FIG. **2** shows a schematic diagram of a downstream processing that incorporates an iteration of the present esterification process. In particular, FIG. **2** depicts an example of using succinic acid or any other kind of carboxylic acid derived from a fermentation broth is extracted and reacted with an alcohol in the presence of excess CO_2 to generate esters. According to this iteration of the process, glucose, corn steep liquor, or other sugars, and $Mg(OH)_2$/NaOH are introduced into a fermentation reactor **21** and fermented **23** to produce carboxylic acids. A fermentation broth liquid **25** containing a mixture of carboxylic acids, salts (e.g., succinic acid and its sodium or magnesium salt), and other by-products is filtered **27** to remove cell mass and other insoluble matter **27***a*. The fermentation is performed at a low pH value, in which one starts at a higher pH (e.g., pH ~7 or 8) and during the course of the fermentation, the pH value drops to about 2-3. One will produce a mixture of salts and free acid present, for example, in a ratio range of about 9:1 w/w to 7:3 w/w of salt to acid. The fermentation broth is retrieved from a fermentation reactor at a pH value of less than the pKa of the carboxylic acids, (e.g., pH 5). Typically, the fermentation broth is at a pH value in a range between about 1.5 and about 4.5.

The broth extract is then dried **29** to a powder. When drying the mixed acid filtrate should remove as much water as possible. The drying step can be accomplished, for instance, by means of spray drying, drum drying, or cryo-desiccation. As with esterification in general, relatively low water content is desired, otherwise the reversible reaction will tend to hydrolyze back to the dicarboxylic acid. In the present process, a maximum residual moisture content of about 5% by weight should be maintained. One would expect an increase in ester yield of up to about 98 or 99% with samples that contain less than 3% wt. of water.

The dried powder (average moisture content between about 1 wt. % and 5 wt. %, desirably ≤3 wt. %) is then reacted **31** with an alcohol **33** which serves as an alkylating agent, in excess CO_2 at a temperature between about 180° C. to about 250° C. for a duration of about 4 hours or more to esterify the carboxylic acids. In this example, succinic acid is reacted in methanol and CO_2 to generate dimethyl succinate. Along with the free carboxylic acid, any remaining free amino acids which were in the fermentation broth are also esterified.

Once the carboxylic acid esters are generated and recovered from the fermentation broth they can be further processed as feed stock in either hydrogenation or hydrogenolysis systems. Hydrogenation or hydrogenolysis can be conducted according to various different methods, systems, and their permutations, such as described in U.S. Pat. No. 7,498,450B2 (relating to homogenous hydrogenation of dicarbocilic acids and/or anhydrides), U.S. Pat. No. 6,433,193B, or 5,969,164, (relating to a process for production of tetrahydrofuran and γ-butyrolactone by hydrogenation of maleic anhydride); U.S. Pat. No. 4,584,419A (relating to process for the production of butane-1,4-diol involving the hydrogenation of a di(C_1 to C_3 alkyl) ester of a C_4 dicarboxylic acid); UK Patent Application No. GB2207914A (relating to a process for production of a mixture of butane 1,4-diol, γ-butyrolactone, and tetrahydrofuran from maleate and fumerate); International Patent Application Nos. WO8800937A (relating to a process for the co-production of butane-1,4-diol and γ-butyrolactone by means of hydrogenation of dialkyl maleate) or WO 82/03854 (relating to a process for hydrogenolysis of a carboxylic acid ester), or an article by S. Varadarajan et al., "Catalytic Upgrading of Fermentation-Derived Organic Acids," Biotechnol. Prog. 1999, 15, 845-854, the content of each of the preceding disclosures is incorporated herein in its entirety by reference.

As the example illustrates in FIG. **2**, when reacted with methanol in accord with the reaction temperatures and pressure parameters defined above, succinic acid esterified to produce dimethyl succinate (as predominant product), $NaHCO_3$, $MgCO_3/Mg(HCO_3)_2$ and excess methanol **35**. The dimethyl succinate and methanol **37** are separated from $NaHCO_3$ and $MgCO_3$ **39**. The carbonates, unlike $CaSO_4$, can be recycled **41** back into the reactor **21**, either for a continuous process or in a fresh batch process. The dimethyl succinate and methanol are further separated **43** from each other with the methanol **33** being recycled **45**. Subsequently, the dimethyl succinate **47** is subjected to either hydrogenation or hydrogenolysis **49** and transformed into a variety of biofuel products **51**, including alkanes and/or alcohols, for instance: ethane, ethanol, propane, propanol, butane, or butanol.

Another advantage of the present process is that it can simplify the transport and processing of crops for fermentation products. For instance, with a dried fermentation broth powder one is freed from issues associated with working with wet or liquid stock. A dried fermentation broth powder can be more economically shipped to a location different from where the fermentation broth is made or obtained. This will enable the reaction for ester synthesis to be performed at a remote location different from where the fermentation broth is obtained, and expand the geography of where the final processing facilities can be situated.

Section II.—Examples

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Examples prepared according to the present esterification method are integrated into a process for isolating free carboxylic acid from a fermentation broth. The method involves generally the following steps: a) filtering a crude fermentation broth to remove cell mass and other biological debris from a fermentation broth; b) desiccating the fermentation broth; c) reacting the dried fermentation broth with an excess of methanol (CH_3OH) or ethanol (C_2H_5OH) and carbon dioxide (CO_2) at a temperature about 150° C. up to the near critical or critical temperature and under near critical or critical pressure of the alcohol and/or CO_2 reagents, to produce a mixture of monoesters and diesters and carbonate ($NaHCO3/MgCO_3$); d) filtering the reaction product to remove by-products; and e) purifying by distilling the esters.

The fermentation broth filtrate was dried to remove all or nearly all of the water to produce a powder of mixed organics. Using a spray dryer or drum dryer, one aerosolizes the raw solution containing mixed carboxylic acids to desiccate into a powder. The desiccated powder is suspended in