic acid (TPA).

[0045] Fe and Ce are found to be promising candidates as co-catalyst for the p-xylene oxidation in terms of lesser CO_x formation, particularly at a 190°C reaction temperature. When using these materials as a co-catalyst:

- Fe exhibited decreased CO_x and heavies formation but 4-CBA formation is higher.
- Ce exhibited reduced CO_x and 4-CBA formation but heavies formation is higher.

[0046] The role of co-catalyst at reduced amounts of Co, Mn, and Br was evaluated using Fe, Ce, Zr, and Ru. Also studied were the combination of Fe+Ce and Fe+Zr on the p-xylene oxidation product distribution, at reduced amounts of Co-Mn-Br of 300-100-332 respectively. All the results proved that presence of Fe and Ce were able to reduce CO_x and heavies formation. 4-CBA formation is reduced with the use of Zr as co-catalyst, but the CO_x and heavies formation was higher.

Table 3

Ex.	Catalyst composition				Product distribution					
	Co (ppm)	Mn (ppm)	Co-catalyst (ppm)	Br (ppm)	COx (mol. %)	TPA (wt. %)	4-CBA (wt. %)	p-Toluic acid (wt. %)	Heavies (wt. %)	
3	400	400	--	730	0.187	92.36	4.32	0.96	2.36	
4	400	400	Zr (50)	730	0.1948	92.51	3.84	1.01	2.64	
5	400	400	Pd (50)	730	0.1812	91.98	4.3	0.98	2.73	
6	400	400	Mo (50)	730	0.199	92.49	4.58	1.03	1.91	
7	400	400	Ce (50)	730	0.1668	92.16	4.91	1.22	1.71	
8	400	400	Ce (100)	730	0.1671	92.11	4.82	1.23	1.84	
9	400	400	Ag (50)	730	0.1839	92.33	4.52	1.04	2.11	
10	400	400	Zr (50), Ce (50)	730	0.1997	92.85	4.13	1	2.01	
11	400	400	--	730	0.2091	94.85	1.37	0.35	3.4	
12	400	400	Fe (50)	730	0.0937	96.62	2.6	0.39	0.38	
13	400	400	Ag (100)	730	0.1849	94.95	1.26	0.34	3.43	
14	400	400	Ce (50)	730	0.1742	95.06	1.27	0.35	3.31	
15*	400	400	Cu (50)	730	0.0624	64.86	12.81	33.26	0.49	
16	300	100	--	359	0.1771	96.22	1.73	0.3	1.74	
17	300	100	--	166	0.1759	96.83	1.74	0.3	1.13	
18	300	100	Fe (50)	332	0.1304	97.38	2.03	0.37	0.23	
19	300	100	Ce (50)	166	0.1612	97.03	1.87	0.35	0.75	
20	300	100	Fe (50) + Ce (50)	332	0.1277	97.5	1.92	0.33	0.25	
21	300	100	Fe (50) + Zr (50)	332	0.1620	97.18	2.06	0.4	0.37	
22	300	100	Fe (50) + Zr (25)	332	0.1565	97.41	1.86	0.32	0.41	
23	300	100	Zr (50)	332	0.2169	96.69	1.64	0.33	1.34	
24	300	100	Ru (50)	332	0.1862	--	--	--	--	
25	300	100	Fe (25)	332	0.1386	--	--	--	--	
26	300	100	Fe (50)	332	0.1333	97.45	1.94	0.34	0.27	

*Not to be limited by theory, the reaction was incomplete, it is believed to be due to the presence of Cu.

[0047] Hence, the presence of small amounts of co-catalysts in Co-Mn-Br catalyst exhibited wide ranges of performances. Specific consumption improvement and impurity reduction is clearly demonstrated by the incorporation of co-catalyst in Co-Mn-Br catalytic system for paraxylene oxidation. This study also proves that the reaction temperature has more influence on TPA quality and on the heavies formation. Cu as a co-catalyst showed inhibiting role in paraxylene oxidation process. Among the various co-catalysts tested, Fe and Ce showed promising performance by increasing product quality.

[0048] As shown in the Examples, the present methods using a catalyst including cobalt and manganese at a weight ratio equal to or greater than 1:1, or equal to or greater than 2:1, preferably equal to or greater than 3:1 and a co-catalyst including cerium can reduce the amount of reactant and solvent used, increase the selectivity for the aromatic dicarboxylic acids, reduce the amount of at least one of carbon monoxide, carbon dioxide, and C₁₀₊ hydrocarbons in the reaction product, and increase the purity of the aromatic dicarboxylic acids as compared to previous methods for oxidizing dimethyl aromatic compounds outside the presence of such a catalyst and co-catalyst. Moreover, the amount of catalyst, preferably the amount of bromine, can be reduced as compared to such previous methods.

[0049] This disclosure further encompasses the following aspects.

[0050] Aspect 1. A method for oxidizing a dimethyl aromatic compound comprising: reacting the dimethyl aromatic compound and an oxidant in the presence of a catalyst and a co-catalyst in a solvent to produce a reaction product comprising an aromatic dicarboxylic acid, wherein the catalyst comprises cobalt, manganese, and bromine, and wherein a weight ratio of cobalt to manganese is equal to or greater than 1:1, or equal to or greater than 2:1, preferably equal to or greater than 3:1, and wherein the co-catalyst comprises at least one of cerium or iron, preferably comprises cerium, and wherein the co-catalyst is present in an amount in a range of 10 ppm to 200 ppm, or 20 ppm to 190 ppm, preferably 30 ppm to 180 ppm, based on a total weight of the dimethyl aromatic compound and the solvent, and wherein the aromatic dicarboxylic acid is present in the reaction product in an amount equal to or greater than 70 wt.%, or equal to or greater than 90 wt.%, preferably equal to or greater than 92 wt.%, more preferably equal to or greater than 94 wt.%, based on a total weight of solids in the reaction product.

[0051] Aspect 2. The method of Aspect 1, wherein the dimethyl aromatic compound comprises *para*-xylene, *meta*-xylene, *ortho*-xylene, 2,6-dimethylnaphthalene, or a combination comprising at least one of the foregoing, preferably *para*-xylene.

[0052] Aspect 3. The method of any one or more of the preceding aspects, wherein a total amount of cobalt and manganese is equal to or less than 1,000 ppm, or equal to or less than 900 ppm, preferably equal to or less than 800 ppm, based on the total weight of the dimethyl aromatic compound and the solvent.

[0053] Aspect 4. The method of any one or more of the preceding aspects, wherein bromine is present in an amount equal to or less than 800 ppm, or equal to or less than 600 ppm, preferably equal to or less than 400 ppm, based on the total weight of the dimethyl aromatic compound and the solvent.

[0054] Aspect 5. The method of any one or more of the preceding aspects, wherein the bromine comprises hydrobromic acid.

[0055] Aspect 6. The method of any one or more of the preceding aspects, wherein the total moles of carbon monoxide and carbon dioxide present in the reaction product is reduced by equal to or greater than 5 mole %, or equal to or greater than 10 mole %, preferably equal to or greater than 15 moles %, as compared to the total moles of carbon monoxide and carbon dioxide present in a reaction product obtained from a method for oxidizing a dimethyl aromatic compound outside the presence of the catalyst and the co-catalyst.

[0056] Aspect 7. The method of any one or more of the preceding aspects, wherein C₁₀₊ hydrocarbons are present in the reaction product in an amount equal to or less than 1.5 wt.%, or equal to or less than 1.0 wt.%, preferably equal to or less than 0.5 wt.%, based on the total weight of solids in the reaction product.

[0057] Aspect 8. The method of any one or more of the preceding aspects, wherein the oxidant comprises air.

[0058] Aspect 9. The method of any one or more of the preceding aspects, wherein the solvent comprises at least one of water and a C₁-C₇ aliphatic carboxylic acid, preferably acetic acid.

[0059] Aspect 10. The method of any one or more of the preceding aspects, wherein the weight ratio of solvent to dimethyl aromatic compound is in a range of 15:1 to 1:1, or 10:1 to 1:1, preferably 5:1 to 1:1.

[0060] Aspect 11. The method of any one or more of the preceding aspects, wherein a molar ratio of bromine to cobalt and manganese is in a range of 0.3:1 to 3:1, or 0.3:1 to 2:1, preferably 0.3:1 to 1:1.

[0061] Aspect 12. The method of any one or more of the preceding aspects, wherein the reacting is at a temperature in a range of 170°C to 200°C, or 180°C to 200°C, preferably 190°C to 200°C.

[0062] Aspect 13. The method of any one or more of the preceding aspects, wherein the reacting is at a pressure in a range of 1 MegaPascals to 1.8 MegaPascals, or 1 MegaPascals to 1.7 MegaPascals, preferably 1 MegaPascals to 1.6 MegaPascals.

[0063] Aspect 14. The method of any one or more of the preceding aspects, wherein the reacting is in a continuous stirred-tank reactor and a residence time is in a range of 20 minutes to 200 minutes, or 40 minutes to 150 minutes, preferably 60 minutes to 100 minutes.

[0064] Aspect 15. The method of any one or more of the preceding aspects, wherein during the reacting, a reaction mixture comprising the dimethyl aromatic compound, the oxidant, the catalyst, the co-catalyst, and the solvent are substantially free of ammonium acetate, *meta*-xylene, and ionic liquid comprising at least one of a bromide anion or an iodide anion; preferably the reaction mixture is substantially free of ammonium acetate, *meta*-xylene, and ionic liquid comprising a bromide anion; more preferably, no ammonium acetate, *meta*-xylene, and ionic liquid comprising a bromide anion.

[0065] Aspect 16. The method of any one or more of the preceding aspects, further comprising crystallizing the reaction product.

[0066] Aspect 17. The method of any one or more of the preceding aspects, further comprising separating the solvent, the catalyst, and the co-catalyst from the reaction product, and recycling the solvent, the catalyst, and the co-catalyst to the step of reacting.

[0067] Aspect 18. The method of any one or more of the preceding aspects, further comprising reacting the dimethyl aromatic compound and hydrogen in the presence of a hydrogenation catalyst.

[0068] Aspect 19. The method of any one or more of the preceding aspects, wherein the reaction mixture (comprising the dimethyl aromatic compound, the oxidant, the catalyst, the co-catalyst, and the solvent) comprises a total amount of cobalt and manganese of equal to or less than 1,000 ppm, preferably equal to or less than 900 ppm, more preferably equal to or less than 800 ppm, based on a total weight of the reactant mixture.

[0069] Aspect 20. The method of any one or more of the preceding aspects, wherein the catalyst comprises a molar ratio of bromine to (cobalt and manganese) in a range of 0.3:1 to 3:1, preferably 0.3:1 to 2:1, more preferably 0.3:1 to 1:1.

[0070] Aspect 21. The method of any one or more of the preceding aspects, wherein the catalyst is free of Cu.

[0071] Aspect 22. A reaction mixture for the oxidation of dimethyl aromatic compound by the method of any one or more of the preceding aspects, wherein the reaction mixture

comprises: the dimethyl aromatic compound; the oxidant; the catalyst; the co-catalyst; and the solvent.

[0072] Aspect 23. A reaction product produced by the method of any one or more of Aspects 1-21, or using the reaction mixture of Aspect 22.

[0073] Aspect 24. A catalyst system for the oxidation of a dimethyl aromatic compound, the catalyst system comprising: a catalyst comprising cobalt, manganese, and bromine, wherein a weight ratio of cobalt to manganese is equal to or greater than 1:1, or equal to or greater than 2:1, preferably equal to or greater than 3:1; and a co-catalyst comprising at least one of cerium or iron, preferably comprises cerium.

[0074] Aspect 25. A reaction mixture for the oxidation of a dimethyl aromatic compound, the reaction mixture comprising: the catalyst system of Aspect 24; the dimethyl aromatic compound; an oxidant; and a solvent, wherein the co-catalyst is present in an amount in a range of 10 ppm to 200 ppm, or 20 ppm to 190 ppm, preferably 30 ppm to 180 ppm, based on a total weight of the dimethyl aromatic compound and the solvent, wherein a total amount of cobalt and manganese is equal to or less than 1,000 ppm, or equal to or less than 900 ppm, preferably equal to or less than 800 ppm, based on the total weight of the dimethyl aromatic compound and the solvent, wherein bromine is present in an amount equal to or less than 800 ppm, or equal to or less than 600 ppm, preferably equal to or less than 400 ppm, based on the total weight of the dimethyl aromatic compound and the solvent, and wherein a molar ratio of bromine to cobalt and manganese is in a range of 0.3:1 to 3:1, or 0.3:1 to 2:1, preferably 0.3:1 to 1:1.

[0075] The compositions, methods, and articles can alternatively comprise, consist of, or consist essentially of, any appropriate components or steps herein disclosed. The compositions, methods, and articles can additionally, or alternatively, be formulated so as to be devoid, or substantially free, of any steps, components, materials, ingredients, adjuvants, or species that are otherwise not necessary to the achievement of the function or objectives of the compositions, methods, and articles.

[0076] The singular forms “a,” “an,” and “the” include plural referents unless the context clearly dictates otherwise. “Or” means “and/or” unless clearly indicated otherwise by context. The terms “first,” “second,” and the like, “primary,” “secondary,” and the like, as used herein do not denote any order, quantity, or importance, but rather are used to distinguish one element from another.

[0077] The endpoints of all ranges directed to the same component or property are inclusive and independently combinable (e.g., ranges of “less than or equal to 25 wt%, or 5 wt%

to 20 wt%,” is inclusive of the endpoints and all intermediate values of the ranges of “5 wt% to 25 wt%,” etc.). Disclosure of a narrower range or more specific group in addition to a broader range is not a disclaimer of the broader range or larger group.

[0078] The suffix “(s)” is intended to include both the singular and the plural of the term that it modifies, thereby including at least one of that term (e.g., the colorant(s) includes at least one colorants). “Optional” or “optionally” means that the subsequently described event or circumstance can or cannot occur, and that the description includes instances where the event occurs and instances where it does not. Unless defined otherwise, technical and scientific terms used herein have the same meaning as is commonly understood by one of skill in the art to which this disclosure belongs. A “combination” is inclusive of blends, mixtures, alloys, reaction products, and the like.

[0079] While typical embodiments have been set forth for the purpose of illustration, the foregoing descriptions should not be deemed to be a limitation on the scope herein. Accordingly, various modifications, adaptations, and alternatives can occur to one skilled in the art without departing from the spirit and scope herein.

WHAT IS CLAIMED IS:

CLAIMS

1. A method for oxidizing a dimethyl aromatic compound comprising:
reacting the dimethyl aromatic compound and an oxidant in the presence of a catalyst and a co-catalyst in a solvent to produce a reaction product comprising an aromatic dicarboxylic acid,
wherein the catalyst comprises cobalt, manganese, and bromine, and
wherein a weight ratio of cobalt to manganese is equal to or greater than 1:1, or equal to or greater than 2:1, preferably equal to or greater than 3:1, and
wherein the co-catalyst comprises at least one of cerium or iron, preferably comprises cerium, and
wherein the co-catalyst is present in an amount in a range of 10 ppm to 200 ppm, or 20 ppm to 190 ppm, preferably 30 ppm to 180 ppm, based on a total weight of the dimethyl aromatic compound and the solvent, and
preferably wherein the aromatic dicarboxylic acid is present in the reaction product in an amount equal to or greater than 70 wt.%, or equal to or greater than 90 wt.%, preferably equal to or greater than 92 wt.%, more preferably equal to or greater than 94 wt.%, based on a total weight of solids in the reaction product.
2. The method of Claim 1, wherein the dimethyl aromatic compound comprises *para*-xylene, *meta*-xylene, *ortho*-xylene, 2,6-dimethylnaphthalene, or a combination comprising at least one of the foregoing, preferably *para*-xylene.
3. The method of any one or more of the preceding claims, wherein a total amount of cobalt and manganese is equal to or less than 1,000 ppm, or equal to or less than 900 ppm, preferably equal to or less than 800 ppm, based on the total weight of the dimethyl aromatic compound and the solvent; and/or wherein bromine is present in an amount equal to or less than 800 ppm, or equal to or less than 600 ppm, preferably equal to or less than 400 ppm, based on the total weight of the dimethyl aromatic compound and the solvent.
4. The method of any one or more of the preceding claims, wherein the co-catalyst comprises cerium, preferably wherein the co-catalyst is cerium.

5. The method of any one or more of the preceding claims, wherein the bromine comprises hydrobromic acid.
6. The method of any one or more of the preceding claims, wherein the total moles of carbon monoxide and carbon dioxide present in the reaction product is reduced by equal to or greater than 5 mole %, or equal to or greater than 10 mole %, preferably equal to or greater than 15 moles %, as compared to the total moles of carbon monoxide and carbon dioxide present in a reaction product obtained from a method for oxidizing a dimethyl aromatic compound outside the presence of the catalyst and the co-catalyst.
7. The method of any one or more of the preceding claims, wherein C₁₀₊ hydrocarbons are present in the reaction product in an amount equal to or less than 1.5 wt.%, or equal to or less than 1.0 wt.%, preferably equal to or less than 0.5 wt.%, based on the total weight of solids in the reaction product.
8. The method of any one or more of the preceding claims, wherein the catalyst is free of copper.
9. The method of any one or more of the preceding claims, wherein the solvent comprises at least one of water and a C₁-C₇ aliphatic carboxylic acid, preferably acetic acid.
10. The method of any one or more of the preceding claims, wherein the weight ratio of solvent to dimethyl aromatic compound is in a range of 15:1 to 1:1, or 10:1 to 1:1, preferably 5:1 to 1:1.
11. The method of any one or more of the preceding claims, wherein a molar ratio of bromine to cobalt and manganese is in a range of 0.3:1 to 3:1, or 0.3:1 to 2:1, preferably 0.3:1 to 1:1.
12. The method of any one or more of the preceding claims, wherein the reacting is at a temperature in a range of 170°C to 200°C, or 180°C to 200°C, preferably 190°C to 200°C.
13. The method of any one or more of the preceding claims, wherein the reacting is at a pressure in a range of 1 MegaPascals to 1.8 MegaPascals, or 1 MegaPascals to 1.7 MegaPascals, preferably 1 MegaPascals to 1.6 MegaPascals.

14. The method of any one or more of the preceding claims, wherein the reacting is in a continuous stirred-tank reactor and a residence time is in a range of 20 minutes to 200 minutes, or 40 minutes to 150 minutes, preferably 60 minutes to 100 minutes.

15. The method of any one or more of the preceding claims, wherein during the reacting, a reaction mixture comprising the dimethyl aromatic compound, the oxidant, the catalyst, the co-catalyst, and the solvent is substantially free of ammonium acetate, *meta*-xylene, and ionic liquid comprising a bromide anion and an iodide anion.

16. The method of any one or more of the preceding claims, further comprising crystallizing the reaction product.

17. The method of any one or more of the preceding claims, further comprising separating the solvent, the catalyst, and the co-catalyst from the reaction product, and recycling the solvent, the catalyst, and the co-catalyst to the step of reacting.

18. The method of any one or more of the preceding claims, further comprising reacting the dimethyl aromatic compound and hydrogen in the presence of a hydrogenation catalyst.

19. A catalyst system for the oxidation of a dimethyl aromatic compound, the catalyst system comprising:

a catalyst comprising cobalt, manganese, and bromine, wherein a weight ratio of cobalt to manganese is equal to or greater than 1:1, or equal to or greater than 2:1, preferably equal to or greater than 3:1; and

a co-catalyst comprising at least one of cerium or iron, preferably comprises cerium.

20. A reaction mixture for the oxidation of a dimethyl aromatic compound, the reaction mixture comprising:

- the catalyst system of Claim 19;
- the dimethyl aromatic compound;
- an oxidant; and
- a solvent;

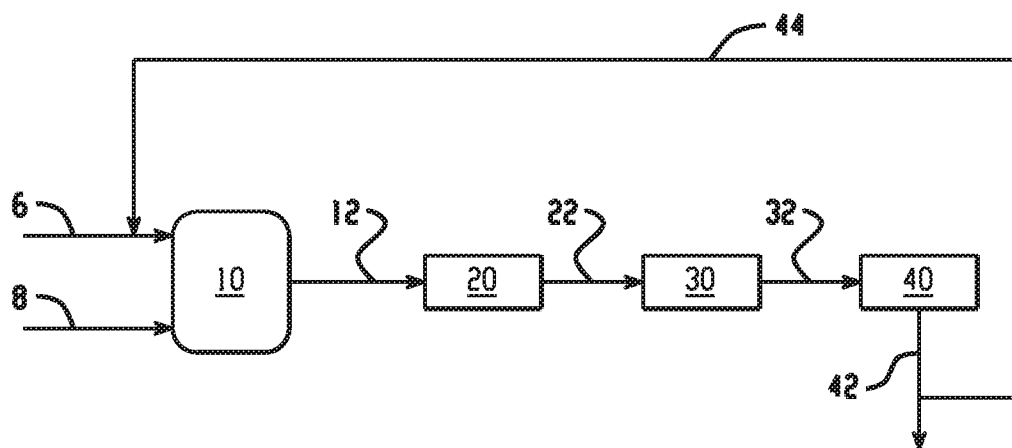
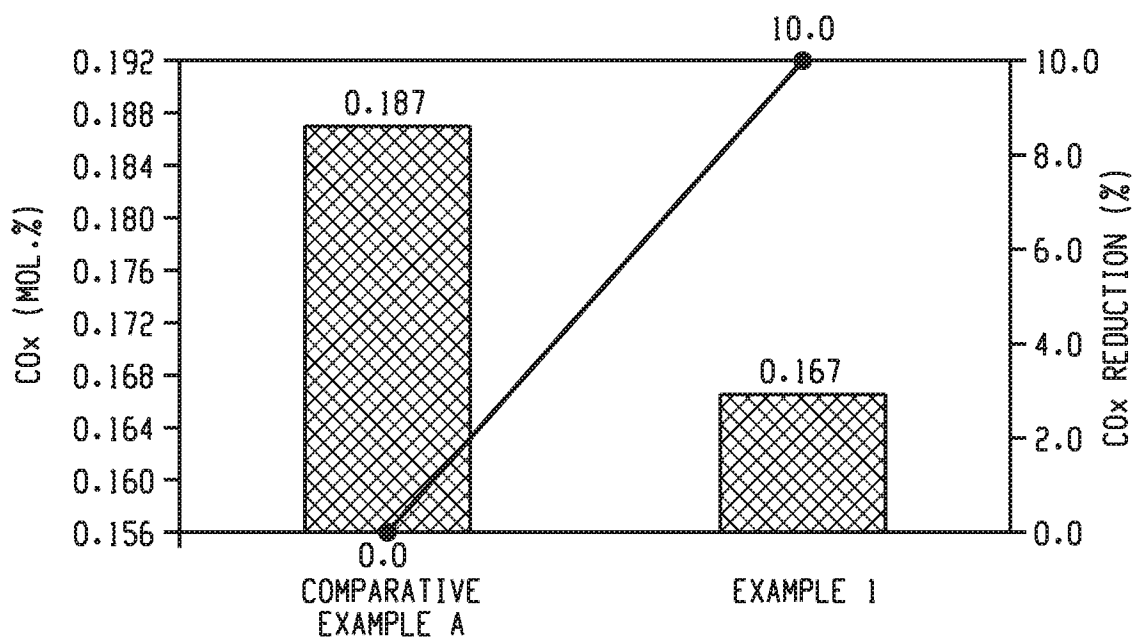
wherein the co-catalyst is present in an amount in a range of 10 ppm to 200 ppm, or 20 ppm to 190 ppm, preferably 30 ppm to 180 ppm, based on a total weight of the dimethyl aromatic compound and the solvent;

wherein a total amount of cobalt and manganese is equal to or less than 1,000 ppm, or equal to or less than 900 ppm, preferably equal to or less than 800 ppm, based on the total weight of the dimethyl aromatic compound and the solvent;

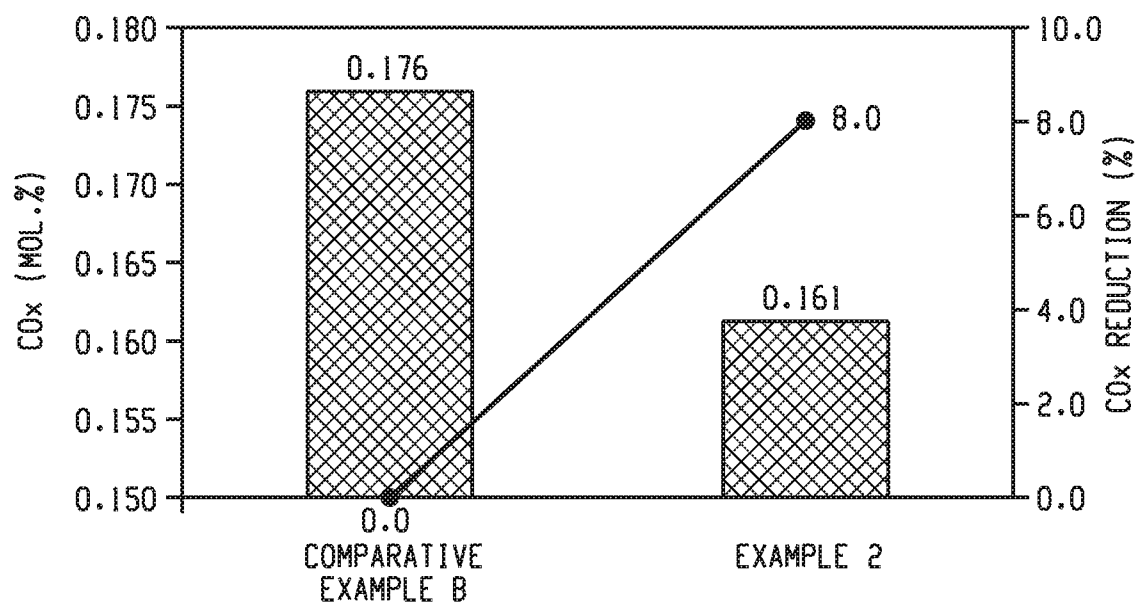
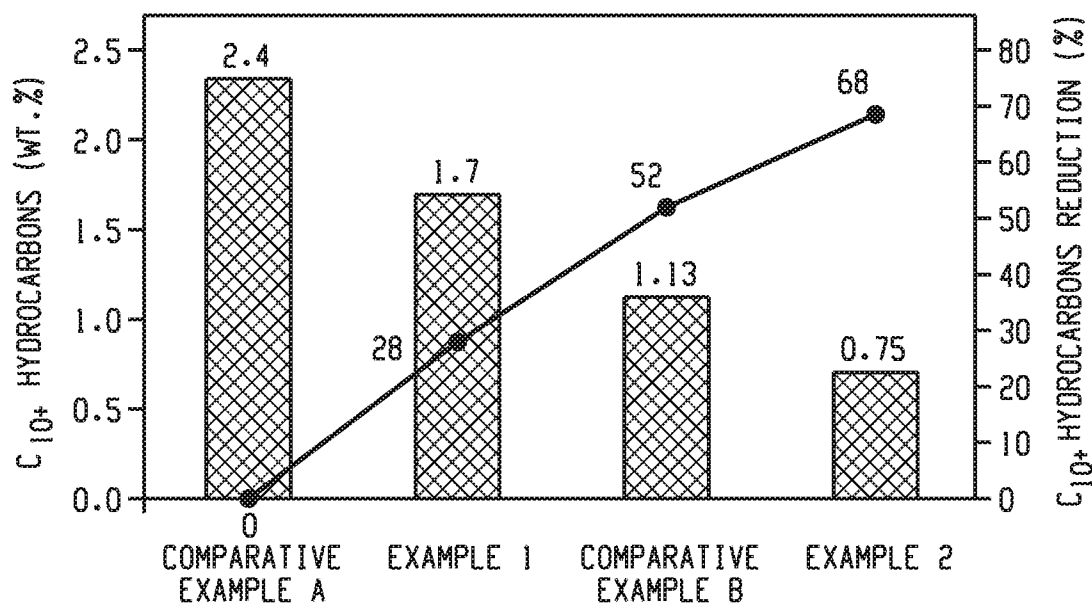
wherein bromine is present in an amount equal to or less than 800 ppm, or equal to or less than 600 ppm, preferably equal to or less than 400 ppm, based on the total weight of the dimethyl aromatic compound and the solvent; and

wherein a molar ratio of bromine to cobalt and manganese is in a range of 0.3:1 to 3:1, or 0.3:1 to 2:1, preferably 0.3:1 to 1:1.

1/2

*Fig. 1**Fig. 2A*

2/2

*Fig. 2B**Fig. 3*

INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2019/061047

A. CLASSIFICATION OF SUBJECT MATTER INV. B01J27/08 B01J27/128 C07C51/265 C07C63/26 C07C63/16 C07C63/24 C07C63/38 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) B01J C07C Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) EPO-Internal											
C. DOCUMENTS CONSIDERED TO BE RELEVANT <table border="1" style="width: 100%; border-collapse: collapse;"> <thead> <tr> <th style="width: 10%;">Category*</th> <th style="width: 70%;">Citation of document, with indication, where appropriate, of the relevant passages</th> <th style="width: 20%;">Relevant to claim No.</th> </tr> </thead> <tbody> <tr> <td style="text-align: center; vertical-align: top;">X</td> <td style="vertical-align: top;"> US 5 453 538 A (BROEKER JEFFREY L [US] ET AL) 26 September 1995 (1995-09-26) cited in the application abstract examples table 1 claims 1-14 figures 1-3 column 2, lines 25-37 column 3, lines 12-37 column 6, lines 45-48 </td> <td style="text-align: center; vertical-align: top;">1-20</td> </tr> <tr> <td style="text-align: center; vertical-align: top;">A</td> <td style="vertical-align: top;"> ----- US 2015/087859 A1 (LANGE DAVID MILTON [US] ET AL) 26 March 2015 (2015-03-26) abstract paragraphs [0031], [0034], [0039] claims 1-25 ----- </td> <td style="text-align: center; vertical-align: top;">1-20</td> </tr> </tbody> </table>			Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.	X	US 5 453 538 A (BROEKER JEFFREY L [US] ET AL) 26 September 1995 (1995-09-26) cited in the application abstract examples table 1 claims 1-14 figures 1-3 column 2, lines 25-37 column 3, lines 12-37 column 6, lines 45-48	1-20	A	----- US 2015/087859 A1 (LANGE DAVID MILTON [US] ET AL) 26 March 2015 (2015-03-26) abstract paragraphs [0031], [0034], [0039] claims 1-25 -----	1-20
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.									
X	US 5 453 538 A (BROEKER JEFFREY L [US] ET AL) 26 September 1995 (1995-09-26) cited in the application abstract examples table 1 claims 1-14 figures 1-3 column 2, lines 25-37 column 3, lines 12-37 column 6, lines 45-48	1-20									
A	----- US 2015/087859 A1 (LANGE DAVID MILTON [US] ET AL) 26 March 2015 (2015-03-26) abstract paragraphs [0031], [0034], [0039] claims 1-25 -----	1-20									
☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.											
* Special categories of cited documents : "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family											
Date of the actual completion of the international search 27 March 2020	Date of mailing of the international search report 08/04/2020										
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Delanghe, Patrick										

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/IB2019/061047

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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