CLAIMS

We Claim:

1. A process for recovering and using carboxylic acids from a fermentation broth, the process comprises: a) obtaining a fermentation broth having an adjusted pH of less than 5, containing at least one free carboxylic acid or a mixture of carboxylic acids~~, or at least one free carboxylic acid and an associated alkali or alkaline earth metal salts thereof~~; b) drying said fermentation broth containing free carboxylic acid into a powder, and c) synthesizing an ester by reacting said carboxylic acid in said powder with an alcohol solvent under a CO_2 atmosphere in substantial absence of any other acid catalyst at either a reaction temperature or pressure or both which corresponds to supercritical, critical, or near critical conditions for at least one of said alcohol or CO_2.

2. The process according to claim 1, further comprising converting said ester back to a free carboxylic acid.

3. The process according to claim 1, wherein said fermentation broth contains cell mass and insoluble compounds and further comprises filtering said fermentation broth to remove said cell mass and insoluble compounds either before drying or after ester synthesis.

4. The process according to claim 1, further comprising concentrating said ester.

5. The process according to claim 3, wherein said fermentation broth is part of a continuous fermentation process, and further comprising recycling said insoluble compounds back into said fermentation broth.

6. The process according to claim 3, wherein said fermentation broth is part of a batch fermentation process, and further comprising recycling said insoluble compounds into a second fermentation reactor.

7. The process according to claim 1, wherein said alcohol has an R-group of C_1-C_{20} that is at least a saturated, unsaturated, cyclic, or aromatic species.

8. The process according to claim 1, wherein said alcohol is a C_2-C_6-diol.

9. The process according to claim 1 , wherein said carboxylic acid is selected from: formic acid, acetic acid, propionic acid, lactic acid, butyric acid, isobutyric acid, valeric acid, hexanoic acid, heptanoic acid, decanoic acid, lauric acid, myristic acid, and C_{15}-C_{18} fatty acids, fumaric acid, itaconic acid, malic acid, succinic acid, maleic acid, malonic acid, glutaric acid, glucaric acid, oxalic acid, adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid,

dodecanedioic acid, glutaconic acid, ortho-phthalic acid, isophthalic acid, terephthalic acid, citric acid, isocitric acid, aconitic acid, tricarballylic acid, and trimesic acid.

10. The process according 10 claim 1, wherein said carboxylic acid is a polycarboxylic acid.

11. The process according to claim 10, wherein said polycarboxylic acid is a dicarboxylic or a tricarboxylic acid.

12. The process according to claim 11, wherein said synthesized ester is predominantly at least a diester.

13. The process according to claim 1, wherein said reaction temperature is between about 150°C and about 250°C, and said pressure is between about 400 psi and 3,000 psi.

14. The process according to claim 1 , wherein said free carboxylic acids are not subject to activation with a halide to form an acyl halide.

~~15. The process according to claim 1, wherein said fermentation broth is at a pH of less than 5.~~

~~16~~15. The process according to claim 1, wherein said fermentation broth is at a pH in a range between about 1.5 and about 4.5.

~~17~~16. The process according to claim 1, wherein said drying is by means of at least one of the following: spray drying, drum drying, or cryodesiccation.

~~18~~17. The process according to claim 1, wherein said mixture of free carboxylic acid contains at least a diacid, triacid, or polyacid, and said reaction with alcohol yields a minimum of 50% conversion of said diacid, triacid, or polyacid to a corresponding ester of the free carboxylic acid.

~~19~~18. The process according to claim 1 , wherein said process further comprising purifying said ester to at least about 90% purity.

~~20~~19. The process according to claim ~~19~~18, wherein said purifying is by at least one of the following: crystallization, chromatography, or distillation.

~~21~~20. The process according to claim 1, further comprises subjecting said ester to hydrogenation to produce a compound selected from one of the following: 1,4-butane- diol (BDO), tetrahydrofuran (THF), γ-butyrolactone (GBL), or N-Methyl-2-pyrrolidone (NMP).

~~22~~21. The process according to claim 1, further comprises subjecting said ester to hydrogenation or hydrogenolysis to produce a biofuel compound.

~~23~~22. The process according to claim 1, wherein the ester is further converted into pharmaceutical, cosmetic, food or feed ingredient, or polymer materials.

~~24~~23. The process according to claim 1, wherein said dried fermentation broth powder is shipped to a location different from where said fermentation broth is sourced.

~~25~~24. The process according to claim 1, wherein said reaction for ester synthesis is performed at a remote location different from where said fermentation broth is sourced.

~~26~~25. The process according to claim 1, wherein said dried fermentation broth powder is shipped to a location different from where said fermentation brow is sourced.

~~27~~26. The process according to claim 1, wherein said ester synthesis is performed at a remote location different from where said fermentation broth is sourced.

~~28~~27. An esterification method for a polycarboxylic acid comprising: providing a solution of at least one free carboxylic acid from a fermentation broth having an adjusted pH of less than 5; reacting said solution of free carboxylic acids with an alcohol in CO_2 atmosphere without any other acid catalyst; and selecting an operational reaction temperature or a reaction pressure corresponding to supercritical, critical or near critical conditions for at least one of said alcohol or CO_2 to yield an ester corresponding to said free carboxylic acid.

~~29~~28. The esterification method according to claim ~~28~~27, wherein said reaction temperature and pressure conditions preferentially drive said reaction towards formation of diester molecules over monoester molecules when the carboxylic acid is a polyacid.

~~30~~29. The esterification method according to claim ~~28~~27, wherein said reaction temperature is between about 150°C and about 250°C, and said reaction pressure is between 400 psi and about 3,000 psi, and said reaction is run for up to about 12 hours.

~~31~~30. The esterification method according to claim ~~28~~27, wherein said reaction temperature is in a range between about 180°C and about 24°C, and said reaction pressure is between about 950 psi and about 2,400 psi.

~~32~~31. The esterification method according to claim ~~28~~27, wherein said temperature is in a range between about 200°C to about 235°C, and said operational temperature is between about 1,000 psi and about 2,350 psi.

~~33~~32. The esterification method according to claim ~~28~~27, wherein said polycarboxylic acid is selected from: fumaric acid, itaconic acid, malic acid, succinic acid, maleic acid, malonic acid, glutaric acid, glucaric acid, oxalic acid, adipic acid, pimelic acid, suberic acid, and azelaic acid, sebacic acid, dodecanedioic acid, glutaconic acid, ortho-phthalic acid, isophthalic acid, terephthalic acid, citric acid, isocitric acid, aconitic acid, tricarballylic acid, and trimesic acid.

~~34~~33. The esterification method according to claim ~~28~~27, wherein said solution of free carboxylic acids further includes alkali or alkaline earth metal salts of said carboxylic acids.

~~35~~34. The esterification method according to claim ~~28~~27, wherein said free carboxylic acids are dicarboxylic acids.

~~36~~35. The esterification method according to claim ~~28~~27, wherein said free carboxylic acids are derived from a fermentation process conducted at a pH of less than the pKa of said carboxylic acids.

~~37~~36. The esterification method according to claim ~~28~~27, further comprises purifying said ester; and regenerating said free carboxylic acid.

~~38~~37. The esterification method according to claim ~~28~~27, wherein said ester is further converted into a pharmaceutical, cosmetic, food or feed ingredient, polymer material or biofuel.

~~39~~38. A method of processing an agricultural product or biomass, comprising: obtaining carbohydrates from said agricultural product or biomass; fermenting said carbohydrates to produce a fermentation broth, said fermentation broth having an adjusted pH of less than 5; drying said fermentation broth to produce a fermentation broth powder, transporting said fermentation broth powder to a second processing site; and reacting at least a free carboxylic acid or a mixture of free carboxylic acids and associated salts thereof in said dried fermentation broth at said second processing site with an alcohol solvent under a CO_2 atmosphere in substantial absence of any other extrinsic catalyst at a reaction temperature and pressure that corresponds to supercritical, critical or near critical conditions for at least the alcohol or CO_2 to synthesize an ester.

~~40~~39. The method according to claim ~~39~~38, wherein said second processing site is located nearer to a source of demand for a product derivable from said fermentation broth powder.

~~41~~40. The method according to claim ~~39~~38, further comprising transforming said synthesized ester to produce a product therefrom.