



(43) International Publication Date
30 September 2010 (30.09.2010)

(10) International Publication Number
WO 2010/111288 A2

- (51) International Patent Classification:
C07C 51/255 (2006.01) B01J 8/00 (2006.01)
C07C 63/00 (2006.01) B01J 12/00 (2006.01)
B01J 19/26 (2006.01)
- (21) International Application Number:
PCT/US2010/028343
- (22) International Filing Date:
23 March 2010 (23.03.2010)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:
61/162,406 23 March 2009 (23.03.2009) US
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- (81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.
- (84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (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, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

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(54) Title: SPRAY PROCESS FOR SELECTIVE OXIDATION

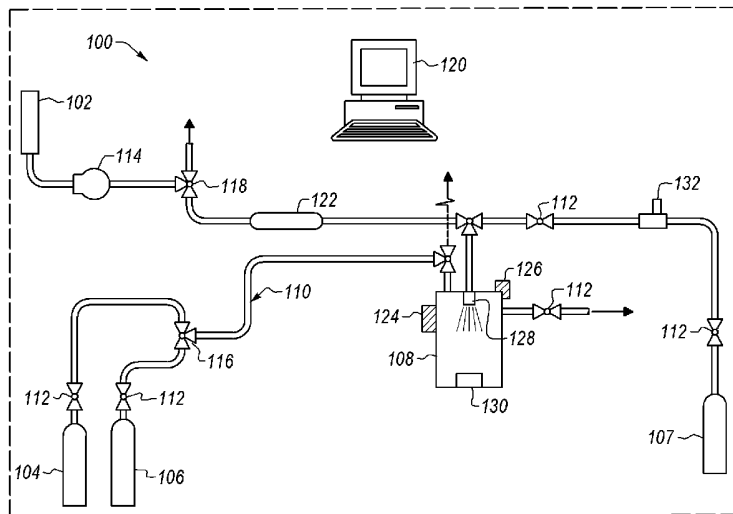


Fig. 1

(57) Abstract: Oxidation process can include: introducing small droplets of liquid reaction mixture having oxidizable reactant, catalyst, and solvent into a reaction zone containing oxygen and diluent gas; and oxidizing the reactant with the oxygen at a suitable reaction temperature and a suitable reaction pressure to produce an oxidized product. The liquid reaction mixture can have an aromatic feedstock having an oxidizable substituent as the oxidizable reactant. The oxidized product can include an aromatic compound having at least one carboxylic acid. For example, the aromatic feedstock can include a benzene ring having at least one oxidizable alkyl substituent, furan hetero-ring having at least one oxidizable alkyl substituent, a naphthalene poly-ring having at least one oxidizable alkyl substituent, derivatives thereof, and mixtures thereof.

WO 2010/111288 A2



Published:

— *without international search report and to be republished upon receipt of that report (Rule 48.2(g))*

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SPRAY PROCESS FOR SELECTIVE OXIDATION**CROSS-REFERENCE**

This patent application claims the benefit of U.S. provisional application 61/162,406, filed on March 23, 2009, entitled "Spray Process For Selective Oxidation," which provisional application is incorporated herein by specific reference in its entirety.

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This invention was made with government support under EEC-0310689 awarded by the National Science Foundation. The government has certain rights in the invention.

BACKGROUND OF THE INVENTION

Oxidation processes are common in industrial processes for preparing various types of substances. Selectivity towards and purity of the desired product, inherent safety and minimization of waste & environmental emissions are constant challenges that industrial oxidation processes face. As such, improvements in oxidation processes and the reaction systems that conduct the oxidation are continually being sought.

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The catalytic liquid-phase oxidation of *para*-xylene to terephthalic acid (hereafter, TPA) with Co/Mn/Br based catalyst, known as the Mid-Century Process, was developed in the 1950s. In 1965, a hydrogenation step to purify TPA was added to help remove 4-carboxybenzaldehyde from the reaction product through conversion to water-soluble *para*-methylbenzyl alcohol and crystallization.

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Another related reaction scheme produces crude TPA at relatively mild oxidation conditions with a metals/bromide catalyst system. The production of isophthalic or TPA from the corresponding xylenes has also been proposed using acetaldehyde as a promoter for the reaction. Since this process does not use bromine as a catalyst promoter, less exotic reactor materials are suitable. Another known process is characterized by the simultaneous oxidation of *para*-xylene and methyl *para*-toluate at mild temperature and comparatively low pressure without acetic acid solvent.

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However, all of these processes share a common shortcoming - an inadequate or non-optimal O₂ mass transfer rate in the liquid phase. The mass transfer is accomplished in a stirred liquid phase reactor, wherein the air is vigorously bubbled through the liquid phase. The crude TPA solid produced via this process is separated and further purified in a subsequent stage to reduce the 4-carboxybenzaldehyde content. Further, roughly 5% of the acetic acid entering the liquid phase reactor is also oxidized (e.g., burned) in this process. Therefore, there still remains a need in the art to have an improved process that

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5 provides increased O₂ mass transfer rate for the production of TPA and other oxidation reactions similar to the ones discussed above.

SUMMARY

Generally, the present invention meets this and other needs through providing an oxidation system and process for selective oxidation through a spray process where each
10 droplet can function as a micro-reactor for selective oxidation of a substrate. While the reaction proceeds within the liquid droplet, some reactions may occur in the vapor or gas phase, such that the majority of reaction occurs substantially in the liquid phase of the droplets.

In one embodiment, an oxidation process can include: introducing small droplets
15 of a liquid reaction mixture having an oxidizable reactant, a catalyst, and a solvent into a gaseous reaction zone containing oxygen and a diluent gas; and oxidizing the reactant with the oxygen at a suitable reaction temperature and a suitable reaction pressure to produce an oxidized product. The liquid reaction mixture can have an aromatic feedstock having an oxidizable substituent as the oxidizable reactant. The oxidized product can
20 include an aromatic compound having at least one carboxylic acid. For example, the aromatic feedstock can include a benzene ring having at least one oxidizable alkyl substituent, furan hetero-ring having at least one oxidizable alkyl substituent, a naphthalene poly-ring having at least one oxidizable alkyl substituent, derivatives thereof, and mixtures thereof. Examples of the aromatic feedstock include *para*-xylene, *meta*-
25 xylene, *ortho*-xylene, *pseudo*-cumene, 3-chloro-*meta*-xylene, 2,6-dimethylnaphthalene, 1,5-dimethylnaphthalene, 2,7- dimethylnaphthalene, 5-hydroxymethylfurfural, furfural, 5-formylfurfural, and mixtures thereof as well as similar compounds or derivatives thereof.

In one embodiment, the aromatic feedstock can include *para*-xylene (*p*-xylene) and the oxidized aromatic compound product having at least one carboxylic acid can
30 include terephthalic acid. Alternatively, the aromatic feedstock can include 5-hydroxymethylfurfural and the oxidized product is an aromatic compound having at least one carboxylic acid includes furan-2,5-dicarboxylic acid.

In one embodiment, the oxidized product precipitates from the droplets as a substantially pure solid material.

35 In one embodiment, the aromatic feedstock includes a partially-oxidized derivative of at least one member selected from the group consisting of *p*-toluic acid (PTA), *p*-tolualdehyde (*p*-Ta), *p*-hydroxymethyl benzoic acid, terephthaldehyde, 4-

5 carboxybenzaldehyde (4-CBA), *p*-methylbenzyl alcohol, 5-hydroxymethylfuran-2-carboxylic acid, 2,5-diformylfuran, furfural-5-carboxylic acid, and mixtures thereof.

In one embodiment, the catalyst can include solvent-soluble compositions of palladium, platinum, cobalt, manganese, vanadium, titanium, tin, antimony, bismuth, molybdenum, and mixtures thereof.

10 In one embodiment, the catalyst can further include a co-catalyst dissolved in the liquid reaction mixture. For example, the co-catalyst can include manganese, bromine, or hydrogen bromide.

In one embodiment, the solvent includes acetic acid. Optionally, the acetic acid contains about 0.1 to 10 % water by weight or volume.

15 In one embodiment, the diluent gas is inert. For example, the diluents gas can include nitrogen, carbon dioxide or a noble gas.

In one embodiment, an oxidation intermediate of the oxidizable reactant is added to the liquid reaction mixture. For example, the oxidation intermediate is selected from the group consisting of *p*-toluic acid, *p*-tolualdehyde, *p*-hydroxymethyl benzoic acid, 20 terephthaldehyde, 4-carboxybenzaldehyde, *p*-methylbenzyl alcohol, derivatives thereof, and mixtures thereof.

In one embodiment, the liquid reaction mixture in the small droplet form is contacted with the oxygen at from about 100 to about 300 °C. Also, the process can include preheating the liquid reaction mixture or the gaseous reaction zone to 100-300 °C 25 prior to the liquid reaction mixture being sprayed into contact with the oxygen-containing gas.

In one embodiment, the liquid reaction mixture droplet is contacted with the oxygen for a time period of about 0.1 second to about 60 minutes.

30 In one embodiment, the reaction pressure is in a range of about 1 to about 100 atmospheres.

In one embodiment, the reaction pressure is chosen such that the reaction mixture, dominated by the solvent, begins to boil if the droplet temperature rises (due to heat evolved by the reaction) and attains a certain temperature. However, when the reaction mixture begins to boil, the latent heat of evaporation is removed from the droplet causing 35 it to cool. In this manner, the droplet temperature can be self-controlling and stable.

In one embodiment, the process can include spraying the reaction mixture through a nozzle to form the fine mist spray in the reaction zone containing the gaseous oxidant. The nozzle can be a single fluid-type nozzle that sprays a fine mist into an oxygen-

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