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(54) Title: ORGANOTIN CATALYSTS IN ESTERIFICATION PROCESSES OF FURAN-2,5-DICARBOXYLIC ACID (FDCA)

(57) Abstract: A method for preparing sugar-based mono and diesters is described. The process entails the esterification of 2,5-furan-dicarboxylic acid (FDCA) with an alcohol in the presence of low loadings of a homogeneous organotin (IV) catalyst.

ORGANOTIN CATALYSTS IN ESTERIFICATION PROCESSES OF FURAN-2,5-DICARBOXYLIC ACID (FDCA)

CLAIM OF PRIORITY

[0000] The present Application claims benefit of priority to U.S. Provisional Application No. 62/259,124, filed November 24, 2015, contents of which are incorporated herein.

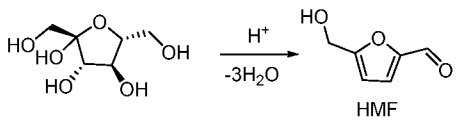
FIELD OF INVENTION

[0001] The present disclosure pertains to processes for improving esterification of sugar-derived furan-2,5-dicarboxylic acid (FDCA). In particular, the invention involves methods for efficient preparation of derivatives of FDCA using organotin catalysts in Fischer-Speier esterification reactions.

BACKGROUND

[0002] Petroleum traditionally has been a primary source of raw material for making organic monomer precursors for common polymeric materials. However, with concerns about climate change and carbon dioxide emissions from fossil fuel sources, researchers have turned to bio-based, renewable carbon sources for plausible surrogate molecules. Carbohydrates, sometimes simply termed sugars, are a prodigious class of bio-based compounds that present a diverse array of extended, carbon-chained building blocks. For over 150 years, scientists have explored various chemical means for adapting the properties of sugars to an array of applications, including polymers. Dehydrative cyclization is a common transformation that sugars can undergo, particularly at elevated temperatures and in the presence of a catalyst, producing furan-based substances. For example, the common sugar, fructose, readily cyclizes at low pH to produce a versatile precursor, 5-hydroxymethyl-2-furfural, HMF. This process is illustrated in Scheme A.

Scheme A. Catalytic dehydrative cyclization of fructose to HMF



By virtue of its unique functionality, HMF can, in turn, be modified into other interesting molecular entities, such as furan-2,5-dimethanol (FDM), 2,5-bishydroxymethyl tetrahydrofuran (bHMTHF), diformylfuran (DFF), and 2,5-furandicarboxylic acid (FDCA). FDCA, in particular, has recently received considerable interest by myriad research groups as potentially renewable replacement for petro-based terephthalic acid in polymer applications.

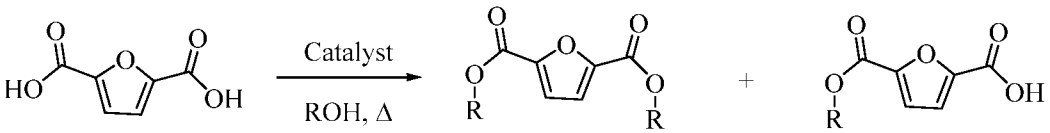
[0003] Synthetic chemists have long sought to overcome challenges posed by the physical attributes of FDCA (e.g., its limited solubility in many common organic solvents and an extremely high melting point (>300°C)). The high melting point of FDCA is a particular encumbrance when one desires to employ melt polymerization processes. Simple chemical modifications, such as esterification, often enables one to overcome barriers that arise from such physical properties. Esterification of FDCA with methanol to make dimethyl 2,5-furandicarboxylate (FDME) allows chemists to work with an appreciably more "manageable" derivative chemical compound that has a melting point at 112°C, and boiling point of 140-145°C (10 torr), and facile solubility in a multitude of common organic solvents.

[0004] Over the years, esterification by autocatalysis has been demonstrated by several research groups in many publications. The inherent inefficiency of this process, however, arises from the need to use high temperatures and long, protracted reaction times to attain copacetic conversions of FDCA and yields of the target esters. This phenomenon of the esterification process has been a drawback which adds significantly to the cost of manufacture on an industrial or commercial scale operation. One conventional approach to enhance the esterification process has been to employ Brønsted acid catalysis, which on one hand greatly improves FDCA conversions and ester yields, but on another hand also readily drives alcohol condensation to undesired, low molecular weight ethers. This generation of byproducts can reduce the overall yield of desired ester product, and can encumber downstream processing, particularly relating to recycling and waste. Alternatively, Lewis acid catalysis in esterification have also been used, but Lewis acid catalysts often suffer from limited activity (lability), and a propensity to generate undesired Brønsted acids when in an aqueous matrix. In order to offset the specified hindrances of common esterification methods, alternate catalysts are needed.

SUMMARY OF INVENTION

[0005] The present disclosure describes, in part, a catalytic process for converting furan-2,5 dicarboxylic acid (FDCA) into monoalkylfuran-2,5-dicarboxylate (FDMAE) and dialkylfuran-2,5-dicarboxylate (FDAE), according to a reaction depicted in Figure 1.

Scheme 1. Esterification of FDCA to FDMAE and FDAE



FDCA FDAE FDMAE

wherein the R-group is an aliphatic, having C_1-C_{20} chain, or aromatic group, such as at least one of the following: alkyl, alkenyl, alkynyl, allyl, or aryl. In general, the process involves: reacting FDCA with at least an alcohol or a mixture of different alcohols in the presence of a homogeneous organotin acid catalyst for a time and temperature sufficient to fully esterify the FDCA and produce an intermediate

mono- or di-ester; and removing any unreacted alcohol. The reaction can be in either an alcohol and/or diester solvent matrix. The process can generate relatively high conversions of FDCA and yields at reduced temperatures (e.g., ~125°C-225°C) and at lower catalyst loadings (e.g., ≤ 1.0 mol. % relative to starting amount of FDCA) of the organotin catalysts. The tin ion in the organotin catalyst is Sn (IV), and has at least one tin-carbon covalent bond. The process can convert FDCA at least 85 mol.% to a mono- or di-ester. Furthermore, the organotin catalysts manifest markedly reduced side product activities relative to Brønsted acid counterparts in forming undesired alcohol condensations to ethers.

[0006] Additional features and advantages of the present synthesis method and material compounds will be disclosed in the following detailed description. It is understood that both the foregoing summary and the following detailed description and examples are merely representative of the invention, and are intended to provide an overview for understanding the invention as claimed.

DETAILED DESCRIPTION OF INVENTION

Section I. Description

[0007] The present disclosure describes, in part, a highly efficient process for preparation of mono- and di-esters of furan-2,5-dicarboxylic acid (FDCA). According to embodiments, the process involves plying homogeneous organotin catalysts to produce both the mono- and di-esters of FDCA from reactions with aliphatic and aromatic alcohols, such as ethanol, propanol, butanol, 2-ethylhexanol, phenol, benzyl alcohol, and 5-hydroxymethylfurfural (HMF). The process comprises: reacting FDCA with at least an alcohol or a mixture of different alcohols in either an alcohol or diester solvent matrix in the presence of a homogeneous organotin catalyst at a loading level of up to 5 or 10 mol.% for a reaction time and temperature sufficient to esterify said FDCA and produce a di-ester species at a FDCA conversion of at least 80 mol.%, and a di-ester yield of at least 5 mol.% greater than a comparable amount of Brønsted acid catalyst. The process produces less side products in amount of less than 0.05 mol.%, typically about 0.03-0.04 mol.%., and minimal to no decarboxylation.

[0008] The homogeneous organotin catalysts are generally in the (+4) oxidation state. The organotin catalyst can include at least one of the following: butylstannoic acid (BSA), dibutyltin oxide (DBTO), dibutyltin diacetate, butyltin tris 2-ethylhexanoate, dibutyltin maleate, dibutyltin dilaurate, dioctyltin oxide, dibutyltin bis(1-thioglyceride), dibutyltin dichloride, and monobutyltin dihydroxychloride. In certain particularly favored embodiments, the organotin catalyst can be selected from: butylstannoic acid, dibutyltin oxide, dibutyltin diacetate, butyltin tris 2-ethylhexanoate. Not necessarily limiting, the ligand complex surrounding the metal ion can have a cluster size with about 2-20 carbons, typically 2 or 4 to about 10 or 12 carbons, more typically about 2-8 carbons.

[0009] According to certain embodiments of the process the organotin catalyst loading level can be in a range from about 0.01 mo.% to about 5 mol.% (e.g., 2 mol.%, 3 mol.% or 4 mol.%). Typically,

the catalyst loading level is in a range from about 0.05 mol.% to about 1.5 mol.%; more typically, the range is about 0.01 mol% to about 1 mol.%, preferably about 0.1 mol% to about 0.5 mol%.

[0010] Differentiated from heterogeneous catalysts, which are generally immobilized on carbon or aluminum scaffolds, homogeneous organometallic catalysts are monophasic with the reagents and can demonstrate advantages in catalyzing processes *vis-à-vis* supported metal catalyst species. One benefit of homogeneous catalysts over insoluble heterogeneous catalysts, particular to the application in the present method, is that the homogeneous species does not require filtration after use, which imparts improved economics, as an extra unit operation for such is avoided.

[0011] An advantageous feature of the current process with homogeneous organotin catalysis is that few side products are generated. This is a salient difference between the two kinds of catalysts. With the present organotin catalysts one can generate higher FDME yields than when using sulfuric acid (e.g., ~93% vs. ~87% respectively). Brønsted acids are significantly different and detrimental for producing more side-products, lower yields, and can trigger side reaction pathways – such as noticeable yields of dimethyl ether (DME) with Brønsted acid versus Lewis acid (~2-3 orders of magnitude more). This effect has not been sufficiently recognized or appreciated. Conventionally, a sulfuric acid catalyst produces a great amount of DME, nearly 2 mol% in yield. Furthermore, in conventional processes, one uses catalyst in amounts that can be up to about 50 mol.% relative to the starting amount of FDCA. The tin catalysts generate significantly less, only about 0.03 mol.% yield of DME. In contrast for instance, strong Brønsted acid (e.g., HCl, H_2SO_4) catalyzed processes one effects significant amounts of flammable, gaseous alkyl and aryl ethers from alcohol condensations, which would need to perform extensive downstream separation or purification processing to remove both side products and the catalysts themselves before the product mixture could be used in synthesis of other or additional compounds. At such amounts, downstream processing will require catalyst removal.

[0012] Using the homogeneous organotin catalysts, the process can achieve a FDCA conversion of at least 3% or 5% greater, or a mono- or di-ester yield of at least 8 mol.% or 10 mol.% greater than a process reacted using a comparable amount of Brønsted acid catalyst. The homogeneous organotin catalyzed process enables the conversion of FDCA to the corresponding di-esters in reasonably high mole yields of at least 75 mol.%-82 mol.% (e.g., ~77 mol.%, 80 mol.%), typically 85 mol.%-89 mol.% or greater. Typically, the molar yield ranges from about 85% or 87% to about 99%+, or any combination of ranges therein (e.g., ~86%, 88%, 89%, 90%, 92%, 95%, 97%, 98%), depending on the reaction conditions (i.e., time, temperature pressure), and with the residue being the corresponding monoester. In particular examples, homogeneous organotin catalysts near quantitative conversions of FDCA to a furanic mono and diesters (e.g., 2,5-furandimethyl ester, FDME, when the alcohol is methanol) in yields near 90 mol.%. In certain embodiments, FDCA conversion is at least about 92 mol.%, 95 mol.% or 96 mol.%, or preferably about 99 mol.%. The yield of diester can be at least 50

mole%, typically about 70 mol.% - 97 mol.%, more typically about 80 mol.% or 87 mol.% to about 90 mol.% or 95mol.%.

[0013] A summary of results from catalyst screenings with methanol are summarized in Table 1.

Table 1. Data synopsis from catalyst screening of FDCA esterification in methanol

Catalyst	Vendor/Product #	Product Name	FDCA conversion (mol%)	FDME yield (mol%)	Dimethyl ether yield (mol%, estimated from head space analysis)
Tin (IV)					
Butyltin tris-2-ethylhexanoate	PMC	FASCAT®9102	99.61 ± 0.12	89.46 ± 1.15	0.0363 ± 0.0013
Dibutyltin oxide	SIAL		99.72 ± 0.29	90.05 ± 1.34	0.0351 ± 0.0017
Dibutyltin oxide	PMC	FASCAT®4201	99.77 ± 0.28	90.47 ± 0.98	0.0362 ± 0.0029
Dibutyltin diacetate	PMC	FASCAT®4200	99.55 ± 0.17	90.09 ± 1.23	0.0349 ± 0.0022
Butylstannoic acid	PMC	FASCAT®9100	99.69 ± 0.08	91.21 ± 0.86	0.0334 ± 0.0021
Dibutyltin oxide blend	FOMREZ	FOMREZ®-SUL4	99.64 ± 0.11	89.04 ± 0.41	0.0343 ± 0.0013
Dibutyltin oxide blend	FOMREZ	FOMREZ® SUL-11	99.59 ± 0.19	87.08 ± 1.89	0.0336 ± 0.0011
Dibutyltin dilaurate	PMC	FASCAT®4202	99.06 ± 0.32	82.16 ± 0.97	0.0315 ± 0.0018
Dibutyltin maleate	SIAL		99.19 ± 0.15	84.58 ± 0.86	0.0374 ± 0.0023
Dibutyltin dichloride	PMC	FASCAT®4201	99.26 ± 0.26	86.33 ± 1.16	1.1331 ± 0.0097
Dioctyltin oxide	PMC	FASCAT®8201	98.11 ± 0.29	76.12 ± 0.94	0.0335 ± 0.0027
Monobutyltin dihydroxychloride	PMC	FASCAT®4101	97.63 ± 0.10	80.15 ± 0.59	0.9126 ± 0.1073
Tin dioxide	SIAL		95.91 ± 0.22	64.55 ± 0.70	0.0257 ± 0.0011
Tin (II)					
Stannous octoate	PMC	FASCAT® 2003	96.54 ± 0.12	69.68 ± 1.66	0.0332 ± 0.0021
Stannous oxalate	PMC	FASCAT® 2001	97.17 ± 0.07	78.74 ± 0.77	0.0295 ± 0.0029
Tin acetate	SIAL		99.58 ± 0.16	88.99 ± 0.80	0.0526 ± 0.0014
Tin chloride	PMC	FASCAT®2004	94.11 ± 0.55	81.26 ± 1.69	0.9951 ± 0.1561
Titanates					
Titanium tetrabutoxide	SIAL	TYZOR TBT	98.57 ± 0.15	74.98 ± 1.65	0.0526 ± 0.0014
Titamium tetraisopropoxide	SIAL	TYZOR TTIP	98.31 ± 0.22	72.07 ± 0.89	0.0409 ± 0.0032
Brønsted Acids					
Phosphonic	SIAL		97.42 ± 0.21	71.56 ± 1.15	0.1454 ± 0.0041
p-Toluenesulfonic monohydrate	SIAL		95.16 ± 0.70	67.42 ± 1.43	0.0691 ± 0.0072
Sulfuric	SIAL		99.49 ± 0.09	87.53 ± 1.23	1.6036 ± 0.1284
Autocatalysis			93.94 ± 1.47	64.26 ± 0.82	0.0367 ± 0.0020

[0014] When compared to standard catalyst loadings, the product tolerance for residual organometallic species is usually limited to a organotin catalysts can be used in relatively low loads of about 10 mol.% or less, such as in amounts in a range of about 5 mol.% to 8 mol.% or less, relative to the starting amount of FDCA. Typically, the catalysts amount ranges from about 0.01 mol.% to about 2, 3 or 4 mol.%, desirably, about 0.05 to about 1.0 or 1.8 mol.%. This feature of the present reaction system enables one to allow the catalyst to remain in the product mixture without exigent need for removal, further simplifying downstream demand.

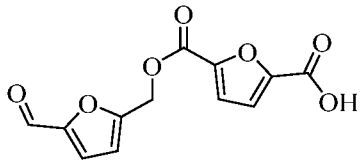
[0015] Esterification of FDCA can be conducted either in an inert atmosphere (e.g., nitrogen or argon) or in air without detrimental effect the reaction. In certain embodiments, the reaction temperature for the present process can be in a range from about 80°C to about 275°C. Typically, the reaction temperature is in a range from about 100°C to about 250°C; more typically about 120°C - 245°C, preferably about 125°C or 150°C to about 225°C or 230°C (e.g., 140°C, 160°C, 215°C,

220°C), more preferably about 175°C or 180°C to about 200°C or 210°C (e.g., 185°C, 195°C, 205°C, 208°C). For instance, one can conduct the reaction in a Parr vessel of any material of composition (MOC) at a temperature in a range from about 125°C to about 250°C, typically about 150°C or 160°C to about 225°C or 235°C, more typically about 170°C to about 200°C (e.g., about 175°C or 180°C to about 190°C or 195°C).

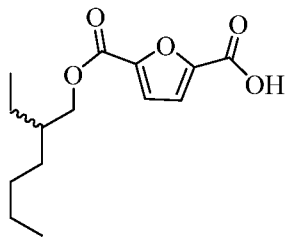
[0016] The reaction time for the esterification process can be up to about 10 or 12 hours. Typically, the reaction time is in a range from about 10 minutes to about 8 hours; more typically, the reaction time is within about 3 or 4 hours, and desirably within about 1-2 hours until equilibrium. In certain embodiments the reaction can reach equilibrium within about 0.5 hours (i.e., 30 minutes) (e.g., ~10, 15, 20 minutes). In an embodiment, for example, esterification can be performed within a 6 hour overall reaction time, typically within about 2 or 4 hours. More typically, the total reaction time ranges from about 1 or 2 hours to about 3 or 4 hours; particular durations can be about 0.5 to 1 hours or about 1-1.5 hours.

[0017] According to the process one can use either an alcohol solvent matrix and/or di-ester matrix is sufficient to dissolve the FDCA. The matrix can constitute about 50 wt.% to about 99 wt.% of alcohol and/or di-ester relative to an amount of FDCA. In other embodiments, the alcohol solvent matrix and/or di-ester solvent matrix can be at about 75 wt.% to about 97 wt.% relative to an amount of FDCA. The alcohols used for esterification of FDCA can be selected from various species, including either an aliphatic, having C_1-C_{20} chain, or aromatic alcohol species, such as at least one of the following: alkyl, alkenyl, alkynyl, allyl, or aryl alcohols. Certain inexpensive and commonly used alcohol species, for example, may include: methanol, ethanol, propanol, isopropanol, n-butanol, *sec*-butanol, isobutanol, n-pentanol, 2-pentanol, 3-pentanol, n-hexanol, isohexanol, 2-ethylhexanol, cyclohexanol, heptanol, octanol, nonanol, decanol, phenol, benzyl alcohol, or 5-hydroxymethylfurfural.

[0018] Mono-ester products produced from the present process can include, for example: 5-(((5-formylfuran-2-yl)methoxy)carbonyl)furan-2-carboxylic acid (FDCA-HMF)



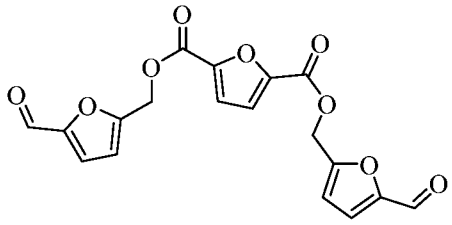
and 5-(((2-ethylhexyl)oxy)carbonyl)furan-2-carboxylic acid (FDCA-2EH)



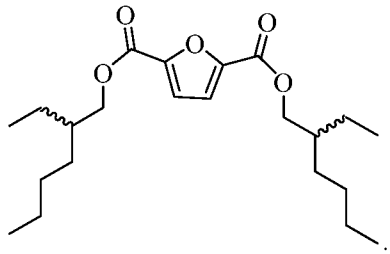
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[0019] Di-ester products made according to the present process may include, for example:

bis((5-formylfuran-2-yl)methyl) furan-2,5-dicarboxylate (FDCA-HMF)



and bis(2-ethylhexyl) furan-2,5-dicarboxylate (FDCA



di(2EH)) .

Section II. Examples

[0020] In the following examples we further demonstrate the present method of preparing mono and dialkyl esters catalyzed by organotin species. For purpose of illustration the particular examples presented herein use methanol in the esterification, producing FDME and FDMME, but the process is not necessarily limited to such as other kinds of alcohols are also applicable.

[0021] A summary of additional examples of organotin catalysts and their efficacy in methanol and FDME solvents, respectively are presented in the appended Tables 2-5. Table 2 presents esterification reactions of FDCA in methanol solvent at 17 wt.% FDCA. In a first group, eight comparative examples are run without a catalyst; in a second group four examples are performed with an organotin catalyst loading of 0.1 mo.%, and six examples in a third group have an organotin catalyst loading of 0.5 mol.%. Generally, reactions with catalyst at temperatures between about 175°C to about 250°C were able to achieve near complete conversion of FCDA (i.e., $\geq$ 95 mol.%) and FDME yields of more than 85 mol.%.

[0022] Table 3 presents esterification reactions of FDCA in methanol solvent at 26 wt.% FDCA. In a first group six comparative examples are run without catalyst, and in a second group four examples have a catalyst loading of 0.5 mol.%. Even at lower temperatures (e.g., ~175°C, 200°C), the presence of the present organotin catalysts helps achieve better FDCA conversion (i.e., near complete) and FDME yield (e.g., $\geq$ 85 mol.%) than that produced at higher temperatures (e.g., 250°C) without catalyst.

[0023] Table 4 presents esterification reactions of FDCA in methanol solvent at 35 wt.% FDCA. In a first group four comparative examples are run without catalyst, and in a second group four examples have a catalyst loading of 0.5 mol.%. Similar to the results in Table 3, the catalyzed reactions performed better than reactions without catalyst; one can achieve about 5 mol.% more FDME yield at

reaction temperatures of about 200°C or higher. This additional yield can be a significant benefit in industrial production.

[0024] Table 5 presents esterification of FDCA in FDME solvent. In the examples using the present organotin catalysts one can achieve similar or better conversion of FDCA, and a significant improvement in FDME yield over examples without catalyst. In some examples, the difference in FDME yield is at least 5 mol.%, others ≥ 10 mol.% or 12 mol.%.

TABLES: Batch Esterifications of FDCA to FDME

I. TABLE 2. Esterification of FDCA in methanol solvent

17 wt.% FDCA (6 g FDCA + 30 g MeOH)

Catalyst Load (mol.%)	Rxn Temp (°C)	Operating Pressure (psi)	Rxn Time (min)	Approximate Time to Equilibrium (min)	FDCA conversion	FDME yield (mol%)	Decarboxylation
None	125	84	90	----	21.59	1.60	N
None	150	170	90	----	71.99	21.90	N
None	175	325	120	----	89.82 ± 0.33	46.06 ± 1.14	N
None	185	360	180	-----	98.58	73.82	N
None	200	500	90	----	95.80	61.10	N
None	210	590	150	135	98.86 ± 0.02	80.17 ± 1.03	N
None	225	750	90	----	98.78 ± 0.03	77.35 ± 1.50	N
None	250	1100	90	30	99.09	82.59	**Y**
0.1	150	165	90	----	79.18	28.30	N
0.1	175	325	90	----	97.21	77.47	N
0.1	200	500	90	60	99.46	85.20	N
0.1	225	750	90	30	99.40 ± 0.23	85.61 ± 1.26	N
0.5	125	84	90	----	40.71	4.98	N
0.5	150	175	90	----	95.87	67.70	N
0.5	175	325	150	120	99.54 ± 0.18	88.49 ± 0.54	N
0.5	200	500	60	15	99.60 ± 0.31	88.98 ± 2.07	N
0.5	225	725	60	Heat up	99.63 ± 0.17	88.76 ± 1.33	N
0.5	250	1100	60	Heat up	99.54 ± 0.13	88.36 ± 1.98	**Y**

TABLE 3.

26 wt.% FDCA (10 g FDCA + 29 g MeOH)

Catalyst Load (mol%)	Rxn Temp (°C)	Operating Pressure (psi)	Rxn Time (min)	Approximate Time to Equilibrium (min)	FDCA conversion (mol%)	FDME yield (mol%)	Decarboxylation
None	175	325	90	----	87.95	48.45	N
None	185	336	180	-----	98.87	75.70	N
None	200	445	90	----	95.72	65.65	N
None	210	590	150	150	98.88	80.16	N
None	225	745	90	----	98.35	73.59	N
None	250	1045	60	45	99.03	80.89	**Y**
0.5	175	310	120	----	99.67	87.52	N
0.5	200	475	90	30	99.52 ± 0.08	87.98 ± 0.61	N
0.5	225	735	60	15	99.62 ± 0.17	87.85 ± 0.57	N
0.5	250	1030	60	Heat up	99.57 ± 0.14	87.54 ± 1.92	**Y**

TABLE 4.

35 wt.% FDCA (15 g FDCA + 28 g MeOH)

Catalyst	Rxn Temp (°C)	Operating Pressure (psi)	Rxn Time (min)	Approximate Time to Equilibrium (min)	FDCA conversion (mol%)	FDME yield (mol%)	Decarboxylation
None	175	230	240	----	80.16	37.79	N
None	200	400	240	----	98.47	78.01	N
None	225	600	180	----	98.19	77.30	N
None	250	920	60	----	98.73	77.65	**Y**
0.5 mol%	175	236	90	----	98.32	77.69	N
0.5 mol%	200	395	90	90	99.08	83.95	N
0.5 mol%	225	600	60	30	99.12	83.99	N
0.5 mol%	250	925	60	Heatup	99.10	83.31	**Y**

II. TABLE 5. Esterification of FDCA in FDME solvent

Trial set	Catalyst	Temp (°C)	P (psi)	MeOH (eq.)	Time (min)	Equilib.	FDCA conv. (mole%)	FDMME yld. (mole %)	FDME yld. (mole %)
1	Y	170	83	2	45	N	67	56	12
2	Y	170	103	4	60	N	95	67	28
3	Y	170	140	8	60	N	97	54	43
4	Y	170	174	12	60	N	98	48	50
5	Y	180	109	4	60	N	96	65	31
6	Y	180	144	8	60	N	97	52	45
7	Y	180	209	12	60	N	98	44	54
8	N	180	121	4	60	N	79	66	13
9	N	180	155	8	60	N	85	67	18
10	N	180	211	12	60	N	89	67	22
11	Y	200	115	4	150	Y (90 min)	97	58	39
12	Y	200	179	8	150	Y (45 min)	99	36	63
13	Y	200	301	12	60	Y (30 min)	99	34	65
14	N	200	112	4	60	N	94	74	20
15	N	200	185	8	60	N	96	63	33
16	N	200	297	12	60	N	97	60	37
17	Y	220	135	4	150	Y (30 min)	97	58	39
18	Y	220	220	8	45	Y (15 min)	99	36	63
19	Y	220	375	12	60	Y (15 min)	*99*	34	65
20	N	220	134	4	150	Y (30 min)	96	74	23
21	N	220	221	8	45	Y (45 min)	98	61	37
22	N	220	379	12	60	Y (30 min)	98	54	44

I. Highly effective catalysts

A. Methanol solvent

[0025]

1) Butylstannoic acid catalyzed esterification of FDCA to FDME and FDMME

Experimental: A 75 cc 316SS Parr vessels, each equipped with a glass enclosed magnetic stir bar, was charged with 10 g of FDCA (0.064 mol), 40 g of methanol (1.25 mol), and 50 mg of butylstannoic acid (FASCAT®9100). While stirring at 875 rpm, the suspension was heated to 200°C for 60 minutes, including a 30 minute heat up requirement. After this time, the reaction was quickly quenched by immersion of the vessel in an ice bath. The solid residual material was dried and analyzed (UPLC-PDA). The compositional analysis was as follows: 0.6 mole% FDCA, 8.2 mole% FDMME, 91.2 mole% FDME, 0.03 mole% DME. No decarboxylation products, MF and FA, were descried.

[0026]

2) Dibutyltin oxide catalyzed esterification of FDCA to FDME and FDMME

Experimental: A 75 cc 316SS Parr vessels, each equipped with a glass enclosed magnetic stir bar, was charged with 10 g of FDCA (0.064 mol), 40 g of methanol (1.25 mol), and 50 mg of dibutyltin oxide (FASCAT®9201). While stirring at 875 rpm, the suspension was heated to 200°C for 60 minutes, including a 30 minute heat up requirement. After this time, the reaction was quickly quenched by immersion of the vessel in an ice bath. The solid residual material was dried and analyzed (UPLC-PDA). The compositional analysis was as follows: 0.5 mole% FDCA, 9.0 mole% FDMME, 90.5 mole% FDME, 0.04 mole% DME. No decarboxylation products, MF and FA, were descried.

[0027]

3) Dibutyltin diacetate catalyzed esterification of FDCA to FDME and FDMME

Experimental: A 75 cc 316SS Parr vessels, each equipped with a glass enclosed magnetic stir bar, was charged with 10 g of FDCA (0.064 mol), 40 g of methanol (1.25 mol), and 50 mg of dibutyltin diacetate (FASCAT®4200). While stirring at 875 rpm, the suspension was heated to 200°C for 60 minutes, including a 30 minute heat up requirement. After this time, the reaction was quickly quenched by immersion of the vessel in an ice bath. The solid residual material was dried and analyzed (UPLC-PDA). The compositional analysis was as follows: 0.6 mole% FDCA, 9.1 mole% FDMME, 90.4 mole% FDME, 0.04 mole% DME. No decarboxylation products, MF and FA, were descried.

[0028]

4) Butyltin tris 2-ethylhexanoate catalyzed esterification of FDCA to FDME and FDMME.

Experimental: A 75 cc 316SS Parr vessels, each equipped with a glass enclosed magnetic stir bar, was charged with 10 g of FDCA (0.064 mol), 40 g of methanol (1.25 mol), and 50 mg of butyltin tris 2-

ethylhexanoate (FASCAT®9102). While stirring at 875 rpm, the suspension was heated to 200°C for 60 minutes, including a 60 minute heat up requirement. After this time, the reaction was quickly quenched by immersion of the vessel in an ice bath. The solid residual material was dried and analyzed (UPLC-PDA). The compositional analysis was as follows: 0.6 mole% FDCA, 9.3 mole% FDMME, 90.4 mole% FDME, 0.05 mole% DME. No decarboxylation products, MF and FA, were descried.

[0029]

5) Comparative Example: No Catalyst Added.

Experimental: A 75 cc 316SS Parr vessels, each equipped with a glass enclosed magnetic stir bar, was charged with 10 g of FDCA (0.064 mol), 40 g of methanol (1.25 mol), While stirring at 875 rpm, the suspension was heated to 200°C for 60 minutes, including a 30 minute heat up requirement. After this time, the reaction was quickly quenched by immersion of the vessel in an ice bath. The solid residual material was dried and analyzed (UPLC-PDA). The compositional analysis was as follows: 6.1 mole% FDCA, 38.5 mole% FDMME, 55.4 mole% FDME, DME 0.01 mole%. No decarboxylation products, MF and FA, were descried.

B. Highly effective catalysts in FDME solvent, 8 mole equivalents methanol

[0030]

1) Butylstannoic acid catalyzed esterification of FDCA to FDME and FDMME

Experimental: A 75 cc 316SS Parr vessels, each equipped with a glass enclosed magnetic stir bar, was charged with 10 g of FDCA (0.064 mol), 30 g of FDME, 16.4 g of methanol and 50 mg of butylstannoic acid (FASCAT®9100). While stirring at 875 rpm, the suspension was heated to 200°C for 60 minutes, including a 30 minute heat up requirement. After this time, the reaction was quickly quenched by immersion of the vessel in an ice bath. The solid residual material was dried and analyzed (UPLC-PDA). The compositional analysis was as follows: 1.1 mole% FDCA, 36.1 mole% FDMME, 62.8 mole% FDME, 0.04 mole% DME. No decarboxylation products, MF and FA, were descried.

[0031]

2) Dibutyltin oxide catalyzed esterification of FDCA to FDME and FDMME

Experimental: A 75 cc 316SS Parr vessels, each equipped with a glass enclosed magnetic stir bar, was charged with 10 g of FDCA (0.064 mol), 30 g FDME, 16.4 g of methanol and 50 mg of dibutyltin oxide (FASCAT® 9201). While stirring at 875 rpm, the suspension was heated to 200°C for 60 minutes, including a 30 minute heat up requirement. After this time, the reaction was quickly quenched by immersion of the vessel in an ice bath. The solid residual material was dried and analyzed (UPLC-PDA). The compositional analysis was as follows: 1.5 mole% FDCA, 36.5 mole% FDMME, 62.0 mole% FDME, 0.06 mole% DME. No decarboxylation products, MF and FA, were descried.

[0032]

3) Comparative example, no added catalyst

Experimental: A 75 cc 316SS Parr vessels, each equipped with a glass enclosed magnetic stir bar, was charged with 10 g of FDCA (0.064 mol), 30 g of FDME, and 16.4 g of methanol. While stirring at 875 rpm, the suspension was heated to 200°C for 60 minutes, including a 30 minute heat up requirement. After this time, the reaction was quickly quenched by immersion of the vessel in an ice bath. The solid residual material was dried and analyzed (UPLC-PDA). The compositional analysis was as follows: 3.5 mole% FDCA, 63.5 mole% FDMME, 33.0 mole% FDME, 0.04 mole% DME. No decarboxylation products, MF and FA, were descried.

II. Moderately effective catalysts

A. Methanol solvent

[0033]

1) Dibutyltin maleate catalyzed esterification of FDCA to FDME and FDMME

Experimental: A 75 cc 316SS Parr vessels, each equipped with a glass enclosed magnetic stir bar, was charged with 10 g of FDCA (0.064 mol), 40 g of methanol (1.25 mol), and 50 mg of dibutyltin maleate (Sigma Aldrich). While stirring at 875 rpm, the suspension was heated to 200°C for 60 minutes, including a 30 minute heat up requirement. After this time, the reaction was quickly quenched by immersion of the vessel in an ice bath. The solid residual material was dried and analyzed (UPLC-PDA). The compositional analysis was as follows: 0.7 mole% FDCA, 10.4 mole% FDMME, 88.9 mole% FDME, 0.04 mole% DME. No decarboxylation products, MF and FA, were descried.

[0034]

2) Dibutyltin dilaurate catalyzed esterification of FDCA to FDME and FDMME

Experimental: A 75 cc 316SS Parr vessels, each equipped with a glass enclosed magnetic stir bar, was charged with 10 g of FDCA (0.064 mol), 40 g of methanol (1.25 mol), and 50 mg of dibutyltin dilaurate (FASCAT® 4202). While stirring at 875 rpm, the suspension was heated to 200°C for 60 minutes, including a 30 minute heat up requirement. After this time, the reaction was quickly quenched by immersion of the vessel in an ice bath. The solid residual material was dried and analyzed (UPLC-PDA). The compositional analysis was as follows: 0.6 mole% FDCA, 10.6 mole% FDMME, 88.8 mole% FDME, 0.07 mole% DME. No decarboxylation products, MF and FA, were descried.

[0035]

3) Stannous acetate catalyzed esterification of FDCA to FDME and FDMME

Experimental: A 75 cc 316SS Parr vessels, each equipped with a glass enclosed magnetic stir bar, was charged with 10 g of FDCA (0.064 mol), 40 g of methanol (1.25 mol), and 50 mg of stannous acetate

(Sigma Aldrich). While stirring at 875 rpm, the suspension was heated to 200°C for 60 minutes, including a 30 minute heat up requirement. After this time, the reaction was quickly quenched by immersion of the vessel in an ice bath. The solid residual material was dried and analyzed (UPLC-PDA). The compositional analysis was as follows: 0.8 mole% FDCA, 11.2 mole% FDMME, 88.0 mole% FDME, 0.05 mole% DME. No decarboxylation products, MF and FA, were descried.

[0036]

4) Dioctyltin oxide catalyzed esterification of FDCA to FDME and FDMME

Experimental: A 75 cc 316SS Parr vessels, each equipped with a glass enclosed magnetic stir bar, was charged with 10 g of FDCA (0.064 mol), 40 g of methanol (1.25 mol), and 50 mg of dioctyltin oxide (FASCAT® 8201). While stirring at 875 rpm, the suspension was heated to 200°C for 60 minutes, including a 30 minute heat up requirement. After this time, the reaction was quickly quenched by immersion of the vessel in an ice bath. The solid residual material was dried and analyzed (UPLC-PDA). The compositional analysis was as follows: 0.9 mole% FDCA, 12.6 mole% FDMME, 86.5 mole% FDME, 0.07 mole% DME. No decarboxylation products, MF and FA, were descried.

[0037]

5) Dibutyltin bis(1-thioglyceride) catalyzed esterification of FDCA to FDME and FDMME

Experimental: A 75 cc 316SS Parr vessels, each equipped with a glass enclosed magnetic stir bar, was charged with 10 g of FDCA (0.064 mol), 40 g of methanol (1.25 mol), and 50 mg of dioctyltin oxide (FASCAT® 4224). While stirring at 875 rpm, the suspension was heated to 200°C for 60 minutes, including a 30 minute heat up requirement. After this time, the reaction was quickly quenched by immersion of the vessel in an ice bath. The solid residual material was dried and analyzed (UPLC-PDA). The compositional analysis was as follows: 1.1 mole% FDCA, 13.8 mole% FDMME, 85.1 mole% FDME, 0.03 mole% DME. No decarboxylation products, MF and FA, were descried.

B. FDME solvent, 8 mole equivalents methanol

[0038]

1) Dibutyltin dilaurate catalyzed esterification of FDCA to FDME and FDMME

Experimental: A 75 cc 316SS Parr vessels, each equipped with a glass enclosed magnetic stir bar, was charged with 10 g of FDCA (0.064 mol), 30 g of FDME, 16.4 g of methanol (1.25 mol), and 50 mg of dibutyltin dilaurate (FASCAT® 4202). While stirring at 875 rpm, the suspension was heated to 200°C for 60 minutes, including a 30 minute heat up requirement. After this time, the reaction was quickly quenched by immersion of the vessel in an ice bath. The solid residual material was dried and analyzed (UPLC-PDA). The compositional analysis was as follows: 1.8 mole% FDCA, 16.1 mole% FDMME, 82.1 mole% FDME, 0.05 mole% DME. No decarboxylation products, MF and FA, were descried.

[0039]

2) Dioctyltin oxide catalyzed esterification of FDCA to FDME and FDMME

Experimental: A 75 cc 316SS Parr vessels, each equipped with a glass enclosed magnetic stir bar, was charged with 10 g of FDCA (0.064 mol), 40 g of methanol (1.25 mol), and 50 mg of dioctyltin oxide (FASCAT® 8201). While stirring at 875 rpm, the suspension was heated to 200°C for 60 minutes, including a 30 minute heat up requirement. After this time, the reaction was quickly quenched by immersion of the vessel in an ice bath. The solid residual material was dried and analyzed (UPLC-PDA). The compositional analysis was as follows: 1.9 mole% FDCA, 22.0 mole% FDMME, 76.1 mole% FDME, 0.07 mole% DME. No decarboxylation products, MF and FA, were descried.

III. Comparative Ineffective Catalysts

A. In Methanol solvent

[0040]

1) Dibutyltin dichloride catalyzed esterification of FDCA to FDME and FDMME

Experimental: A 75 cc 316SS Parr vessels, each equipped with a glass enclosed magnetic stir bar, was charged with 10 g of FDCA (0.064 mol), 40 g of methanol (1.25 mol), and 50 mg of dibutyltin dichloride (FASCAT® 4201). While stirring at 875 rpm, the suspension was heated to 200°C for 60 minutes, including a 30 minute heat up requirement. After this time, the reaction was quickly quenched by immersion of the vessel in an ice bath. The solid residual material was dried and analyzed (UPLC-PDA). The compositional analysis was as follows: 0.7 mole% FDCA, 13.0 mole% FDMME, 86.3 mole% FDME, 1.4 mole% DME. No decarboxylation products, MF and FA, were descried.

[0041]

2) Monobutyltin dihydroxychloride catalyzed esterification of FDCA to FDME and FDMM

Experimental: A 75 cc 316SS Parr vessels, each equipped with a glass enclosed magnetic stir bar, was charged with 10 g of FDCA (0.064 mol), 40 g of methanol (1.25 mol), and 50 mg of monobutyltin dihydroxyoxychloride (FASCAT® 4101). While stirring at 875 rpm, the suspension was heated to 200°C for 60 minutes, including a 30 minute heat up requirement. After this time, the reaction was quickly quenched by immersion of the vessel in an ice bath. The solid residual material was dried and analyzed (UPLC-PDA). The compositional analysis was as follows: 2.4 mole% FDCA, 17.3 mole% FDMME, 80.3 mole% FDME, 0.9 mole% DME. No decarboxylation products, MF and FA, were descried.

[0042]

3) Stannous (II) oxalate catalyzed esterification of FDCA to FDME and FDMME

Experimental: A 75 cc 316SS Parr vessels, each equipped with a glass enclosed magnetic stir bar, was charged with 10 g of FDCA (0.064 mol), 40 g of methanol (1.25 mol), and 50 mg of stannous oxalate

(FASCAT® 2001). While stirring at 875 rpm, the suspension was heated to 200°C for 60 minutes, including a 30 minute heat up requirement. After this time, the reaction was quickly quenched by immersion of the vessel in an ice bath. The solid residual material was dried and analyzed (UPLC-PDA). The compositional analysis was as follows: 2.9 mole% FDCA, 19.0 mole% FDMME, 78.1 mole% FDME, 0.04 mole% DME. No decarboxylation products, MF and FA, were descried.

[0043]

4) Stannous chloride catalyzed esterification of FDCA to FDME and FDMME

Experimental: A 75 cc 316SS Parr vessels, each equipped with a glass enclosed magnetic stir bar, was charged with 10 g of FDCA (0.064 mol), 40 g of methanol (1.25 mol), and 50 mg of stannous chloride (FASCAT® 2004). While stirring at 875 rpm, the suspension was heated to 200°C for 60 minutes, including a 30 minute heat up requirement. After this time, the reaction was quickly quenched by immersion of the vessel in an ice bath. The solid residual material was dried and analyzed (UPLC-PDA). The compositional analysis was as follows: 3.3 mole% FDCA, 19.1 mole% FDMME, 77.6 mole% FDME, 1.2 mole% DME. No decarboxylation products, MF and FA, were descried.

[0044]

5) Stannic chloride catalyzed esterification of FDCA to FDME and FDMME

Experimental: A 75 cc 316SS Parr vessels, each equipped with a glass enclosed magnetic stir bar, was charged with 10 g of FDCA (0.064 mol), 40 g of methanol (1.25 mol), and 50 mg of stannic chloride (FASCAT® 4400). While stirring at 875 rpm, the suspension was heated to 200°C for 60 minutes, including a 30 minute heat up requirement. After this time, the reaction was quickly quenched by immersion of the vessel in an ice bath. The solid residual material was dried and analyzed (UPLC-PDA). The compositional analysis was as follows: 1.9 mole% FDCA, 13.6 mole% FDMME, 84.5 mole% FDME, 1.7 mole% DME. No decarboxylation products, MF and FA, were descried.

[0045]

6) Stannous (II) octoate catalyzed esterification of FDCA to FDME and FDMME

Experimental: A 75 cc 316SS Parr vessels, each equipped with a glass enclosed magnetic stir bar, was charged with 10 g of FDCA (0.064 mol), 40 g of methanol (1.25 mol), and 50 mg of stannous octoate (FASCAT® 2003). While stirring at 875 rpm, the suspension was heated to 200°C for 60 minutes, including a 30 minute heat up requirement. After this time, the reaction was quickly quenched by immersion of the vessel in an ice bath. The solid residual material was dried and analyzed (UPLC-PDA). The compositional analysis was as follows: 3.0 mole% FDCA, 18.5 mole% FDMME, 78.5 mole% FDME, 0.03 mole% DME. No decarboxylation products, MF and FA, were descried.

[0046]

7) Titanium (IV) tetraisopropoxide catalyzed esterification of FDCA to FDME and FDMME

Experimental: A 75 cc 316SS Parr vessels, each equipped with a glass enclosed magnetic stir bar, was charged with 10 g of FDCA (0.064 mol), 40 g of methanol (1.25 mol), and 50 mg of titanium tetraisopropoxide (TYZOR® TTIP). While stirring at 875 rpm, the suspension was heated to 200°C for 60 minutes, including a 30 minute heat up requirement. After this time, the reaction was quickly quenched by immersion of the vessel in an ice bath. The solid residual material was dried and analyzed (UPLC-PDA). The compositional analysis was as follows: 5.1 mole% FDCA, 22.2 mole% FDMME, 72.7 mole% FDME, 0.01 mole% DME. No decarboxylation products, MF and FA, were descried.

[0047]

8) Titanium tetrabutoxide catalyzed esterification of FDCA to FDME and FDMME

Experimental: A 75 cc 316SS Parr vessels, each equipped with a glass enclosed magnetic stir bar, was charged with 10 g of FDCA (0.064 mol), 40 g of methanol (1.25 mol), and 50 mg of titanium tetrabutoxide (TYZOR® TBT). While stirring at 875 rpm, the suspension was heated to 200°C for 60 minutes, including a 30 minute heat up requirement. After this time, the reaction was quickly quenched by immersion of the vessel in an ice bath. The solid residual material was dried and analyzed (UPLC-PDA). The compositional analysis was as follows: 5.0 mole% FDCA, 22.0 mole% FDMME, 73.0 mole% FDME, 0.01 mole% DME. No decarboxylation products, MF and FA, were descried.

B. In FDME solvent, 8 mole equivalents methanol

[0048]

1) Titanium tetraisopropoxide catalyzed esterification of FDCA to FDME and FDMME

Experimental: A 75 cc 316SS Parr vessels, each equipped with a glass enclosed magnetic stir bar, was charged with 10 g of FDCA (0.064 mol), 30 g of FDME, 16.4 g of methanol and 50 mg of titanium tetraisopropoxide (TYZOR® TTIP). While stirring at 875 rpm, the suspension was heated to 200°C for 60 minutes, including a 30 minute heat up requirement. After this time, the reaction was quickly quenched by immersion of the vessel in an ice bath. The solid residual material was dried and analyzed (UPLC-PDA). The compositional analysis was as follows: 6.4 mole% FDCA, 50.3 mole% FDMME, 43.3 mole% FDME, 0.01 mole% DME. No decarboxylation products, MF and FA, were descried.

[0049]

2) Stannic chloride catalyzed esterification of FDCA to FDME and FDMME

Experimental: A 75 cc 316SS Parr vessels, each equipped with a glass enclosed magnetic stir bar, was charged with 10 g of FDCA (0.064 mol), 40 g of methanol (1.25 mol), and 50 mg of stannic chloride (FASCAT® 4400). While stirring at 875 rpm, the suspension was heated to 200°C for 60 minutes, including a 30 minute heat up requirement. After this time, the reaction was quickly quenched by immersion of the vessel in an ice bath. The solid residual material was dried and analyzed (UPLC-PDA).

The compositional analysis was as follows: 5.8 mole% FDCA, 44.7 mole% FDMME, 49.5 mole% FDME, 0.6 mole% DME. No decarboxylation products, MF and FA, were descried.

IV. Comparative Brønsted Acids

A. Sulfuric acid catalyzed esterification of FDCA to FDME and FDMME

[0050]

Experimental: A 75 cc 316SS Parr vessels, each equipped with a glass enclosed magnetic stir bar, was charged with 10 g of FDCA (0.064 mol), 40 g of methanol (1.25 mol), and 50 mg of sulfuric acid (Sigma Aldrich). While stirring at 875 rpm, the suspension was heated to 200°C for 60 minutes, including a 30 minute heat up requirement. After this time, the reaction was quickly quenched by immersion of the vessel in an ice bath. The solid residual material was dried and analyzed (UPLC-PDA). The compositional analysis was as follows: 0.7 mole% FDCA, 11.2 mole% FDMME, 88.1 mole% FDME, 2.5 mole% DME. No decarboxylation products, MF and FA, were descried.

B. Triflic acid catalyzed esterification of FDCA to FDME and FDMME

[0051]

Experimental: A 75 cc 316SS Parr vessels, each equipped with a glass enclosed magnetic stir bar, was charged with 10 g of FDCA (0.064 mol), 40 g of methanol (1.25 mol), and 50 mg of triflic acid (Sigma Aldrich). While stirring at 875 rpm, the suspension was heated to 200°C for 60 minutes, including a 30 minute heat up requirement. After this time, the reaction was quickly quenched by immersion of the vessel in an ice bath. The solid residual material was dried and analyzed (UPLC-PDA) The compositional analysis was as follows: 0.5 mole% FDCA, 10.7 mole% FDMME, 88.8 mole% FDME, 2.6 mole% DME. No decarboxylation products, MF and FA, were descried.

C. *p*-Toluenesulfonic acid catalyzed esterification of FDCA to FDME and FDMME

[0052]

Experimental: A 75 cc 316SS Parr vessels, each equipped with a glass enclosed magnetic stir bar, was charged with 10 g of FDCA (0.064 mol), 40 g of methanol (1.25 mol), and 50 mg of *p*-toluenesulfonic acid (Sigma Aldrich). While stirring at 875 rpm, the suspension was heated to 200°C for 60 minutes, including a 30 minute heat up requirement. After this time, the reaction was quickly quenched by immersion of the vessel in an ice bath. The solid residual material was dried and analyzed (UPLC-PDA). The compositional analysis was as follows: 2.6 mole% FDCA, 17.1 mole% FDMME, 80.3 mole% FDME, 1.1 mole% DME. No decarboxylation products, MF and FA, were descried.

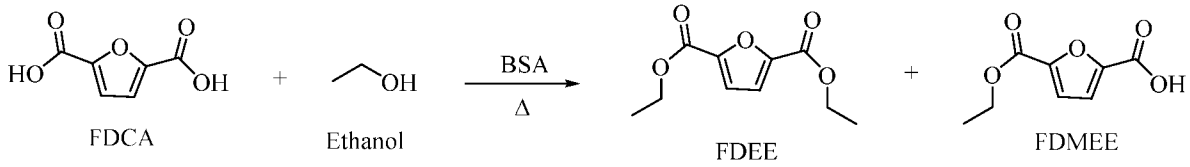
D. Phosphonic acid

[0053]

Experimental: A 75 cc 316SS Parr vessels, each equipped with a glass enclosed magnetic stir bar, was charged with 10 g of FDCA (0.064 mol), 40 g of methanol (1.25 mol), and 50 mg of phosphonic acid (Sigma Aldrich). While stirring at 875 rpm, the suspension was heated to 200°C for 60 minutes, including a 30 minute heat up requirement. After this time, the reaction was quickly quenched by immersion of the vessel in an ice bath. The solid residual material was dried and analyzed (UPLC-PDA). The compositional analysis was as follows: 3.2 mole% FDCA, 17.9 mole% FDMME, 78.9 mole% FDME, 0.9 mole% DME. No decarboxylation products, MF and FA, were descried.

V. FDCA esterification with other alcohols, example effectiveness of select catalyst butylstannoic acid

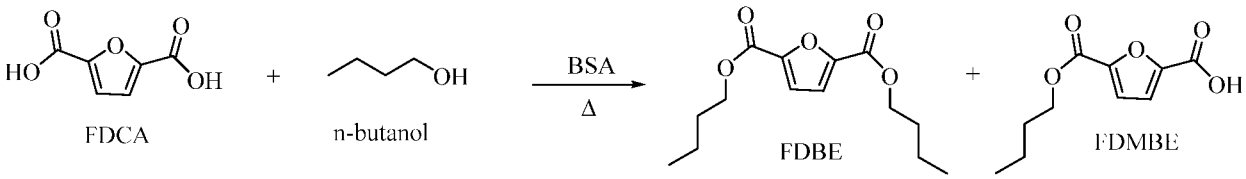
A. FDCA esterification with ethanol to FDEE and FDMEE



[0054]

Experimental: A 75 cc 316SS Parr vessels, each equipped with a glass enclosed magnetic stir bar, was charged with 10 g of FDCA (0.064 mol), 40 g of ethanol and 50 mg of butylstannoic acid (FASCAT® 9100). While stirring at 875 rpm, the suspension was heated to 200°C for 60 minutes, including a 30 minute heat up requirement. After this time, the reaction was quickly quenched by immersion of the vessel in an ice bath. The liquid residual material was dried and analyzed by ^{1}H NMR (400 MHz, d^{6}-DMSO). The compositional analysis was as follows: 0.8 mole% FDCA, 15.4 mole% FDMEE, 83.8 mole% FDEE. No decarboxylation products, MF and FA, were descried.

B. FDCA esterification with n-butanol to FDBE and FDMBE

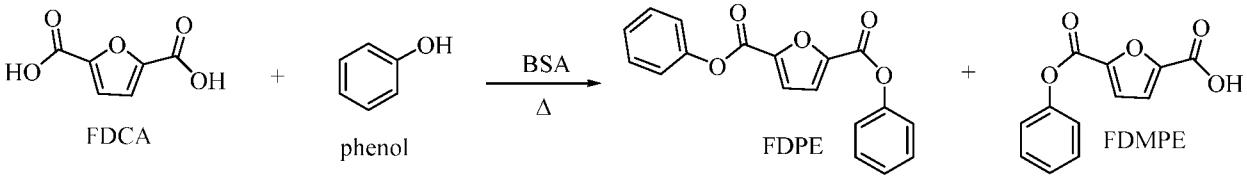


[0055]

Experimental: A 75 cc 316SS Parr vessels, each equipped with a glass enclosed magnetic stir bar, was charged with 10 g of FDCA (0.064 mol), 40 g of n-butanol and 50 mg of butylstannoic acid (FASCAT® 9100). While stirring at 875 rpm, the suspension was heated to 200°C for 60 minutes, including a 30

minute heat up requirement. After this time, the reaction was quickly quenched by immersion of the vessel in an ice bath. The liquid residual material was dried and analyzed by ^{1}H NMR (400 MHz, d^6-DMSO). The compositional analysis was as follows: 0.8 mole% FDCA, 17.2 mole% FDMBE, 82.0 mole% FDBE. No decarboxylation products, MF and FA, were descried.

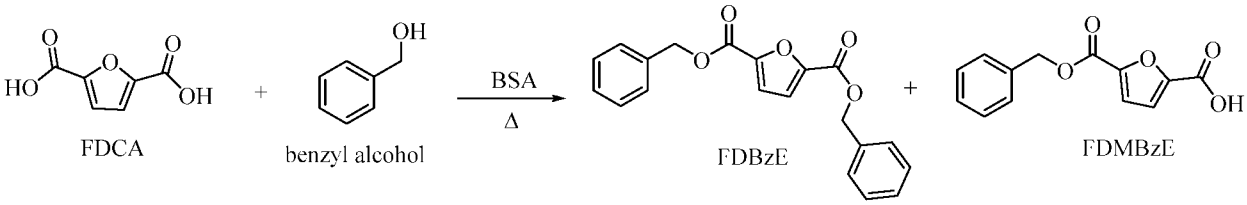
C. FDCA esterification with phenol to FDPE and FDMPE



[0056]

Experimental: A 75 cc 316SS Parr vessels, each equipped with a glass enclosed magnetic stir bar, was charged with 10 g of FDCA (0.064 mol), 40 g of phenol and 50 mg of butylstannoic acid (FASCAT® 9100). While stirring at 875 rpm, the suspension was heated to 200°C for 60 minutes, including a 30 minute heat up requirement. After this time, the reaction was quickly quenched by immersion of the vessel in an ice bath. The liquid residual material was dried and analyzed by ^{1}H NMR (400 MHz, d^6-DMSO). The compositional analysis was as follows: 1.2 mole% FDCA, 15.5 mole% FDMPE, 82.1 mole% FDPE. No decarboxylation products, MF and FA, were descried.

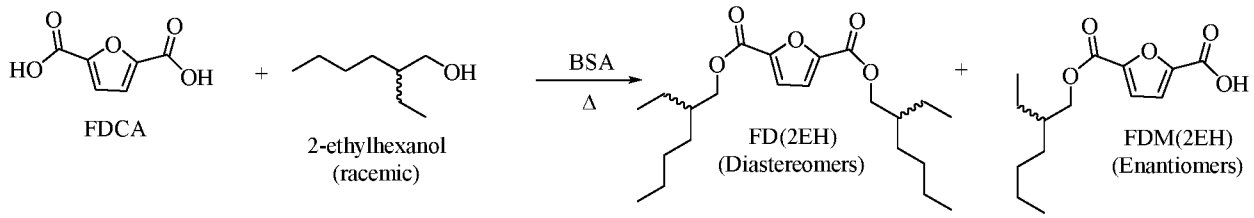
D. FDCA esterification with benzyl alcohol to FDBzE and FDMBzE



[0057]

Experimental: A 75 cc 316SS Parr vessels, each equipped with a glass enclosed magnetic stir bar, was charged with 10 g of FDCA (0.064 mol), 40 g of benzyl alcohol and 50 mg of butylstannoic acid (FASCAT® 9100). While stirring at 875 rpm, the suspension was heated to 200°C for 60 minutes, including a 30 minute heat up requirement. After this time, the reaction was quickly quenched by immersion of the vessel in an ice bath. The liquid residual material was dried and analyzed by ^{1}H NMR (400 MHz, d^6-DMSO). The compositional analysis was as follows: 1.9 mole% FDCA, 21.1 mole% FDMBzE, 73.0 mole% FDBzE. No decarboxylation products, MF and FA, were descried.

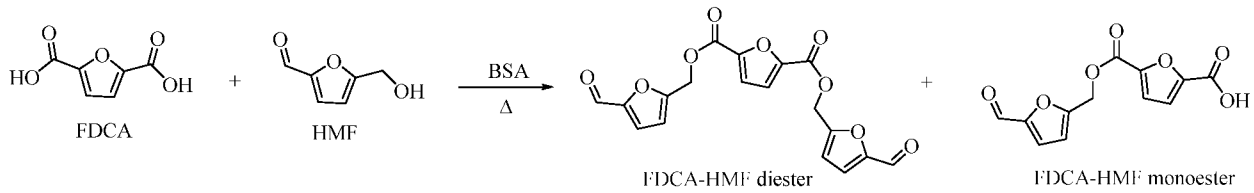
E. FDCA esterification with 2-ethylhexanol to FD(2EH)and FDM(2EH).



[0058]

Experimental: A 75 cc 316SS Parr vessels, each equipped with a glass enclosed magnetic stir bar, was charged with 10 g of FDCA (0.064 mol), 40 g of 2-ethylhexanol and 50 mg of butylstannoic acid (FASCAT® 9100). While stirring at 875 rpm, the suspension was heated to 200°C for 60 minutes, including a 30 minute heat up requirement. After this time, the reaction was quickly quenched by immersion of the vessel in an ice bath. The liquid residual material was dried and analyzed by ^{1}H NMR (400 MHz, d^{6}-DMSO). The compositional analysis was as follows: 3.2 mole% FDCA, 21.1 mole% FDM(2EH), 75.7 mole% FD(2EH). No decarboxylation products, MF and FA, were descried.

F. FDCA esterification with 5-hydroxymethyl-2-furfural (HMF) to FDCA-HMF monoester and FDCA-HMF diester.



[0059]

Experimental: A 75 cc 316SS Parr vessels, each equipped with a glass enclosed magnetic stir bar, was charged with 10 g of FDCA (0.064 mol), 40 g of HMF and 50 mg of butylstannoic acid (FASCAT® 9100). While stirring at 875 rpm, the suspension was heated to 200°C for 60 minutes, including a 30 minute heat up requirement. After this time, the reaction was quickly quenched by immersion of the vessel in an ice bath. The liquid residual material was dried and analyzed by ^{1}H NMR (400 MHz, d^{6}-DMSO). The compositional analysis was as follows: 2.1 mole% FDCA, 26.0 mole FDCA-HMF monoester, 68.7 mole% FDCA-HMF diester. No decarboxylation products, MF and FA, were descried.

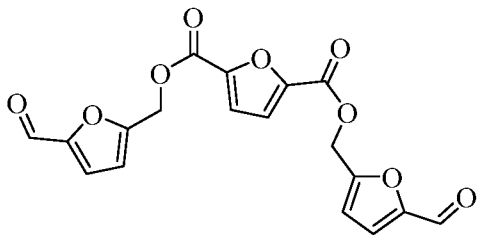
[0060] Although the present invention has been described generally and by way of examples, it is understood by those persons skilled in the art that the invention is not necessarily limited to the embodiments specifically disclosed, and that modifications and variations can be made without departing from the spirit and scope of the invention. Thus, unless changes otherwise depart from the scope of the invention as defined by the following claims, they should be construed as included herein.

CLAIMS

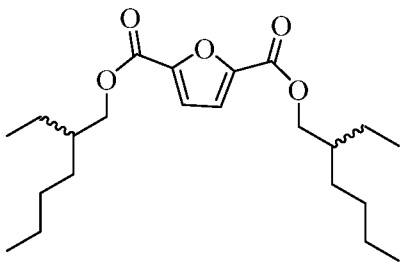
We claim:

1. A process of preparing esters of furan-2,5-dicarboxylic acid (FDCA) comprising: reacting FDCA with at least an alcohol or a mixture of different alcohols in either an alcohol or diester solvent matrix in the presence of a homogeneous organotin catalyst at a loading level of up to 10 mol.% for a reaction time and temperature sufficient to esterify said FDCA and produce a di-ester species at a FDCA conversion of at least 80 mol.%, and a di-ester yield of at least 5 mol.% greater than a comparable amount of Brønsted acid catalyst.
2. The process according to claim 1, wherein said alcohol is either an aliphatic, having C_1-C_{20} chain, or aromatic alcohol species.
3. The process according to claim 2, wherein said alcohol is selected from the group consisting of: methanol, ethanol, propanol, isopropanol, n-butanol, sec-butanol, isobutanol, n-pentanol, 2-pentanol, 3-pentanol, n-hexanol, isohexanol, 2-ethylhexanol, heptanol, octanol, nonanol, decanol, phenol, benzyl alcohol, and 5-hydroxymethylfurfural.
4. The process according to claim 1, wherein either said alcohol solvent matrix or di-ester matrix is sufficient to dissolve said FDCA, at about 50 wt.% to about 99 wt.% relative to an amount of FDCA.
5. The process according to claim 4, wherein either said alcohol solvent matrix or di-ester solvent matrix is at about 75 wt.% to about 97 wt.% relative to an amount of FDCA.
6. The process according to claim 1, wherein a tin ion of said organotin catalyst is Sn (IV).
7. The process according to claim 1, wherein said organotin catalyst has at least one tin-carbon covalent bond.
8. The process according to claim 1 or 6, wherein said organotin catalyst is selected from the group consisting of: butylstannoic acid, dibutyltin oxide, dibutyltin diacetate, butyltin tris 2-ethylhexanoate, dibutyltin maleate, dibutyltin dilaurate, dioctyltin oxide, dibutyltin bis(1-thioglyceride), dibutyltin dichloride, and monobutyltin dihydroxychloride.
9. In certain particularly favored embodiments, the organotin catalyst can be selected from: butylstannoic acid, dibutyltin oxide, dibutyltin diacetate, butyltin tris 2-ethylhexanoate.
10. The process according to claim 1, wherein said process using a homogeneous organotin catalyst achieves a FDCA conversion of at least 5% greater, or a mono- or di-ester yield of at least 10 mol.% greater than a process reacted using a comparable amount of Brønsted acid catalyst.
11. The process according to claim 1, wherein said loading level of organotin catalyst is in a range from about 0.01 mo.% to about 5 mol.%.

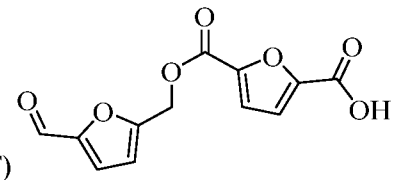
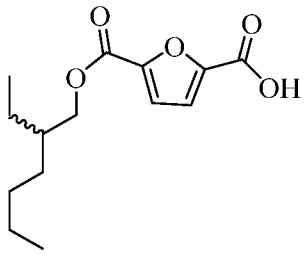
12. The process according to claim 11, wherein said loading level of said organotin catalysts is in a range from about 0.01 mol.% to about 1.5 mol.%.
13. The process according to claim 1, wherein said reaction time is up to about 12 hours.
14. The process according to claim 13, wherein said reaction time is in a range from about 10 minutes to about 8 hours.
15. The process according to claim 1, wherein said reaction temperature is in a range from about 80°C to about 275°C.
16. The process according to claim 15, wherein said reaction temperature is in a range from about 110°C to about 250°C.
17. The process according to claim 1, wherein said FDCA conversion is at least 85 mol.% to a mono- or di-ester.
18. The process according to claim 22, wherein said FDCA conversion is at least about 90 mol.% to about 99 mol.%.
19. The process according to claim 1, wherein said yield of diester is at least 70 mol.%.
20. The process according to claim 19, wherein said yield of diester is about 80 mol.% to about 95 mol.%.
21. The process according to claim 1, wherein said di-ester includes: bis((5-formylfuran-2-yl)methyl) furan-2,5-dicarboxylate (FDCA-HMF)



and bis(2-ethylhexyl) furan-2,5-dicarboxylate (FDCA



di(2EH)).

22. The process according to claim 1, wherein mono-ester includes: 5-(((5-formylfuran-2-yl)methoxy)carbonyl)furan-2-carboxylic acid (FDCA-HMF)  and 5-(((2-ethylhexyl)oxy)carbonyl)furan-2-carboxylic acid (FDCA-2EH) .

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US16/62491

A. CLASSIFICATION OF SUBJECT MATTER
IPC - C08L 67/02; B29C 47/88 (2016.01)
CPC - B29C 47/8845, 47/0019; C08G 63/181, 63/199

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)
See Search History document

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
See Search History document

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
See Search History document

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2015/0307704 A1 (DOW GLOBAL TECHNOLOGIES LLC) 29 October 2015; abstract; paragraphs [0029]-[0035], [0044], [0070]-[0071]	1-7, 8/1, 8/6, 9-22
Y	US 2015/0315166 A1 (ARCHER DANIELS MIDLAND COMPANY) 05 November 2015; paragraphs [0031]-[0033], [0036], [0039]	1-7, 8/1, 8/6, 9-22
Y	US 2014/0128623 A1 (EASTMAN CHEMICAL COMPANY) 08 May 2014; abstract; paragraphs [0002], [0018], [0027], [0053]	21-22

☐ 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	Date of mailing of the international search report
29 December 2016 (29.12.2016)	03 FEB 2017
Name and mailing address of the ISA/ Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-8300	Authorized officer Shane Thomas PCT Helpdesk: 571-272-4300 PCT OSP: 571-272-7774

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