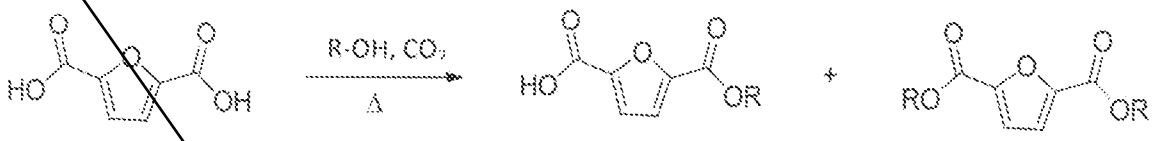
CLAIMS

We Claim:

1. A method of producing one or more furan dicarboxylates, the method comprises: reacting furan dicarboxylic acid (FDCA) with at least an alcohol or a mixture of different alcohols in a CO_2 atmosphere in substantial absence of any other extrinsic catalyst, according to the following:



to yield a mixture of esters, wherein R-group is at least a saturated, unsaturated, cyclic, or aromatic group.

2. The method according to claim 1, wherein the R-group is C_1 to C_{20}.
3. The method according to claim 1, wherein said CO_2 functions as a self-generating acid catalyst *in situ* and regenerates back to a reagent during ester synthesis.
4. The method according to claim 1, wherein said reaction of FDCA with an alcohol in CO_2 is performed under temperature and pressure conditions that are either supercritical, critical or near-critical for at least one of said alcohol or mixture of alcohols or CO_2.
5. The method according to claim 3, wherein said synthesis is performed at a temperature between about 150°C and 250°C, at a pressure of about 400 psi up to about 3000 psi.
6. The method according to claim 1, wherein said mixture of esters includes monoesters and diesters.
7. The method according to claim 1, further comprises reacting said mixture of esters in a second esterification reaction to regenerate said alcohol, and recycling said alcohol back to react with additional FDCA.
8. The method according to claim 1, further comprises separating mono-alkyl esters from di-alkyl esters by means of either crystallization or acid-base extraction.
9. The method according to claim 1, wherein said alcohol is a C_2-C_6-diol.
10. A method of synthesizing a furan diester, the method comprises: reacting furan dicarboxylic acid (FDCA) with an alcohol in CO_2 atmosphere in the substantial absence of any other acid catalyst under operational conditions that are at either supercritical, critical, or near critical temperatures and pressures for the alcohol or CO_2 gas.
11. The method according to claim 10, wherein said operational conditions, temperatures, and pressures are modified selectively to drive said synthesis reaction toward formation of diester molecules.

12. The method according to claim 10, wherein said operational conditions is at a reaction temperature between about 160°C and 250°C, at an reaction pressure of between about 400 psi and 3000 psi.
13. The method according to claim 10, further comprising separating monoesters from diesters by means of an ion exchange resin, acid-base extraction, distillation, or crystallization.
14. The method according to claim 10, wherein said alcohol is a C_2-C_6-diol.
15. A method of processing furan dicarboxylic acid (FDCA), the method comprises: reacting FDCA with a first alcohol in CO_2 atmosphere in the substantial absence of any other catalyst to produce a first ester mixture; reacting said first ester mixture with a second alcohol in a transesterification reaction to produce a second ester mixture.
16. The method according to claim 15, wherein further comprises regenerating said first alcohol, and recycling said first alcohol back to react with additional FDCA.
17. The method according to claim 15, wherein said first alcohol is a C_1 to C_{20} alcohol.
18. The method according to claim 17, wherein said first alcohol is: methanol, ethanol or propanol.
19. The method according to claim 15, wherein said second alcohol is a C_2-C_{12} alcohol.
20. The method according to claim 19, wherein said second alcohol is a C_2-C_6-diol.
21. The method according to claim 15, wherein said first ester mixture includes either mono-esters or diesters of any one of the following species: methyl furan dicarboxylate, ethyl furan dicarboxylate, or propyl furan dicarboxylate.
22. The method according to claim 15, wherein said reaction of FDCA with an alcohol in CO_2 is performed under operational conditions either at supercritical, critical or near-critical reaction temperatures and pressures for said alcohol or CO_2.
23. The method according to claim 15, wherein said reaction of FDCA with an alcohol in CO_2 is performed at a reaction temperature of between about 150°C and 250°C, at a reaction pressure of about 400 psi up to about 3000 psi.
24. The method according to claim 23, wherein said reaction of FDCA with an alcohol in CO_2 is performed at a reaction temperature between about 170°C and about 230°C, at a reaction pressure of about 920 psi to about 2500 psi.
25. The method according to claim 15, wherein said first ester mixture is transesterified by means of base-catalyzed or enzymatic reactions.
26. The method according to claim 15, wherein said transesterification reaction is performed at about 80°C to about 90°C.
27. The method according to claim 15, wherein a boiling point of said second alcohol is at least 10°C to 20°C greater than that of said first alcohol.

28. The method according to claim 15, wherein said transesterification reaction is performed under reduced pressure at said boiling point of said first alcohol.

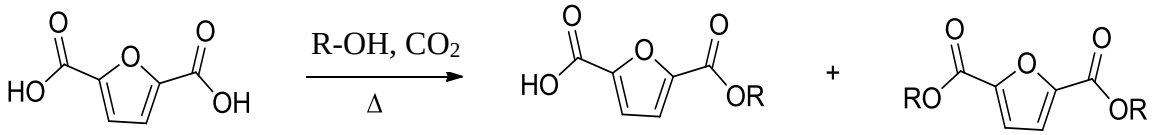
29. The method according to claim 15, wherein said transesterification reaction is by means of a lipase enzymatic reaction.

30. The method according to claim 29, wherein said lipase is of *Candida antartica*.

CLAIMS

We Claim:

1. A method of producing one or more furan dicarboxylates, the method comprises: reacting furan dicarboxylic acid (FDCA) with at least an alcohol or a mixture of different alcohols in a CO_2 atmosphere in substantial absence of any other extrinsic catalyst, according to the following:



to yield a mixture of esters, wherein R-group is at least a saturated, unsaturated, cyclic, or aromatic group, wherein said CO_2 functions as a self-generating acid catalyst *in situ* and regenerates back to a reagent during ester synthesis.

2. The method according to claim 1, wherein said reaction of FDCA with an alcohol in CO_2 is performed under temperature and pressure conditions that are either supercritical, critical or near-critical for at least one of said alcohol or mixture of alcohols or CO_2.
3. The method according to claim 2, wherein said synthesis is performed at a temperature between about 150°C and 250°C, at a pressure of about 400 psi up to about 3000 psi.
4. The method according to claim 1, further comprises reacting said mixture of esters in a second esterification reaction to regenerate said alcohol, and recycling said alcohol back to react with additional FDCA.
5. The method according to claim 1, wherein the R-group is C_1 to C_{20}.
6. The method according to claim 1, wherein said alcohol is a C_2-C_6-diol.
7. A method of synthesizing a furan diester, the method comprises: reacting furan dicarboxylic acid (FDCA) with an alcohol in CO_2 atmosphere in the substantial absence of any other acid catalyst under operational conditions that are at either supercritical, critical, or near critical temperatures and pressures for the alcohol or CO_2 gas.
8. The method according to claim 7, wherein said operational conditions, temperatures, and pressures are modified selectively to drive said synthesis reaction toward formation of diester molecules.
9. A method of processing furan dicarboxylic acid (FDCA), the method comprises: reacting FDCA with a first alcohol in CO_2 atmosphere in the substantial absence of any other catalyst to produce

a first ester mixture; reacting said first ester mixture with a second alcohol in a transesterification reaction to produce a second ester mixture.

10. The method according to claim 9, wherein further comprises regenerating said first alcohol, and recycling said first alcohol back to react with additional FDCA.
11. The method according to claim 9, wherein said first alcohol is a C_1 to C_{20} alcohol.
12. The method according to claim 9, wherein said second alcohol is a C_2-C_{12} alcohol.
13. The method according to claim 9, wherein said first ester mixture includes either mono-esters or diesters of any one of the following species: methyl furan dicarboxylate, ethyl furan dicarboxylate, or propyl furan dicarboxylate.
14. The method according to claim 9, wherein said reaction of FDCA with an alcohol in CO_2 is performed under operational conditions either at supercritical, critical or near-critical reaction temperatures and pressures for said alcohol or CO_2.
15. The method according to claim 9, wherein said reaction of FDCA with an alcohol in CO_2 is performed at a reaction temperature of between about 150°C and 250°C, at a reaction pressure of about 400 psi up to about 3000 psi.
16. The method according to claim 15, wherein said reaction of FDCA with an alcohol in CO_2 is performed at a reaction temperature between about 170°C and about 230°C, at a reaction pressure of about 920 psi to about 2500 psi.
17. The method according to claim 9, wherein said first ester mixture is transesterified by means of base-catalyzed or enzymatic reactions.
18. The method according to claim 9, wherein said transesterification reaction is performed at about 80°C to about 90°C.
19. The method according to claim 9, wherein a boiling point of said second alcohol is at least 10°C to 20°C greater than that of said first alcohol.
20. The method according to claim 9, wherein said transesterification reaction is by means of a lipase enzymatic reaction.
21. The method according to claim 20, wherein said lipase is of *Candida antartica*.