USING SILICA-ZIRCONIA CATALYSTS IN PROCESSES TO PURIFY FATTY ACID ETHYL ESTER COMPOSITIONS

CROSS-REFERENCE TO RELATED APPLICATION

[0001] This application claims the benefit of priority to U.S. Provisional Application No. 63/567,375 filed on March 19, 2024, the contents of which are incorporated by reference herein in their entirety.

TECHNICAL FIELD

[0002] The present disclosure is directed to methods of using silica-zirconia catalysts in processes to reduce an amount of glycidol, glycidyl esters, or both glycidol and glycidyl esters in a composition containing fatty acid ethyl esters. The present disclosure is also directed to silica-zirconia catalysts and methods of making silica-zirconia catalysts.

BACKGROUND

[0003] Glycidyl esters are known carcinogens and mutagens found in processed edible oil. These heat-generated contaminants form at temperatures as low as 200°C; however, much higher temperatures are required during the deodorization process to remove various volatile components from the oil. After crude oil is refined, bleached, and deodorized (RBD), additional oil processing is required to lower the glycidol and/or glycidyl ester concentrations to acceptable regulatory limits. These reduction methods include a wide variety of process combinations including, but not limited to, contacting the oil with an enzyme, shear mixing the oil with an acid, rebleaching the oil, and/or rerunning the deodorization at a lower temperature, but for an extended period of time. These known methods are not only inefficient and costly to operate, but further degrade the oil quality and reduce market price.

[0004] There remains a need in the art for effective methods for reducing heat-generated contaminants, such as glycidol and/or glycidyl esters, from compositions containing fatty acid ethyl esters.

[0005] This disclosure addresses the aforementioned need in the art. The methods described herein reduce an amount of glycidol, glycidyl ester, or both glycidol and glycidyl ester within a composition containing fatty acid ethyl esters, thereby providing an effective, environmentally-friendly method without the shortcomings of previously known methods. The methods disclosed herein advantageously (1) require much lower processing temperatures, (2) require shorter processing time, (3) do not increase free fatty acid content of edible oils, (4) do not result in any significant oxidation as measured by the p-anisidine value and/or the peroxide value and/or the total oxidation value of the treated fatty acid ethyl ester-containing composition, and (5) do not result in extensive double bond isomerization.

SUMMARY

[0006] In one aspect, provided herein are methods for reducing an amount of (i) glycidol, (ii) glycidyl ester, or (iii) both glycidol and glycidyl ester within a fatty acid ethyl ester-containing composition. In some embodiments, the method for reducing an amount of (i) glycidol, (ii) glycidyl ester, or (iii) both glycidol and glycidyl ester within a fatty acid ethyl ester-containing composition comprises: contacting the fatty acid ethyl ester-containing composition with an effective amount of silica-zirconia catalyst to reduce the amount of (i) glycidol, (ii) glycidyl ester, or (iii) both glycidol and glycidyl ester in the composition, wherein the amount of (i) glycidol, (ii) glycidyl ester, or (iii) both glycidol and glycidyl ester is reduced. In some embodiments, wherein the amount of (i) glycidol, (ii) glycidyl ester, or (iii) both glycidol and glycidyl ester is reduced without affecting other components of the composition comprising the fatty acid ethyl ester (i.e., without increasing a free fatty acid content of the fatty acid ethyl ester-containing composition, without any significant oxidation of the fatty acid ethyl ester-containing composition, as measured by the p-anisidine value and/or the peroxide value and/or the total oxidation value of the treated fatty acid ethyl ester-containing composition, and without extensive double bond isomerization of the fatty acid ethyl ester).

[0007] In some embodiments, the method advantageously uses a relatively short reaction time (e.g., less than or up to 60 minutes) and a relatively low reaction temperature (e.g., typically from room temperature up to about 100 °C). The method may further comprise heating the fatty acid ethyl ester-containing composition and the silica-zirconia particles, so as to more effectively reduce the glycidol, the glycidyl ester, or both the glycidol and the

glycidyl ester using the disclosed silica-zirconia catalysts. Unexpectedly, it has been found that the incorporation of an effective amount of the silica-zirconia catalyst particles described herein provides superior catalytic activity in reducing glycidol, glycidyl ester, or both glycidol and glycidyl ester present in a fatty acid ethyl ester-containing composition.

[0008] In some embodiments, the method for reducing an amount of glycidol, the glycidyl ester, or both the glycidol and the glycidyl ester within a fatty acid ethyl ester-containing edible oil provides an edible oil, desirably, with a low level of glycidol and/or glycidyl esters, i.e. less than 0.2 ppm, and with little to no change in (i) an initial free fatty acid content of the edible oil (as measured by the content of oleic acid) or (ii) an initial lipid oxidation level of the edible oil as measured by one or more of (a) p-anisidine value (AV) of the edible oil as measured by American Oil Chemists' Society (AOCS) Official Method Cd 18-90, (b) peroxide value (PV) of the edible oil as measured by AOCS Official Method Cd 8-53, and (c) total oxidation value (Totox or TV) as measured by TV = 2PV + AV, and without extensive double bond isomerization of the fatty acid ethyl ester.

[0009] In some embodiments, silica-zirconia catalyst comprises zirconia located on at least a portion of the surface of the porous silica particles. In some embodiments, the silica-zirconia catalyst comprises zirconia located in at least a portion of the pores of the porous silica particles. In some embodiments, the silica-zirconia catalyst comprises zirconia located substantially in the pores of the porous silica particles.

[0010] In some embodiments, the silica-zirconia catalyst comprises particles having a median particle size of from about 0.1 micron (μm) to about 10,000 μm. In some embodiments, the silica-zirconia catalyst comprises particles having a median particle size of from about 80.0 μm to about 400 μm. In some embodiments, the silica-zirconia catalyst comprises particles having a pore volume of at least about 0.01 cubic centimeters/gram (cc/g) as determined by Barrett-Joyner-Halenda (BJH) method. In some embodiments, the silica-zirconia catalyst comprises particles having a pore volume of at least about 0.5 cc/g as determined by Barrett-Joyner-Halenda (BJH) method. In some embodiments, the silica-zirconia catalyst comprises particles having a pore volume of from about 0.5 cc/g to about 3.0 cc/g, or greater as determined by Barrett-Joyner-Halenda (BJH) method. In some embodiments, the silica-zirconia catalyst comprises particles having an average pore diameter

of at least about 0.1 nanometers (nm) up to about 1000 nm as determined by a mercury intrusion test procedure using an Autopore IV 9520 available from Micromeritics Instrument Corp. In some embodiments, the silica-zirconia catalyst comprises particles having an average pore diameter of from about 1.0 nm to about 100.0 nm. In some embodiments, the silica-zirconia catalyst comprises particles having an average pore diameter of from about 2.0 nm to about 50.0 nm. In some embodiments, the silica-zirconia catalyst comprises particles having a BET particle surface area of about 10 m^2/g up to about 2000 m^2/g, or greater. In some embodiments, the silica-zirconia catalyst comprises particles having a BET particle surface area of at least about 25.0 m^2/g. In some embodiments, the silica-zirconia catalyst comprises particles having a BET particle surface area of about 50.0 m^2/g up to about 800 m^2/g. In some embodiments, the porous silica particles comprise silica gel, precipitated silica, or fumed silica particles.

[0011] In some embodiments, the silica-zirconia catalyst comprises particles comprising at least about 0.01 weight percent (wt%) of zirconia based on a total weight of the silica-zirconia catalyst. In some embodiments, the silica-zirconia catalyst comprises particles comprising from about 1.0 wt% to about 50.0 wt% of zirconia based on a total weight of the silica-zirconia catalyst. In some embodiments, the silica-zirconia catalyst comprises particles comprising from about 1.5 wt% to about 15.0 wt% of zirconia based on a total weight of the silica-zirconia catalyst.

[0012] In some embodiments, the silica-zirconia catalyst exhibits a pH $\leq$ 9. In some embodiments, the silica-zirconia catalyst exhibits a pH of from about 1 to about 9.

[0013] In some embodiments, the silica-zirconia catalyst comprises particles formed by: impregnating porous silica particles with a soluble zirconium compound in water; drying the impregnated porous silica particles at about 105°C for about 2 hours; and calcining the dried impregnated porous silica particles at about 500°C for about 4 hours. In some embodiments, said impregnating step allows contact between the porous silica particles and the soluble zirconium compound for about 30 minutes. In some embodiments, said method further comprises: after said impregnating step and before said drying step, allowing the impregnated porous silica particles to mill for about 60 minutes. In some embodiments, said method further comprises: mixing the composition comprising the fatty acid ethyl ester and the silica-zirconia

catalyst. In some embodiments, said contacting step occurs at room temperature. In some embodiments, said mixing step occurs at room temperature. In some embodiments, said method further comprises heating the composition comprising the fatty acid ethyl ester and the silica-zirconia catalyst up to a temperature of at least about 40.0 °C. In some embodiments, said method further comprises heating the composition comprising the fatty acid ethyl ester and the silica-zirconia catalyst up to a temperature of about 150.0 °C. In some embodiments, said heating step comprises: heating the composition comprising the fatty acid ethyl ester and the silica-zirconia catalyst up to an uppermost temperature; and maintaining the uppermost temperature for at least about 10.0 minutes. In some embodiments, said heating step comprises: heating the composition comprising the fatty acid ethyl ester and the silica-zirconia catalyst up to an uppermost temperature; and maintaining the uppermost temperature for about 30.0 minutes. In some embodiments, said heating step and said mixing step occur simultaneously. In some embodiments, said contacting step comprises mixing the composition comprising the fatty acid ethyl ester and the silica-zirconia catalyst under an inert gas flow. In some embodiments, the inert gas comprises nitrogen, argon, carbon dioxide, or any combination thereof. In some embodiments, said contacting step comprises mixing the composition comprising the fatty acid ethyl ester and the silica-zirconia catalyst under vacuum.

[0014] In some embodiments, the amount of silica-zirconia catalyst comprises at least about 0.01 wt% of the silica-zirconia catalyst based on a total weight of the silica-zirconia catalyst and the composition comprising the fatty acid ethyl ester. In some embodiments, the amount of silica-zirconia catalyst comprises from about 0.5 wt% to about 10.0 wt% of the silica-zirconia catalyst based on a total weight of the silica-zirconia catalyst and the composition comprising the fatty acid ethyl ester. In some embodiments, the amount of silica-zirconia catalyst comprises from about 1.0 wt% to about 3.0 wt% of the silica-zirconia catalyst based on a total weight of the silica-zirconia catalyst and the composition comprising the fatty acid ethyl ester.

[0015] In some embodiments, the method reduces the amount of (i) glycidol, (ii) glycidyl ester, or (iii) both glycidol and glycidyl ester to a level of less than about 10.0 parts per million (ppm) of (i) glycidol, (ii) glycidyl ester, or (iii) both glycidol and glycidyl ester in the composition comprising the fatty acid ethyl ester. In some embodiments, the method reduces

the amount of (i) glycidol, (ii) glycidyl ester, or (iii) both glycidol and glycidyl ester to a level of less than about 5.0 ppm of (i) glycidol, (ii) glycidyl ester, or (iii) both glycidol and glycidyl ester in the composition comprising the fatty acid ethyl ester. In some embodiments, the method reduces the amount of (i) glycidol, (ii) glycidyl ester, or (iii) both glycidol and glycidyl ester to a level of less than about 1.0 ppm of (i) glycidol, (ii) glycidyl ester, or (iii) both glycidol and glycidyl ester in the composition comprising the fatty acid ethyl ester. In some embodiments, the method reduces the amount of (i) glycidol, (ii) glycidyl ester, or (iii) both glycidol and glycidyl ester to a level of less than about 0.5 ppm of (i) glycidol, (ii) glycidyl ester, or (iii) both glycidol and glycidyl ester in the composition comprising the fatty acid ethyl ester. In some embodiments, the method reduces the amount of (i) glycidol, (ii) glycidyl ester, or (iii) both glycidol and glycidyl ester to a level of less than about 0.2 ppm of (i) glycidol, (ii) glycidyl ester, or (iii) both glycidol and glycidyl ester in the composition comprising the fatty acid ethyl ester.

[0016] In some embodiments, the method reduces the amount of (i) glycidol, (ii) glycidyl ester, or (iii) both glycidol and glycidyl ester within the composition comprising the fatty acid ethyl ester by at least about 50 weight percent (wt%). In some embodiments, the method reduces the amount of (i) glycidol, (ii) glycidyl ester, or (iii) both glycidol and glycidyl ester within the composition comprising the fatty acid ethyl ester by at least about 80.00 wt%. In some embodiments, the method reduces the amount of (i) glycidol, (ii) glycidyl ester, or (iii) both glycidol and glycidyl ester within the composition comprising the fatty acid ethyl ester by up to about 99.99 wt%.

[0017] In some embodiments, the composition comprising the fatty acid ethyl ester comprises (i) an oil or (ii) both an oil and an organic solvent. In some embodiments, the composition comprising the fatty acid ethyl ester comprises (i) a fatty acid ethyl ester-containing oil or (ii) both a fatty acid ethyl ester-containing oil and an organic solvent capable of dissolving fatty acid ethyl ester(s).

[0018] In some embodiments, the oil comprises an edible oil, wherein the edible oil is plant-derived oil (such as soybean oil, palm oil, corn oil, canola oil, rapeseed oil, sunflower oil, or olive oil), animal-derived oil, microbial-derived oil (such as algal oil), or a combination

thereof. In some embodiments, the organic solvent comprises heptane, hexane, toluene, diethyl ether, an alcohol, or any combination thereof.

[0019] In some embodiments, the composition comprising the fatty acid ethyl ester comprises one or more of omega-3 fatty acid ethyl esters and/or omega-6 fatty acid ethyl esters. In some embodiments, the omega-3 fatty acid ethyl esters are selected from the group consisting of α-linolenic acid ethyl ester, stearidonic acid ethyl ester, docosapentaenoic acid ethyl ester, docosahexaenoic acid ethyl ester, and eicosapentaenoic acid ethyl ester; and the omega-6 fatty acid ethyl esters are selected from the group consisting of linoleic acid and arachidonic acid.

[0020] In some embodiments, the contacting step is performed in a continuous reactor. In some embodiments, the continuous reactor is a packed bed reactor, a rotating bed reactor, a continuous stirred tank reactor (CSTR), a plug flow reactor, or a fluidized bed reactor. In some embodiments, the continuous reactor is a packed bed reactor or CSTR. In some embodiments, the contacting step occurs at a gravimetric space velocity of about 1 hr^{-1} to about 500 hr^{-1}. In some embodiments, the silica-zirconia catalyst is present in the continuous reactor at a weight percent relative to the amount of the treated composition of less than about 2%.

[0021] In another aspect, provided herein is a method of producing a purified fatty acid ethyl ester-containing edible oil, said method comprising performing the method described herein for reducing an amount of (i) glycidol, (ii) glycidyl ester, or (iii) both glycidol and glycidyl ester on an initial composition comprising a fatty acid ethyl ester to provide the purified fatty acid ethyl ester-containing edible oil. In some embodiments, the method further comprises subjecting an initial oil to a refined-bleached-deodorized (RBD) treatment to provide an intermediate oil prior to contact with the silica-zirconia catalyst described herein. In some embodiments, the method further comprises subjecting the intermediate oil to ethanolysis to provide the initial composition comprising a fatty acid ethyl ester. In some embodiments, the initial composition comprising a fatty acid ethyl ester has an initial free fatty acid content, as measured as a content of oleic acid, and said method changes the initial free fatty acid content, as measured by AOCS Official Method Ca 5a-40, by less than about 20%. In some embodiments, the initial composition comprising a fatty acid ethyl ester has an initial free fatty acid content, as measured as a content of oleic acid, and said method changes the

initial free fatty acid content, as measured by AOCS Official Method Ca 5a-40, by less than about 10%. In some embodiments, the initial composition comprising a fatty acid ethyl ester has an initial p-anisidine value (AV), and said method changes the initial p-anisidine value (AV) by less than 10 units, as measured by AOCS Official Method Cd 18-90. In some embodiments, the initial composition comprising a fatty acid ethyl ester has an initial peroxide value (PV), and said method changes the initial peroxide value by less than 10 units, as measured by AOCS Official Method Cd 8-53. In some embodiments, the purified fatty acid ethyl ester-containing edible oil has a total oxidation value of less than 10 units. In some embodiments, the purified fatty acid ethyl ester-containing edible oil demonstrates substantially no degradation, as measured by UV absorbance at 233 nm compared to the initial composition comprising a fatty acid ethyl ester.

[0022] In another aspect, provided herein are compositions comprising (i) a fatty acid ethyl ester-containing composition and (ii) the herein-disclosed silica-zirconia particulate catalyst. In some embodiments, the composition comprises (i) an oil and (ii) the herein-disclosed silica-zirconia catalyst. The composition may further comprise glycidol, the glycidyl ester, or both the glycidol and the glycidyl ester (i.e., the composition prior to being subjected to the herein-disclosed method of reducing an amount of glycidol, the glycidyl ester, or both the glycidol and the glycidyl ester) or may have a minimal or negligible amount of glycidol, the glycidyl ester, or both the glycidol and the glycidyl ester (i.e., the composition after being subjected to the herein-disclosed method of reducing an amount of glycidol, the glycidyl ester, or both the glycidol and the glycidyl ester). In some embodiments, the fatty acid ethyl ester-containing composition contains one or more omega-3 fatty acid ethyl esters and or omega-6 fatty acid ethyl esters, such as, but not limited to, docosahexaenoic acid (DHA) ethyl ester and eicosapentaenoic acid (EPA) ethyl ester.

BRIEF DESCRIPTION OF THE DRAWINGS

[0023] **FIG. 1** compares the first order reaction rate constants for reactions described in Examples 1 - 4.

[0024] **FIG. 2** shows that total glycidol reduction in the reaction with DHA/EPA ethyl esters proceeded at the same rate as the reaction with RBD palm oil.

DETAILED DESCRIPTION

[0025] Various embodiments are described hereinafter. It should be noted that the specific embodiments are not intended as an exhaustive description or as a limitation to the broader aspects discussed herein. One aspect described in conjunction with a particular embodiment is not necessarily limited to that embodiment and can be practiced with any other embodiment(s).

[0026] Unless defined otherwise, all technical and scientific terms used herein generally have the same meaning as commonly understood by one of ordinary skill in the art to which this technology belongs.

[0027] It must be noted that as used herein and in the appended claims, the singular forms "a", "and", and "the" include plural referents unless the context clearly dictates otherwise. Thus, for example, reference to "an oxide" includes a plurality of such oxides and reference to "oxide" includes reference to one or more oxides and equivalents thereof known to those skilled in the art, and so forth.

[0028] As used herein, the term "about" modifies, for example, the quantity of an ingredient in a coated particle and/or composition, concentrations, volumes, process temperatures, process times, recoveries or yields, flow rates, and like values, and ranges thereof, employed in describing the embodiments of the disclosure, and refers to variation in the numerical quantity that may occur, for example, through typical measuring and handling procedures; through inadvertent error in these procedures; through differences in the ingredients used to carry out the methods; and like proximate considerations. The term "about" also encompasses amounts that differ due to aging of a formulation with a particular initial concentration or mixture, and amounts that differ due to mixing or processing a formulation with a particular initial concentration or mixture. If there are uses of the term which are not clear to persons of ordinary skill in the art, given the context in which it is used, "about" will mean up to plus or minus 10% of the particular term. Whether modified by the term "about", the claims appended hereto include equivalents.

[0029] As used herein, the term "fatty acid ethyl ester-containing composition" (also referred to herein as "a composition comprising a fatty acid ethyl ester") is preferably any liquid containing one or more fatty acid ethyl esters, and optionally, one or more additional composition components. In some embodiments of the present technology, the glycidol, the glycidyl ester, or both the glycidol and the glycidyl ester are present within an edible oil comprising one or more omega-3 fatty acid ethyl esters and/or one or more omega-6 fatty acid ethyl esters.

[0030] As used herein, a "batch reactor" refers to a closed system, where the reactor is filled with media and reactants. The reactants are allowed to react in the reactor for a fixed time. No feed is added or product withdrawn during this time. The reaction products are removed at the end of the reaction. The reactor may have an agitator and an internal heating or cooling system. In some cases, a batch reactor may be operated in semi-batch mode where one chemical is charged to the reactor and a second chemical is added slowly.

[0031] As used herein, the term "BET particle surface area" is defined as meaning a particle surface area as measured by the Brunauer Emmet Teller (BET) nitrogen adsorption method.

[0032] As used herein, the term "crystalline" means a solid material whose constituent atoms, molecules, or ions are arranged in an ordered pattern extends in all three directions, which may be measured by X-ray diffraction or differential scanning calorimetry. As used herein, the term "amorphous" means a solid material whose constituent atoms, molecules, or ions are arranged in a random, non-ordered pattern extends in all three directions, which may be determined by X-ray diffraction or differential scanning calorimetry.

[0033] As used herein, a "continuous reactor" refers to a reactor that is characterized by a continuous flow of reactants into and a continuous flow of products from the reaction system (*e.g.*, a packed bed reactor, a rotating bed reactor, a continuous stirred tank reactor (CSTR), a plug flow reactor, or a fluidized bed reactor).

[0034] As used herein, the term "gravimetric space velocity" refers to mass flow rate of a composition comprising reactants (grams/hour) per mass of the catalyst (grams) given by the following equation:

$$Gravimetric\ Space\ Velocity = \frac{m_o}{m_c * t} \qquad [\text{hour}^{-1}]$$

where m_o is the mass (g) of oil treated over a given time, t (hour), with a given mass of catalyst, m_c (g).

[0035] As used herein, the term "particle size" refers to median particle size (D50, which is a volume distribution with 50 volume percent of the particles are smaller than this number and 50 volume percent of the particles are bigger than this number in size) measured by dynamic light scattering when the particles are slurried in water or an organic solvent such as acetone or ethanol.

[0036] As used herein, the term "pore volume" refers to the median pore volume of a plurality of particles (*e.g.*, the silica-zirconia particles disclosed herein) as determined using the Barrett-Joyner-Halenda (BJH) nitrogen porosimetry as described in DIN 66134, which is incorporated by reference herein in its entirety.

[0037] Described herein is a method for reducing an amount of (i) glycidol, (ii) glycidyl ester, or (iii) both glycidol and glycidyl ester within a composition comprising a fatty acid ethyl ester, said method comprising: contacting the composition comprising a fatty acid ethyl ester with an effective amount of a particulate silica-zirconia catalyst to reduce the amount of (i) glycidol, (ii) glycidyl ester, or (iii) both glycidol and glycidyl ester in the composition, the silica-zirconia catalyst comprising porous silica particles impregnated with zirconia, wherein the amount of (i) glycidol, (ii) glycidyl ester, or (iii) both glycidol and glycidyl ester is reduced.

[0038] In one aspect, the amount of (i) glycidol, (ii) glycidyl ester, or (iii) both glycidol and glycidyl ester is reduced without affecting other components of the composition comprising the fatty acid ethyl ester. In another aspect, the amount of (i) glycidol, (ii) glycidyl ester, or (iii) both glycidol and glycidyl ester is reduced without increasing a free fatty acid content of the fatty acid ethyl ester-containing composition, without any significant oxidation

of the fatty acid ethyl ester-containing composition as measured by the p-anisidine value and/or the peroxide value and/or the total oxidation value of the treated fatty acid ethyl ester-containing composition, and without extensive double bond isomerization of the fatty acid ethyl ester.

[0039] In one aspect, the silica-zirconia catalyst comprises zirconia located on at least a portion of the surface of the porous silica particles. In another aspect, the silica-zirconia catalyst comprises zirconia located in at least a portion of the pores of the porous silica particles. In yet another aspect, the silica-zirconia catalyst comprises zirconia located substantially in the pores of the porous silica particles.

[0040] In one aspect, the silica-zirconia catalyst comprises particles having a median particle size of from about 0.1 micron (μm) to about 10,000 μm. In another aspect, the silica-zirconia catalyst comprises particles having a median particle size of from about 80.0 μm to about 400 μm.

[0041] In one aspect, the silica-zirconia catalyst comprises particles having a pore volume of at least about 0.01 cubic centimeters/gram (cc/g) as determined by Barrett-Joyner-Halenda (BJH) method. In another aspect, the silica-zirconia catalyst comprises particles having a pore volume of at least about 0.5 cc/g as determined by Barrett-Joyner-Halenda (BJH) method. In yet another aspect, the silica-zirconia catalyst comprises particles having a pore volume of from about 0.5 cc/g to about 3.0 cc/g, or greater as determined by Barrett-Joyner-Halenda (BJH) method.

[0042] In one aspect, the silica-zirconia catalyst comprises particles having an average pore diameter of at least 0.1 nanometers (nm) up to about 1000 nm as determined by a mercury intrusion test procedure using an Autopore IV 9520 available from Micromeritics Instrument Corp. In another aspect, the silica-zirconia catalyst comprises particles having an average pore diameter of from about 1.0 nm to about 100.0 nm. In yet another aspect, the silica-zirconia catalyst comprises particles having an average pore diameter of from about 2.0 nm to about 50.0 nm.

[0043] In one aspect, the silica-zirconia catalyst comprises particles having a BET particle surface area of about 10 m^2/g up to about 2000 m^2/g, or greater. In another aspect, the silica-zirconia catalyst comprises particles having a BET particle surface area of at least about 25.0 m^2/g. In yet another aspect, the silica-zirconia catalyst comprises particles having a BET particle surface area of about 50.0 m^2/g up to about 800 m^2/g.

[0044] In one aspect, the porous silica particles comprise silica gel, precipitated silica, or fumed silica particles. In another aspect, the silica-zirconia catalyst comprises particles comprising at least about 0.01 weight percent (wt%) of zirconia based on a total weight of the silica-zirconia catalyst. In yet another aspect, the silica-zirconia catalyst comprises particles comprising from about 1.0 wt% to about 50.0 wt% of zirconia based on a total weight of the silica-zirconia catalyst. In a further aspect, the silica-zirconia catalyst comprises particles comprising from about 1.5 wt% to about 15.0 wt% of zirconia based on a total weight of the silica-zirconia catalyst.

[0045] In one aspect, the silica-zirconia catalyst comprises particles formed by: impregnating porous silica particles with a soluble zirconium compound in water; drying the impregnated porous silica particles at about 105°C for about 2 hours; and calcining the dried impregnated porous silica particles at about 500°C for about 4 hours. In another aspect, said impregnating step allows contact between the porous silica particles and the soluble zirconium compound for about 30 minutes. In a further aspect, said method further comprises, after said impregnating step and before said drying step, allowing the impregnated porous silica particles to mill for about 60 minutes. In yet another aspect, said method further comprises mixing the composition comprising the fatty acid ethyl ester and the silica-zirconia catalyst.

[0046] In one aspect, said contacting step occurs at room temperature. In another aspect, said mixing step occurs at room temperature. In a further aspect, said method further comprises heating the composition comprising the fatty acid ethyl ester and the silica-zirconia catalyst up to a temperature of at least about 40.0 °C. In yet another aspect, said method further comprises heating the composition comprising the fatty acid ethyl ester and the silica-zirconia catalyst up to a temperature of about 150.0 °C.

[0047] In one aspect, said heating step comprises: heating the composition comprising the fatty acid ethyl ester and the silica-zirconia catalyst up to an uppermost temperature; and maintaining the uppermost temperature for at least about 10.0 minutes. In another aspect, said heating step comprises: heating the composition comprising the fatty acid ethyl ester and the silica-zirconia catalyst up to an uppermost temperature; and maintaining the uppermost temperature for about 30.0 minutes. In yet another aspect, said heating step and said mixing step occur simultaneously.

[0048] In one aspect, said contacting step comprises: mixing the composition comprising the fatty acid ethyl ester and the silica-zirconia catalyst under an inert gas flow. In another aspect, the inert gas comprises nitrogen, argon, carbon dioxide, or any combination thereof. In a further aspect, said contacting step comprises: mixing the composition comprising the fatty acid ethyl ester and the silica-zirconia catalyst under vacuum.

[0049] In one aspect, the amount of silica-zirconia catalyst comprises at least about 0.01 wt% of the silica-zirconia catalyst based on a total weight of the silica-zirconia catalyst and the composition comprising the fatty acid ethyl ester. In another aspect, the amount of silica-zirconia catalyst comprises from about 0.5 wt% to about 10.0 wt% of the silica-zirconia catalyst based on a total weight of the silica-zirconia catalyst and the composition comprising the fatty acid ethyl ester. In yet another aspect, the amount of silica-zirconia catalyst comprises from about 1.0 wt% to about 3.0 wt% of the silica-zirconia catalyst based on a total weight of the silica-zirconia catalyst and the composition comprising the fatty acid ethyl ester.

[0050] In one aspect, the silica-zirconia catalyst exhibits a pH $\leq$ 9. In another aspect, the silica-zirconia catalyst exhibits a pH of from about 1 to about 9.

[0051] In one aspect, the method reduces the amount of (i) glycidol, (ii) glycidyl ester, or (iii) both glycidol and glycidyl ester to a level of less than about 10.0 parts per million (ppm) of (i) glycidol, (ii) glycidyl ester, or (iii) both glycidol and glycidyl ester in the composition comprising the fatty acid ethyl ester. In another aspect, the method reduces the amount of (i) glycidol, (ii) glycidyl ester, or (iii) both glycidol and glycidyl ester to a level of less than about 5.0 ppm of (i) glycidol, (ii) glycidyl ester, or (iii) both glycidol and glycidyl ester in the composition comprising the fatty acid ethyl ester. In a further aspect, the method reduces the

amount of (i) glycidol, (ii) glycidyl ester, or (iii) both glycidol and glycidyl ester to a level of less than about 1.0 ppm of (i) glycidol, (ii) glycidyl ester, or (iii) both glycidol and glycidyl ester in the composition comprising the fatty acid ethyl ester. In yet another aspect, the method reduces the amount of (i) glycidol, (ii) glycidyl ester, or (iii) both glycidol and glycidyl ester to a level of less than about 0.5 ppm of (i) glycidol, (ii) glycidyl ester, or (iii) both glycidol and glycidyl ester in the composition comprising the fatty acid ethyl ester. In yet a further aspect, the method reduces the amount of (i) glycidol, (ii) glycidyl ester, or (iii) both glycidol and glycidyl ester to a level of less than about 0.2 ppm of (i) glycidol, (ii) glycidyl ester, or (iii) both glycidol and glycidyl ester in the composition comprising the fatty acid ethyl ester.

[0052] In one aspect, the method reduces the amount of (i) glycidol, (ii) glycidyl ester, or (iii) both glycidol and glycidyl ester within the composition comprising the fatty acid ethyl ester by at least about 50 weight percent (wt%). In another aspect, the method reduces the amount of (i) glycidol, (ii) glycidyl ester, or (iii) both glycidol and glycidyl ester within the composition comprising the fatty acid ethyl ester by at least about 80.00 wt%. In a further aspect, the method reduces the amount of (i) glycidol, (ii) glycidyl ester, or (iii) both glycidol and glycidyl ester within the composition comprising the fatty acid ethyl ester by up to 99.99 wt%.

[0053] In one aspect, the composition comprising the fatty acid ethyl ester comprises (i) an oil or (ii) both an oil and an organic solvent. In another aspect, the composition comprising the fatty acid ethyl ester comprises (i) a fatty acid ethyl ester-containing oil or (ii) both a fatty acid ethyl ester-containing oil and an organic solvent capable of dissolving fatty acid ethyl ester(s).

[0054] In one aspect, the oil comprises an edible oil, wherein the edible oil is plant-derived oil, animal-derived oil, microbial-derived oil, or a combination thereof. In another aspect, the organic solvent comprises heptane, hexane, toluene, diethyl ether, an alcohol, or any combination thereof.

[0055] In one aspect, the composition comprising the fatty acid ethyl ester comprises one or more of omega-3 fatty acid ethyl esters and/or omega-6 fatty acid ethyl esters. In another aspect, the omega-3 fatty acid ethyl esters are selected from the group consisting of α-linolenic

acid ethyl ester, stearidonic acid ethyl ester, docosapentaenoic acid ethyl ester, docosahexaenoic acid ethyl ester, and eicosapentaenoic acid ethyl ester; and the omega-6 fatty acid ethyl esters are selected from the group consisting of linoleic acid and arachidonic acid.

[0056] In one aspect, the contacting step is performed in a continuous reactor. In another step, the continuous reactor is a packed bed reactor, a rotating bed reactor, a continuous stirred tank reactor (CSTR), a plug flow reactor, or a fluidized bed reactor. In a further aspect, the continuous reactor is a packed bed reactor or CSTR.

[0057] In one aspect, the contacting step occurs at a gravimetric space velocity of about 1 hr^{-1} to about 500 hr^{-1}. In another aspect, the silica-zirconia catalyst is present in the continuous reactor at a weight percent relative to the amount of the treated composition of less than about 2%.

[0058] In one aspect, a method of producing a purified fatty acid ethyl ester-containing edible oil is described herein. The method comprises performing the method of any one of the aspects above on an initial composition comprising a fatty acid ethyl ester to provide the purified fatty acid ethyl ester-containing edible oil. In another aspect, said method further comprises subjecting an initial oil to a refined-bleached-deodorized (RBD) treatment to provide an intermediate oil prior to contact with the silica-zirconia catalyst as described in the method of any one of the preceding aspects. In yet another aspect, said method further comprises subjecting the intermediate oil to ethanolysis to provide the initial composition comprising a fatty acid ethyl ester.

[0059] In one aspect, the initial composition comprising a fatty acid ethyl ester has an initial free fatty acid content as measured as a content of oleic acid, and said method changes the initial free fatty acid content, as measured by AOCS Official Method Ca 5a-40, by less than about 20%. In another aspect, the initial composition comprising a fatty acid ethyl ester has an initial free fatty acid content as measured as a content of oleic acid, and said method changes the initial free fatty acid content, as measured by AOCS Official Method Ca 5a-40, by less than about 10%. In yet a further aspect, the initial composition comprising a fatty acid ethyl ester has an initial p-anisidine value (AV), and said method changes the initial p-anisidine value (AV) by less than 10 units, as measured by AOCS Official Method Cd 18-90. In yet

another aspect, the initial composition comprising a fatty acid ethyl ester has an initial peroxide value (PV), and said method changes the initial peroxide value by less than 10 units, as measured by AOCS Official Method Cd 8-53.

[0060] In one aspect, the purified fatty acid ethyl ester-containing edible oil has a total oxidation value of less than 10 units. In another aspect, the purified fatty acid ethyl ester-containing edible oil demonstrates substantially no degradation as measured by UV absorbance at 233 nm compared to the initial composition comprising a fatty acid ethyl ester.

Methods of Using Silica-Zirconia Catalysts

[0061] In one aspect, provided herein are methods for reducing an amount of glycidol, glycidyl ester, or both glycidol and glycidyl ester within a fatty acid ethyl ester-containing composition. The method may comprise, consist essentially of, or consist of, for example, contacting the fatty acid ethyl ester-containing composition with an effective amount of silica-zirconia catalyst for a time and at a temperature sufficient to reduce the amount of glycidol, glycidyl ester, or both glycidol and glycidyl ester. The method may further comprise mixing the fatty acid ethyl ester-containing composition and the silica-zirconia catalyst, optionally under vacuum or an inert gas with further optional heating. The method typically reduces at least about 50 weight percent (wt%) of the amount of glycidol, glycidyl ester, or both glycidol and glycidyl ester, within a given fatty acid ethyl ester-containing composition, while utilizing a relatively low reaction time and temperature. For example, the reaction time and temperature may be as little as about 60 minutes at a reaction temperature of less than about 100 °C. In some embodiments, the fatty acid ethyl ester-containing composition comprises an edible oil.

[0062] In some embodiments, the disclosed methods for reducing an amount of glycidol, glycidyl ester, or both glycidol and glycidyl ester within a fatty acid ethyl ester-containing composition comprise, consist essentially of, or consist of contacting the fatty acid ethyl ester-containing composition with an effective amount of catalyst at room temperature although other temperatures could be used (e.g., from room temperature, about 20-25 °C, up to about 150.0 °C).

[0063] In some embodiments, a heating step, when used in the disclosed methods, comprises, consists essentially of, or consists of heating the fatty acid ethyl ester-containing composition and the silica-zirconia catalyst up to a temperature of at least about 40.0 °C. In some embodiments, the heating step, when used in the disclosed methods, comprises, consists essentially of, or consists of heating the fatty acid ethyl ester-containing composition and the silica-zirconia catalyst up to a temperature of about 150.0 °C. In some embodiments, the heating step comprises, consists essentially of, or consists of heating the fatty acid ethyl ester-containing composition and the silica-zirconia catalyst to a temperature between about 20.0 °C and about 150.0 °C (or any range of temperatures between about 20.0° C and about 150.0 °C, in increments of 0.1°C, e.g., from about 20.1 °C to about 150.0 °C). The temperature may be about 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33, 34, 35, 36, 37, 38, 39, 40, 41, 42, 43, 44, 45, 46, 47, 48, 49, 50, 51, 52, 53, 54, 55, 56, 57, 58, 59, 60, 61, 62, 63, 64, 65, 66, 67, 68, 69, 70, 71, 72, 73, 74, 75, 76, 77, 78, 79, 80, 81, 82, 83, 84, 85, 86, 87, 88, 89, 90, 91, 92, 93, 94, 95, 96, 97, 98, 99, 100, 110, 120, 130, 140, or 150 °C. This includes a temperature of from about 20 °C to about 30 °C, from about 30 °C to about 40 °C, from about 40 °C to about 50 °C, from about 50 °C to about 60 °C, from about 60 °C to about 70 °C, from about 70 °C to about 80 °C, from about 80 °C to about 90 °C, from about 90 °C to about 100 °C, from about 100 °C to about 110 °C, from about 110 °C to about 120 °C, from about 120 °C to about 130 °C, from about 130 °C to about 140 °C, or from about 140 °C to about 150 °C. In some embodiments, an uppermost temperature for the heating step is about 90 °C.

[0064] Regardless of the uppermost temperature reached during the optional heating step (e.g., about 150.0 °C), the heating step, when used, desirably comprises, consists essentially of, or consists of heating the fatty acid ethyl ester-containing composition and the silica-zirconia catalyst up to a temperature of about 150.0 °C; and maintaining the temperature for at least about 10.0 minutes. In some embodiments, the heating step comprises, consists essentially of, or consists of heating the fatty acid ethyl ester-containing composition and the silica-zirconia catalyst up to the uppermost temperature (e.g., about 150.0 °C); and maintaining the uppermost temperature for about 30.0 minutes. It should be understood that, in the disclosed methods, the uppermost temperature (e.g., about 150.0 °C) of the optional heating step can be maintained at the uppermost temperature (e.g., about 150.0 °C) for any desired amount of time, for example, from about 5.0 minutes to about 60.0 minutes (or any range of

number of minutes between about 5.0 minutes and about 60.0 minutes, in increments of 0.1 minutes, e.g., from about 5.1 minutes to about 59.9 minutes). This includes about 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33, 34, 35, 36, 37, 38, 39, 40, 41, 42, 43, 44, 45, 46, 47, 48, 49, 50, 51, 52, 53, 54, 55, 56, 57, 58, 59, or 60 minutes.

[0065] In some embodiments, the heating step, when used in the disclosed methods, comprises, consists essentially of, or consists of heating the fatty acid ethyl ester-containing composition and the silica-zirconia catalyst (i) under an inert gas flow (i.e., under an inert gas blanket), (ii) under a vacuum, or (iii) both (i) under an inert gas flow and (ii) under a vacuum.

[0066] In some embodiments, the inert gas, when used, comprises, consists essentially of, or consists of nitrogen, argon, carbon dioxide, or any combination thereof.

[0067] In some embodiments, being under vacuum refers to a pressure of from about 0.05 bar to about 0.1 bar, from about 0.10 bar to about 0.20 bar, from about 0.20 bar to about 0.30 bar, from about 0.30 bar to about 0.40 bar, from about 0.40 bar to about 0.50 bar, from about 0.50 bar to about 0.60 bar, from about 0.60 bar to about 0.70 bar, from about 0.70 bar to about 0.80 bar, from about 0.80 bar to about 0.90 bar, or from about 0.90 bar to about 0.95 bar.

[0068] In some embodiments, the heating and mixing steps occur simultaneously.

[0069] The disclosed methods for reducing an amount of glycidol, glycidyl ester, or both glycidol and glycidyl ester within a fatty acid ethyl ester-containing composition are particularly useful when the fatty acid ethyl ester-containing composition comprises, consists essentially of, or consists of (i) a fatty acid ethyl ester-containing oil or (ii) both a fatty acid ethyl ester-containing oil and an organic solvent capable of dissolving fatty acid ethyl ester(s).

[0070] In some embodiments, the fatty acid ethyl ester-containing oil is an edible oil.

[0071] Non-limiting examples of edible oil include, but are not limited to, plant-derived oil (such as soybean oil, palm oil, corn oil, canola oil, rapeseed oil, sunflower oil, or olive oil), animal-derived oil, microbial-derived oil (such as algal oil), or a combination thereof. In some

embodiments, the edible oil has undergone ethanolysis in order to produce fatty acid ethyl esters from triglycerides of polyunsaturated fatty acids.

[0072] In some embodiments, the fatty acid ethyl ester-containing oil comprises, consists essentially of, or consists of one or more of omega-3 fatty acid ethyl esters and/or omega-6 fatty acid ethyl esters.

[0073] In some embodiments, the omega-3 fatty acid ethyl esters are selected from the group consisting of α-linolenic acid ethyl ester, stearidonic acid ethyl ester, docosapentaenoic acid ethyl ester, docosahexaenoic acid ethyl ester, and eicosapentaenoic acid ethyl ester; and the omega-6 fatty acid ethyl esters are selected from the group consisting of linoleic acid and arachidonic acid.

[0074] Suitable organic solvents include, but are not limited to, heptane, hexane, toluene, diethyl ether, an alcohol, or any combination thereof.

[0075] In some embodiments, the disclosed methods for reducing an amount of glycidol, glycidyl ester, or both glycidol and glycidyl ester within a fatty acid ethyl ester-containing composition comprises, consists essentially of, or consists of using an effective amount of silica-zirconia catalyst of at least about 0.01 wt% of the silica-zirconia catalyst based on a total weight of the silica-zirconia catalyst and the fatty acid ethyl ester-containing composition. In some embodiments, the amount of silica-zirconia catalyst used in the disclosed methods is from about 0.5 wt% to about 10.0 wt% of the silica-zirconia catalyst based on a total weight of the silica-zirconia catalyst and the fatty acid ethyl ester-containing composition. In other embodiments, the amount of silica-zirconia catalyst used in the disclosed methods is from about 1.0 wt% to about 3.0 wt% of the silica-zirconia catalyst based on a total weight of the silica-zirconia catalyst and the fatty acid ethyl ester-containing composition. However, it should be understood that any amount of silica-zirconia catalyst may be used in the disclosed methods for reducing an amount of glycidol, glycidyl ester, or both glycidol and glycidyl ester within a fatty acid ethyl ester-containing composition, for example, any amount from about 0.01 wt% to about 10.0 wt% (or any range of weight percents between about 0.01 wt% and about 10.0 wt%, in increments of 0.1 wt%, e.g., from about 0.6 wt% to about 9.9 wt%) of the silica-zirconia catalyst based on a total weight of the silica-zirconia catalyst and the fatty acid

ethyl ester-containing composition. This includes about 0.01, 0.02, 0.03, 0.04, 0.05, 0.06, 0.07, 0.08, 0.09, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 1.1, 1.2, 1.3, 1.4, 1.5, 1.6. 1.7, 1.8, 1.9, 2.0, 2.1, 2.2, 2.3, 2.4, 2.5, 2.6, 2.7, 2.8, 2.9, 3.0, 3.1, 3.2, 3.3, 3.4, 3.5, 3.6, 3.7, 3.8, 3.9, 4.0, 4.1, 4.2, 4.3, 4.4, 4.5, 4.6, 4.7, 4.8, 4.9, 5.0, 5.1, 5.2, 5.3, 5.4. 5.5, 5.6, 5.7, 5.8, 5.9, 6.0, 6.1, 6.2, 6.3, 6.4, 6.5, 6.6, 6.7, 6.8, 6.9, 7.0, 7.1, 7.2, 7.3, 7.4, 7.5, 7.6, 7.7, 7.8, 7.9, 8.0, 8.1, 8.2, 8.3, 8.4, 8.5, 8.6, 8.7, 8.8, 8.9, 9.0, 9.1, 9.2, 9.3, 9.4, 9.5, 9.6, 9.7, 9.8, 9.9, or 10 wt%.

[0076] Unexpectedly, it has been determined that the disclosed methods for reducing an amount of glycidol, glycidyl ester, or both glycidol and glycidyl ester within a fatty acid ethyl ester-containing composition are capable of reducing the amount of glycidol, glycidyl ester, or both glycidol and glycidyl ester within a fatty acid ethyl ester-containing composition to a level of less than about 10.0 parts per million (ppm) of the glycidol, the glycidyl ester, or both the glycidol and the glycidyl ester in the fatty acid ethyl ester-containing composition. This includes about 0.01, 0.05, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 2.0, 3.0, 4.0, 5.0, 6.0, 7.0, 8.0, 9.0, 9.1, 9.2, 9.3, 9.4, 9.5, 9.6, 9.7, 9.8, or 9.9 ppm. In some embodiments, the disclosed methods are capable of reducing the amount of glycidol, glycidyl ester, or both glycidol and glycidyl ester within a fatty acid ethyl ester-containing composition to a level of about 0.1 ppm to less than about 10.0 ppm of the glycidol, the glycidyl ester, or both the glycidol and the glycidyl ester in the fatty acid ethyl ester-containing composition. In some embodiments, the disclosed methods are capable of reducing the amount of glycidol, glycidyl ester, or both glycidol and glycidyl ester within a fatty acid ethyl ester-containing composition to a level of about 0.1 ppm to about 9.9 ppm of the glycidol, the glycidyl ester, or both the glycidol and the glycidyl ester in the fatty acid ethyl ester-containing composition. In some embodiments, the disclosed methods are capable of reducing the amount of glycidol, glycidyl ester, or both glycidol and glycidyl ester within a fatty acid ethyl ester-containing composition to a level of less than about 5.0 ppm (e.g., about 0.1 ppm to about 4.9 ppm) of the glycidol, the glycidyl ester, or both the glycidol and the glycidyl ester in the fatty acid ethyl ester-containing composition. In other embodiments, the disclosed methods are capable of reducing the amount of glycidol, glycidyl ester, or both glycidol and glycidyl ester within a fatty acid ethyl ester-containing composition to a level of less than about 1.0 ppm (e.g., about 0.1 ppm to about 0.9 ppm) of the glycidol, the glycidyl ester, or both the glycidol and the glycidyl ester in the fatty acid ethyl ester-containing composition. In other embodiments, the disclosed methods are

capable of reducing the amount of glycidol, glycidyl ester, or both glycidol and glycidyl ester within a fatty acid ethyl ester-containing composition to a level of less than about 0.5 ppm (e.g., about 0.1 ppm to about 0.4 ppm) of the glycidol, the glycidyl ester, or both the glycidol and the glycidyl ester in the fatty acid ethyl ester-containing composition. In yet other embodiments, the disclosed methods are capable of reducing the amount of glycidol, glycidyl ester, or both glycidol and glycidyl ester within a fatty acid ethyl ester-containing composition to a level of less than about 0.2 ppm (e.g., about 0.1 ppm) of the glycidol, the glycidyl ester, or both the glycidol and the glycidyl ester in the fatty acid ethyl ester-containing composition.

[0077] Unexpectedly, it has been determined that the disclosed methods for reducing an amount of glycidol, glycidyl ester, or both glycidol and glycidyl ester within a fatty acid ethyl ester-containing composition are capable of reducing at least about 50 weight percent (wt%) of the amount of glycidol, glycidyl ester, or both glycidol and glycidyl ester within a fatty acid ethyl ester-containing composition within the above-described reaction parameters (i.e., a reaction temperature of from room temperature to less than about 150 °C, and/or a reaction time of up to about 60 minutes). In some embodiments, the method reduces at least about 80.00 wt% of the amount of glycidol, glycidyl ester, or both glycidol and glycidyl ester within a fatty acid ethyl ester-containing composition. In some embodiments, the disclosed methods are capable of reducing up to about 99.99 wt% of the amount of glycidol, glycidyl ester, or both glycidol and glycidyl ester within a fatty acid ethyl ester-containing composition (or any range of weight percents between about 50.00 wt% and 99.99 wt% in increments of 0.01 wt%, e.g. from about 50.01 wt% to 99.98 wt%) within the above-described reaction parameters (i.e., a reaction temperature of from room temperature to less than about 150 °C, and/or a reaction time of up to about 60 minutes). This includes about 50, 51, 52, 53, 54, 55, 56, 57, 58, 59, 60, 61, 62, 63, 64, 65, 66, 67, 68, 69, 70, 71, 72, 73, 74, 75, 76, 77, 78, 79, 80, 81, 82, 83, 84, 85, 86, 87, 88, 89, 90, 91, 92, 93, 94, 95, 96, 97, 98, or 99 wt%.

[0078] In addition, and unexpectedly, the disclosed methods for reducing an amount of glycidol, glycidyl ester, or both glycidol and glycidyl ester within a fatty acid ethyl ester-containing composition are capable of reducing the amount of glycidol, glycidyl ester, or both glycidol and glycidyl ester within a fatty acid ethyl ester-containing composition to extremely low levels, as discussed above, without negatively impacting a free fatty acid content of the

given fatty acid ethyl ester-containing composition. In some embodiments, the given fatty acid ethyl ester-containing composition (e.g., edible oil) has a free fatty acid content prior to contact with the silica-zirconia catalyst of the present technology, and the disclosed method comprising, consisting essentially of, or consisting of, *inter alia*, contacting the fatty acid ethyl ester-containing composition (e.g., edible oil) with the silica-zirconia catalyst, has a negligible change on the free fatty acid content (i.e., as oleic acid) of the fatty acid ethyl ester-containing composition, as measured by AOCS Official Method Ca 5a-40.

[0079] In some embodiments, the method for reducing an amount of glycidol, glycidyl ester, or both glycidol and glycidyl ester within a fatty acid ethyl ester-containing composition comprises, consists essentially of, or consists of a method of producing an edible oil with a level of glycidol and/or glycidyl esters of less than about 0.2 ppm (e.g., about 0.1 ppm to less about than 0.2 ppm, about 0.1 ppm to about 0.19 ppm) and little to no change in (i) a free fatty acid content of the edible oil (i.e., as oleic acid) and/or (ii) an oxidation level of the edible oil as measured by one or more of (a) the p-anisidine value (AV) of the edible oil as measured, for example, by AOCS Official Method Cd 18-90, (b) the peroxide value of the edible oil as measured, for example, by AOCS Official Method Cd 8-53, and (c) total oxidation value (Totox or TV) as measured by TV = 2PV + AV. TV values are expected to be less than 10 units.

[0080] In some embodiments, the disclosed methods of producing an edible oil (e.g., with a level of glycidol and/or glycidyl esters of less than about 0.2 ppm) changes an initial free fatty acid content of the edible oil (i.e., as measured as content of oleic acid) by less than about 20%, by less than about 19%, by less than about 18%, by less than about 17%, by less than about 16%, by less than about 15%, by less than about 14%, by less than about 13%, by less than about 12%, by less than about 11%, by less than about 10%, by less than about 9%, by less than about 8%, by less than about 7%, by less than about 6%, by less than about 5%, by less than about 4%, by less than about 3%, by less than about 2%, or by less than about 1%. In some embodiments, the disclosed methods of producing an edible oil (e.g., with a level of glycidol and/or glycidyl esters of less than about 0.2 ppm) changes an initial free fatty acid content of the edible oil (i.e., as measured as content of oleic acid) by less than about 10%. In some embodiments, the disclosed methods of producing an edible oil (e.g., with a level of

glycidol and/or glycidyl esters of less than about 0.2 ppm) changes an initial free fatty acid content of the edible oil (i.e., as measured as content of oleic acid) by about 0% to about 10%.

[0081] As discussed in AOCS Official Method Cd 18-90, the subject matter of which is incorporated herein in its entirety, the lipid oxidation level of a given edible oil may be measured by the p-anisidine value (AV) of the edible oil. Processing of edible oils can result in an undesirable series of chemical reactions involving oxygen that degrades the quality of the edible oil. Such undesirable oxidation reactions can generate, for example, primary oxidation products such as peroxides, dienes, free fatty acids, etc., and secondary products such as carbonyls, aldehydes, trienes, etc. The p-anisidine value of the edible oil measures an amount of aldehyde within the edible oil.

[0082] In some embodiments, the disclosed method of producing an edible oil with a level of glycidol and/or glycidyl esters of less than about 0.2 ppm changes an initial p-anisidine value of the edible oil by less than about 10.0 units (e.g., about 0 to less than about 10.0 units, about 0 to about 9.9 units), as measured by AOCS Official Method Cd 18-90. This includes less than about 10 units, less than about 9 units, less than about 8 units, less than about 7 units, less than about 6 units, less than about 5 units, less than about 4 units, less than about 3 units, less than about 2 units, or less than about 1 unit, as measured by AOCS Official Method Cd 18-90. In other embodiments, the disclosed method of producing an edible oil with a level of glycidol and/or glycidyl esters of less than about 0.2 ppm changes an initial p-anisidine value of the edible oil by less than about 1.0 unit (e.g., about 0 to less than about 1.0 unit, about 0 to about 0.9 units), as measured by AOCS Official Method Cd 18-90. In other embodiments, the disclosed method of producing an edible oil with a level of glycidol and/or glycidyl esters of less than about 0.2 ppm changes an initial p-anisidine value of the edible oil by less than about 0.2 units (e.g., about 0 to less than about 0.2 units, about 0 to about 0.19 units), as measured by AOCS Official Method Cd 18-90.

[0083] The oxidation level of a given edible oil may also be measured by the peroxide value (PV) of the edible oil as measured by AOCS Official Method Cd 8-53. As discussed in AOCS Official Method Cd 8-53, the subject matter of which is incorporated herein in its entirety, the peroxide value provides a measure of the amount of peroxides within a given edible oil.

[0084] In some embodiments, the disclosed method of producing an edible oil with a level of glycidol and/or glycidyl esters of less than about 0.2 ppm changes an initial peroxide value of the edible oil by less than about 10.0 units (e.g., about 0 to less than about 10.0 units, about 0 to about 9.9 units), as measured by AOCS Official Method Cd 8-53. This includes less than about 10 units, less than about 9 units, less than about 8 units, less than about 7 units, less than about 6 units, less than about 5 units, less than about 4 units, less than about 3 units, less than about 2 units, or less than about 1 unit, as measured by AOCS Official Method Cd 8-53. In some embodiments, the disclosed method of producing an edible oil with a level of glycidol and/or glycidyl esters of less than about 0.2 ppm changes an initial peroxide value of the edible oil by less than about 7.0 units (e.g., about 0 to less than about 7.0 units, about 0 to about 6.9 units), as measured by AOCS Official Method Cd 8-53. In other embodiments, the disclosed method of producing an edible oil with a level of glycidol and/or glycidyl esters of less than about 0.2 ppm changes an initial peroxide value of the edible oil by less than about 2.0 units (e.g., about 0 to less than about 2.0 units, about 0 to about 1.9 units), as measured by AOCS Official Method Cd 8-53.

[0085] In some embodiments, edible oil is subjected to a refined-bleached-deodorized (RBD) treatment. In conventional methods of producing edible oils, after the RBD treatment, edible oils are subjected to further processing prior to use. The further processing of conventionally-prepared edible oil (i.e., not treated using the herein-described methods) includes, but is not limited to, contacting the oil with an enzyme, shear mixing the oil with an acid, rebleaching the oil, and/or rerunning the deodorization at a lower temperature but for an extended period of time, or any combination of the process steps mentioned. However, edible oils subjected to a RBD treatment and subsequently treated using the herein-described methods of producing an edible oil with a level of glycidol and/or glycidyl esters of less than about 0.2 ppm, typically do not require further processing prior to use (i.e., do not require further processing including, but not limited to, contacting the oil with an enzyme, shear mixing the oil with an acid, rebleaching the oil, and/or rerunning the deodorization at a lower temperature but for an extended period of time, or any combination of the process steps mentioned). In some embodiments, the edible oil is subjected to ethanolysis to convert triglycerides of polyunsaturated fatty acids to fatty acid ethyl esters.

[0086] In another aspect, provided herein are methods of producing a purified fatty acid ethyl ester-containing edible oil, said method comprising performing the method for reducing an amount of (i) glycidol, (ii) glycidyl ester, or (iii) both glycidol and glycidyl ester (as described herein) within an initial composition comprising a fatty acid ethyl ester to provide the purified fatty acid ethyl ester-containing edible oil. In some embodiments, the method further comprises subjecting an initial oil to a refined-bleached-deodorized (RBD) treatment to provide an intermediate oil prior to contact with the silica-zirconia catalyst described herein. In some embodiments, the method further comprises subjecting the intermediate oil to ethanolysis to provide the initial composition comprising a fatty acid ethyl ester. In some embodiments, the initial composition comprising a fatty acid ethyl ester has an initial free fatty acid content as measured as a content of oleic acid, and said method changes the initial free fatty acid content, as measured by AOCS Official Method Ca 5a-40, by less than about 20%. In some embodiments, the initial composition comprising a fatty acid ethyl ester has an initial free fatty acid content as measured as a content of oleic acid, and said method changes the initial free fatty acid content, as measured by AOCS Official Method Ca 5a-40, by less than about 10%. In some embodiments, the initial composition comprising a fatty acid ethyl ester has an initial p-anisidine value (AV), and said method changes the initial p-anisidine value (AV) by less than 10 units, as measured by AOCS Official Method Cd 18-90. In some embodiments, the initial composition comprising a fatty acid ethyl ester has an initial peroxide value (PV), and said method changes the initial peroxide value by less than about 10 units, as measured by AOCS Official Method Cd 8-53. In some embodiments, the purified fatty acid ethyl ester-containing edible oil has a total oxidation value of less than about 10 units. In some embodiments, the purified fatty acid ethyl ester-containing edible oil demonstrates substantially no degradation as measured by UV absorbance at 233 nm compared to the initial composition comprising a fatty acid ethyl ester.

[0087] In some embodiments, the contacting step is performed in a continuous reactor. Accordingly, in another aspect, provided herein are methods including contacting an initial composition comprising (i) a fatty acid ethyl ester and (ii) glycidol, a glycidyl ester, or both glycidol and a glycidyl ester with an effective amount of silica-zirconia catalyst in a continuous reactor to form a treated composition, wherein the silica-zirconia catalyst comprises porous silica particles impregnated with zirconia; and wherein the concentration of (ii) in the treated

composition is lower than a concentration of (ii) in the initial composition. Such methods are useful in reducing the concentration of glycidol, glycidyl ester, or both glycidol and glycidyl ester within the initial composition. These methods reduce at least about 50% of the concentration of glycidol, glycidyl ester, or both glycidol and glycidyl ester, within the initial composition, while utilizing a relatively low reaction time and temperature.

[0088] Unexpectedly, it has been found that utilizing a silica zirconia catalyst in a continuous reactor (*e.g.*, a packed bed reactor) improves the reaction kinetics and slows down the catalyst deactivation of the silica zirconia catalyst, as compared to a silica zirconia catalyst in a batch reactor. In some embodiments, with other reaction parameters consistent with a batch process, utilizing a silica zirconia catalyst in a continuous reactor increases the reaction constant (k) of the silica zirconia catalyst by at least about 1% as compared to that in the batch process examples. This includes about 1%, 2%, 3%, 4%, 5%, 6%, 7%, 8%, 9%, 10%, 11%, or 12% increase in the reaction constant. In some embodiments, the increase is about 8% to about 12%. Consequently, the catalyst life of the silica zirconia catalyst is increased, and the overall silica zirconia dosage amount needed to reduce the same amount of total glycidol is reduced by utilizing a silica zirconia catalyst in a continuous reactor, as compared to a silica zirconia catalyst in a batch reactor.

[0089] Any continuous reactor known to one skilled in the arts may be used. Exemplary continuous reactors include but not limited to a packed bed reactor, a rotating bed reactor, a continuous stirred tank reactor (CSTR), a plug flow reactor, or a fluidized bed reactor.

[0090] In some embodiments, the continuous reactor may be a packed bed reactor. A packed bed reactor, also known as fixed bed reactor, may be a cylindrical tube filled with catalyst pellets (*e.g.*, silica-zirconia catalysts) with reactants (*e.g.*, an initial composition comprising (i) a fatty acid ethyl ester and (ii) glycidol, a glycidyl ester, or both glycidol and a glycidyl ester) undergoing conversion into products while flowing through the bed. The catalyst may be in one or more of multiple configurations such as but not limited to: one large bed, several horizontal beds, several parallel packed tubes, or multiple beds in their own shells. The various configurations may be adapted depending on the need to maintain temperature control within the system. The flow of the reactants in a fixed bed reactor may be downward under the force of gravity.

[0091] In some embodiments, the continuous reactor may be a rotating bed reactor. A rotating bed reactor holds a packed bed fixed within a basket with a central hole. When the basket is spinning immersed in a fluid phase, the inertia forces created by the spinning motion force the fluid outwards, thereby creating a circulating flow through the rotating packed bed. The rotating bed reactor shows relatively high rates of mass/heat transfer and good fluid mixing as compared to a packed bed reactor.

[0092] In some embodiments, the continuous reactor may be a continuous stirred tank reactor (CSTR). A CSTR is an open system, where material is free to enter or exit the system, which operates on a steady-state basis, where the conditions in the reactor do not change with time. Reactants are continuously introduced into the reactor, while products are continuously removed. CSTRs are well mixed, so the contents have relatively uniform properties (such as temperature, density, etc.) throughout. Also, conditions in the reactor's exit stream may be the same as those inside the tank.

[0093] In some embodiments, the continuous reactor may be a fluidized bed reactor. In this type of reactor, a fluid (*e.g.*, an initial liquid composition comprising (i) a fatty acid ethyl ester and (ii) glycidol, a glycidyl ester, or both glycidol and a glycidyl ester) is passed through a solid granular material (*e.g.*, silica-zirconia catalysts) at high enough speeds to suspend the solid and cause it to behave as though it were a fluid. This process, known as fluidization, imparts many important advantages to a packed bed reactor. One key advantage of using a fluidized bed reactor is the ability to achieve a highly uniform temperature in the reactor.

[0094] In some embodiments, the contacting step, when using a continuous reactor, occurs at a gravimetric space velocity of about 0.1 hr^{-1} to about 500 hr^{-1}. In some embodiments, the contacting step when using a continuous reactor occurs at a gravimetric space velocity of about 0.1 $hr^{-1}$to about 5 hr^{-1}, about 5 hr^{-1} to about 10 hr^{-1}, about 10 hr^{-1} to about 20 hr^{-1}, about 20 hr^{-1} to about 30 hr^{-1}, about 30 hr^{-1} to about 40 hr^{-1}, about 40 hr^{-1} to about 50 hr^{-1}, about 50 hr^{-1} to about 60 hr^{-1}, about 60 hr^{-1} to about 70 hr^{-1}, about 70 hr^{-1} to about 80 hr^{-1}, about 80 hr^{-1} to about 90 hr^{-1}, about 90 hr^{-1} to about 100 hr^{-1}, about 100 hr^{-1} to about 110 hr^{-1}, about 110 hr^{-1} to about 120 hr^{-1}, about 120 hr^{-1} to about 180 hr^{-1}, about 180 hr^{-1} to about 240 hr^{-1}, about 240 hr^{-1} to about 300 hr^{-1}, about 300 hr^{-1} to about 360 hr^{-1}, about 360 hr^{-1} to about 420 hr^{-1}, or about 420 hr^{-1} to about 500 hr^{-1}.

[0095] In some embodiments, the method comprises contacting an initial composition comprising (i) a fatty acid ethyl ester and (ii) glycidol, a glycidyl ester, or both glycidol and a glycidyl ester with an effective amount of silica-zirconia catalyst in a continuous reactor under inert gas flow or under vacuum to minimize the oxygen concentration in the atmosphere.

[0096] In some embodiments, the silica-zirconia catalyst is present in the continuous reactor at a weight percent relative to the amount of the treated composition of less than about 2%. In some embodiments, the silica-zirconia catalyst is present in the continuous reactor at a weight percent relative to the amount of the treated composition of less than about 1%, less than about 0.5%, less than about 0.1%, less than about 0.05%, or less than about 0.01%.

Silica-Zirconia Catalysts Used In The Herein-Described Methods

[0097] The silica-zirconia catalyst used in the herein-described methods comprise porous silica particles impregnated with zirconia. As discussed above, in some embodiments, the zirconia is impregnated onto at least a portion of the surface of the porous silica particles. In some embodiments, the zirconia is impregnated in at least a portion of the pores of the porous silica particles. In some embodiments, the zirconia is impregnated so as to be located substantially in the pores of the porous silica particles.

[0098] The silica-zirconia catalysts may be formed by a zirconia coating and/or impregnation step, followed by one or more additional steps such as a drying step, a calcining step, or both. *See* International Application Publication No. WO202026905, which is incorporated herein by reference in its entirety. In some embodiments, the method of making silica-zirconia catalyst suitable for use in the herein-described methods comprises impregnating porous silica particles with a soluble zirconium compound in water (e.g., zirconium acetate in acetic acid with water); drying the impregnated porous silica particles at about 105 °C for about 2 hours; and calcining the dried impregnated porous silica particles at about 500 °C for about 4 hours. Typically, the method of making silica-zirconia catalyst comprises an impregnating step that allows contact between the porous silica particles and the soluble zirconium compound (e.g., zirconium acetate) for a desired period of time, *e.g.*, about 30 minutes or any desired period of time. After the impregnating step and before the drying step, the method of making silica-zirconia catalyst comprises allowing the impregnated porous

silica particles to mill for about 60 minutes. It should be understood that the impregnated porous silica particles may mill (or be milled) for any desired period of time. The zirconia may be impregnated onto at least a portion of the surface of the porous silica particles, and/or at least a portion of the pores of the porous silica particles.

[0099] Suitable porous silica particles useful in the preparation of the silica-zirconia catalysts of the present technology include, but are not limited to, silica gel, precipitated silica, fumed silica, and colloidal silica. Suitable porous silica also includes, but is not limited to, ordered mesoporous silica prepared through an organic template (e.g., a surfactant) during the formation of silica particles, followed by a high temperature treatment to "burn off" the organics. In some embodiments, porous silica particles comprise silica gel, precipitated silica, or fumed silica particles. In some embodiments, porous silica particles comprise silica gel or precipitated silica particles.

[0100] Any commercially available porous silica particles may be used to form the silica-zirconia catalysts of the present technology. Commercially available porous silica particles useful for forming the silica-zirconia catalysts of the present technology include, but are not limited to, particles available from W.R. Grace (Columbia, MD) under the trade designation SYLOID® such as SYLOID® C807 silica gel particles and SYLOID® MX106 precipitated silica particles, SYLOBLOC® silica particles, and DARACLAR® silica particles.

[0101] The porous silica particles used to form the silica-zirconia catalysts described herein comprise porous silica having a purity of at least about 93.0% by weight SiO_2, or at least about 93.5% by weight SiO_2, at least about 94.0% by weight SiO_2, at least about 95.0% by weight SiO_2, at least about 96.0% by weight SiO_2, at least about 97.0% by weight SiO_2, or at least about 98.0% by weight SiO_2, up to 100% by weight SiO_2 based upon the total weight of the porous silica particle. In some embodiments, the purity is about 93.0% by weight SiO_2 to 100% by weight SiO_2 based upon the total weight of the porous silica particle.

[0102] The porous silica particles used to form the silica-zirconia catalysts described herein may have a variety of different symmetrical, asymmetrical or irregular shapes, including chain, rod, or lath shape. The porous silica particles may have different structures including amorphous or crystalline, etc. In some embodiments, the porous silica particles are amorphous.

The porous silica particles may include mixtures of particles comprising different compositions, sizes, shapes or physical structures, or that may be the same except for different surface treatments. Porosity of the porous silica particles may be intraparticle or interparticle in cases where smaller particles are agglomerated to form larger particles.

[0103] In some embodiments, the silica-zirconia catalyst (and independently the porous silica particles used to form the silica-zirconia particles) have a median particle size of from about 0.1 micron (μm) to about 10,000 μm (or any range of median particle size between about 0.1 μm and about 10,000 μm, in increments of 0.1 μm, e.g., from about 0.2 μm to about 9,999.9 μm). In some embodiments, the silica-zirconia catalyst (and independently the porous silica particles used to form the silica-zirconia catalyst) has a median particle size of from about 50 μm to about 75 μm, from about 75 μm to about 100 μm, from about 100 μm to about 125 μm, from about 125 μm to about 150 μm, from about 150 μm to about 175 μm, from about 175 μm to about 200 μm, from about 200 μm to about 225 μm, from about 225 μm to about 250 μm, from about 250 μm to about 275 μm, from about 275 μm to about 300 μm, from about 300 μm to about 325 μm, from about 325 μm to about 350 μm, from about 350 μm to about 375 μm, or from about 375 μm to about 400 μm. In some embodiments, the silica-zirconia particles (and independently the porous silica particles used to form the silica-zirconia particles) has a median particle size of from about 50.0 μm to about 400 μm, about 80.0 μm to about 400 μm, or about 80.0 μm to about 300 μm. In some embodiments, the silica-zirconia particles (and independently the porous silica particles used to form the silica-zirconia particles) has a median particle size of from about 100.0 μm to about 200 μm.

[0104] The silica-zirconia catalyst (and independently the porous silica particles used to form the silica-zirconia catalyst) used in the herein-described methods typically have a pore volume of at least about 0.01 cubic centimeters/gram (cc/g), as determined by Barrett-Joyner-Halenda (BJH) method. In some embodiments, the silica-zirconia catalyst (and independently the porous silica particles used to form the silica-zirconia catalyst) has a pore volume of from about 0.01 cc/g to about 0.1 cc/g, from about 0.1 cc/g to about 0.2 cc/g, from about 0.2 cc/g to about 0.3 cc/g, from about 0.3 cc/g to about 0.4 cc/g, from about 0.4 cc/g to about 0.5 cc/g, from about 0.5 cc/g to about 0.6 cc/g, from about 0.6 cc/g to about 0.7 cc/g, from about 0.7 cc/g to about 0.8 cc/g, from about 0.8 cc/g to about 0.9 cc/g, from about 0.9 cc/g to about 1.0

cc/g, from about 1.0 cc/g to about 1.1 cc/g, from about 1.1 cc/g to about 1.2 cc/g, from about 1.2 cc/g to about 1.3 cc/g, from about 1.3 cc/g to about 1.4 cc/g, from about 1.4 cc/g to about 1.5 cc/g, from about 1.5 cc/g to about 1.6 cc/g, from about 1.6 cc/g to about 1.7 cc/g, from about 1.7 cc/g to about 1.8 cc/g, from about 1.8 cc/g to about 1.9 cc/g, from about 1.9 cc/g to about 2.0 cc/g, from about 2.0 cc/g to about 2.1 cc/g, from about 2.1 cc/g to about 2.2 cc/g, from about 2.2 cc/g to about 2.3 cc/g, from about 2.3 cc/g to about 2.4 cc/g, from about 2.4 cc/g to about 2.5 cc/g, from about 2.5 cc/g to about 2.6 cc/g, from about 2.6 cc/g to about 2.7 cc/g, from about 2.7 cc/g to about 2.8 cc/g, from about 2.8 cc/g to about 2.9 cc/g, or from about 2.9 cc/g to about 3.0 cc/g, as determined by Barrett-Joyner-Halenda (BJH) method. In some embodiments, the silica-zirconia catalyst (and independently the porous silica particles used to form the silica-zirconia catalyst) has a pore volume of from about 0.1 cc/g to about 2.5 cc/g, from about 0.5 cc/g to about 3.0 cc/g, from about 0.5 cc/g to about 2.5 cc/g, or from about 0.8 cc/g to about 2.0 cc/g, as determined by Barrett-Joyner-Halenda (BJH) method. In some embodiments, the silica-zirconia catalyst (and independently the porous silica particles used to form the silica-zirconia catalyst) has a pore volume of at least about 0.5 cc/g, as determined by Barrett-Joyner-Halenda (BJH) method. In some embodiments, the silica-zirconia catalyst (and independently the porous silica particles used to form the silica-zirconia catalyst) has a pore volume of from about 0.5 cc/g to about 3.0 cc/g, or greater, as determined by Barrett-Joyner-Halenda (BJH) method. However, it should be understood that the silica-zirconia catalyst (and independently the porous silica particles used to form the silica-zirconia catalyst) used in the herein-described methods may have a pore volume of from about 0.01 cc/g to about 3.00 cc/g (or greater), as determined by Barrett-Joyner-Halenda (BJH) method (or any range of pore volume between about 0.01 cc/g and about 3.0 cc/g, in increments of 0.01 cc/g, e.g., from about 0.02 cc/g to about 2.99 cc/g). This includes about 0.01, 0.02, 0.03, 0.04, 0.05, 0.06, 0.07, 0.08, 0.09, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 1.1, 1.2, 1.3, 1.4, 1.5. 1.6, 1.7, 1.8, 1.9, 2.0, 2.1, 2.2, 2.3, 2.4, 2.5, 2.6, 2.7, 2.8, 2.9, or 3.0 cc/g.

[0105] The silica-zirconia catalyst (and independently the porous silica particles used to form the silica-zirconia catalyst) used in the herein-described methods may also have a average pore diameter of at least about 0.1 nanometers (nm), as determined by a mercury intrusion test procedure using an Autopore IV 9520 available from Micromeritics Instrument Corp. In some embodiments, the silica-zirconia catalyst (and independently the porous silica particles used to

form the silica-zirconia catalyst) has an average pore diameter of from about 1.0 nm to about 1000.0 nm. In some embodiments, the silica-zirconia catalyst (and independently the porous silica particles used to form the silica-zirconia catalyst) has an average pore diameter of from about 1.0 nm to about 100.0 nm. In other embodiments, the silica-zirconia catalyst (and independently the porous silica particles used to form the silica-zirconia catalyst) has an average pore diameter of from about 2.0 nm to about 50.0 nm. However, it should be understood that the silica-zirconia catalyst (and independently the porous silica particles used to form the silica-zirconia catalyst) used in the herein-described methods may have an average pore diameter ranging from about 0.1 nm to about 1000.0 nm (or greater) (or any range of average pore diameter between about 0.1 nm and about 1000.0 nm, in increments of 0.1 nm, e.g., from about 0.2 nm to about 999.9 nm).

[0106] The silica-zirconia catalyst (and independently the porous silica particles used to form the silica-zirconia catalyst) used in the herein-described methods may also have a BET particle surface area of about 10 m^2/g up to about 2000 m^2/g, or greater. In some embodiments, the silica-zirconia catalyst (and independently the porous silica particles used to form the silica-zirconia catalyst) has a BET particle surface area of at least about 25.0 m^2/g. In some embodiments, the silica-zirconia catalyst (and independently the porous silica particles used to form the silica-zirconia catalyst) has a BET particle surface area of about 50 m^2/g to about 100 m^2/g, about 100 m^2/g to about 150 m^2/g, about 150 m^2/g to about 200 m^2/g, about 200 m^2/g to about 250 m^2/g, about 250 m^2/g to about 300 m^2/g, about 300 m^2/g to about 350 m^2/g, about 350 m^2/g to about 400 m^2/g, about 400 m^2/g to about 450 m^2/g, about 450 m^2/g to about 500 m^2/g, about 500 m^2/g to about 550 m^2/g, about 550 m^2/g to about 600 m^2/g, about 600 m^2/g to about 650 m^2/g, about 650 m^2/g to about 700 m^2/g, about 700 m^2/g to about 750 m^2/g, or about 750 m^2/g to about 800 m^2/g. In some embodiments, the silica-zirconia catalyst (and independently the porous silica particles used to form the silica-zirconia catalyst) has a BET particle surface area of about 50 m^2/g up to about 800 m^2/g, or about 150 m^2/g up to about 450 m^2/g. However, it should be understood that the silica-zirconia catalyst (and independently the porous silica particles used to form the silica-zirconia catalyst) used in the herein-described methods can have any BET particle surface area ranging from about 10 m^2/g to about 2000 m^2/g, or greater (or any range of BET particle surface area values between about 10 m^2/g and about 2000 m^2/g, in increments of 0.1 m^2/g, e.g., from about 10.1 m^2/g to about 1999.9 m^2/g).

[0107] The silica-zirconia catalyst (and independently the porous silica particles used to form the silica-zirconia catalyst) used in the herein-described methods may also be subjected to size reduction. Any known method of reducing the particle size may be used, and include, but are not limited to, a milling step such as ball mill or a mortar pestle grinding step.

[0108] The silica-zirconia catalyst (and independently the porous silica particles used to form the silica-zirconia catalyst) used in the herein-described methods may comprise (i) any of the above-described porous silica particles in combination with (ii) zirconia. As discussed above, the zirconia may be impregnated (i) on at least a portion of the particle surfaces of the porous silica particles, or (ii) within at least a portion of the pores of the porous silica particles, or (iii) on at least a portion of the surface of the porous silica particles and within at least a portion of pores of the porous silica particles, or (iv) substantially within the pores of the porous silica particles. In some embodiments, the zirconia is located substantially within the pores of the silica particles.

[0109] Typically, the silica-zirconia catalyst used in the herein-described methods comprise at least about 0.01 weight percent (wt%) of zirconia based on a total weight of the silica-zirconia catalyst. In some embodiments, the silica-zirconia catalyst comprises from about 0.01 wt.% to about 1.0 wt.%, about 1.0 wt.% to about 5.0 wt.%, from about 5.0 wt.% to about 10.0 wt.%, from about 10.0 wt.% to about 15.0 wt.%, from about 15.0 wt.% to about 20.0 wt.%, from about 20.0 wt.% to about 25.0 wt.%, from about 25.0 wt.% to about 30.0 wt.%, from about 30.0 wt.% to about 35.0 wt.%, from about 35.0 wt.% to about 40.0 wt.%, from about 40.0 wt.% to about 45.0 wt.%, or from 45.0 wt.% to about 50.0 wt.% of zirconia based on a total weight of the silica-zirconia catalyst. In some embodiments, the silica-zirconia catalyst comprises from about 1.0 wt% to about 50.0 wt% of zirconia based on a total weight of the silica-zirconia catalyst. In some embodiments, the silica-zirconia catalyst comprises from about 1.5 wt% to about 15.0 wt%, or from about 1.5 wt% to about 14.3 wt%, of zirconia based on a total weight of the silica-zirconia catalyst. In some embodiments, the silica-zirconia catalyst comprises from about 2.4 wt% to about 5.0 wt% of zirconia based on a total weight of the silica-zirconia catalyst. However, it should be understood that the silica-zirconia catalyst used in the herein-described methods may comprise any amount of zirconia ranging from about 0.01 wt% to about 50.0 wt% (or greater) (or any range of amounts of zirconia between about

0.01 wt% and about 50.0 wt%, in increments of 0.01 wt%, e.g., from about 0.02 wt% to about 49.99 wt%, based on a total weight of the silica-zirconia catalyst).

[0110] In some embodiments, the silica-zirconia catalyst exhibits a pH $\leq$ 9, less than about 9, less than about 8, less than about 7, less than about 6, less than about 5, less than about 4, less than about 3, less than about 2, or less than about 1. In some embodiments, the silica-zirconia catalyst exhibits a pH of about 1 to about 9. In some embodiments, the silica-zirconia catalyst exhibits a pH of about 1 to about 8. In some embodiments, the silica-zirconia catalyst exhibits a pH of about 2 to about 7. In some embodiments, the silica-zirconia catalyst exhibits a pH of about 3 to about 6.

[0111] In some embodiments, the silica-zirconia catalyst (i) has a median particle size of from about 80.0 μm to about 400 μm; (ii) has a pore volume of from about 0.5 cc/g to about 3.0 cc/g, or greater, as determined by Barrett-Joyner-Halenda (BJH) method; (iii) has an average pore diameter of from about 1.0 nm to about 100.0 nm; (iv) has a BET particle surface area of at least about 50.0 m^2/g up to about 800 m^2/g; and (v) comprises from about 1.0 wt% to about 50.0 wt% of zirconia based on a total weight of the silica-zirconia catalyst.

[0112] In some embodiments, the silica-zirconia catalyst (i) has a median particle size of from about 100.0 μm to about 200 μm; (ii) has a pore volume of from about 1.0 cc/g to about 2.0 cc/g, as determined by Barrett-Joyner-Halenda (BJH) method; (iii) has an average pore diameter of from about 15.0 nm to about 30.0 nm; (iv) has a BET particle surface area of at least about 75.0 m^2/g up to about 400 m^2/g; and (v) comprises from about 2.5 wt% to about 15.0 wt% of zirconia based on a total weight of the silica-zirconia catalyst.

Compositions Used In and Produced By The Herein-Described Methods

[0113] In another aspect, provided herein are fatty acid ethyl ester-containing compositions comprising the herein-described silica-zirconia catalyst. As discussed above, typically, a given fatty acid ethyl ester-containing composition (i.e., prior to or after the above described methods for reducing an amount of glycidol, glycidyl ester, or both glycidol and glycidyl ester within a fatty acid ethyl ester-containing composition and/or methods of producing an edible oil, prior to removal of the silica-zirconia catalyst) comprises an amount

greater than about 0.01 wt% , typically from about 0.50 wt% to about 10.0 wt% (or any range of weight percents between about 0.50 wt% and about 10.00 wt%, in increments of 0.01 wt%, e.g., from about 1.00 wt% to about 3.00 wt%) of the herein-described silica-zirconia catalyst based on a total weight of the silica-zirconia catalyst and the fatty acid ethyl ester-containing composition. As discussed above, in some embodiments, the fatty acid ethyl ester-containing composition comprises the herein-described silica-zirconia catalyst in an oil (e.g., an edible oil) or an organic solvent (e.g., a fatty acid ethyl ester-dissolving solvent such as toluene) (i.e., prior to or after the above described methods for reducing an amount of glycidol, glycidyl ester, or both glycidol and glycidyl ester within a fatty acid ethyl ester-containing composition and/or methods of producing an edible oil, prior to removal of the silica-zirconia catalyst). In some embodiments, the fatty acid ethyl ester-containing composition comprises the herein-described silica-zirconia catalyst in an edible oil (i.e., prior to or after the above described methods for reducing an amount of glycidol, glycidyl ester, or both glycidol and glycidyl ester within a fatty acid ethyl ester-containing composition and/or methods of producing an edible oil, prior to removal of the silica-zirconia catalyst).

[0114] In another aspect, provided herein are oils and fatty acid ethyl ester-containing compositions resulting from the above described methods for reducing an amount of glycidol, glycidyl ester, or both glycidol and glycidyl ester within a fatty acid ethyl ester-containing composition and/or methods of producing an edible oil, prior to or after removal of the silica-zirconia catalyst. In some embodiments, the disclosed methods are used to produce an edible oil.

[0115] The present disclosure is further illustrated by the following examples, which are not to be construed in any way as imposing limitations upon the scope thereof. On the contrary, it is to be clearly understood that resort may be had to various other embodiments, modifications, and equivalents thereof which, after reading the description herein, may suggest themselves to those skilled in the art without departing from the spirit of the present disclosure and/or the scope of the appended claims.

EXAMPLES

[0116] Various embodiments are described hereinafter. It should be noted that the specific embodiments are not intended as an exhaustive description or as a limitation to the broader aspects discussed herein. One aspect described in conjunction with a particular embodiment is not necessarily limited to that embodiment and can be practiced with any other embodiment(s).

[0117] **General Reaction Procedure – Batch Reaction**

[0118] Each oil/substrate was charged to a round bottom flask. The overhead mixer was set to 250 rpm. The reactor was flushed with an inert gas, and then an initial sample was taken for GC/MS analysis. The desired amount of silica-zirconia catalyst was added, then the temperature was increased to the desired set point. After the desired amount of time, a final sample was taken, then filtered through a filter disc prior to analysis to remove the solid catalyst.

[0119] The reaction temperature is not limited but is preferably about 45 °C to about 90 °C. Regarding the edible oil industry, keeping the temperature below 90 °C helps prevent oil oxidation, but allows the glycidol and glycidyl esters to be reduced in a sufficient amount of time. Likewise, the reaction time is not limited, but is preferably less than 2 hours to minimize residency time within the refinery.

[0120] **Catalyst Description**

[0121] The silica-zirconia catalysts used in Examples 1-6 below are characterized below. Catalyst A1 was used in Examples 1, 2, 3, 5 (for 50 °C and 80 °C reactions), and 6 (for RBD palm oil). Catalyst A2 was used in Examples 4, 5 (for 70 °C and 90 °C reactions), and 6 (for DHA/EPA ethyl esters).

Catalyst	Pore Diameter (Å)	PV @ 0.9950 (cc/g)	Surface Area (m^2/g)	Particle Size (μm)	Zirconia (wt%)

A1	198	1.5	305	88 to 210	11
A2	209	1.4	273	86 to 242	8.7

[0122] **Example 1 – Reference Reaction 1 – Spiked Soy Bean Oil – Batch Reaction**

[0123] The general reaction procedure described above was followed in this example. Soybean oil (100 g) spiked with 6.9 ppm of glycidyl oleate, was mixed and heated to an uppermost temperature of 90 °C under argon. Silica-zirconia catalyst (2 g) was added under agitation. The total glycidol concentration within the reaction mixture was measured over a 15-minute period as shown in Table 1 below. At 15 minutes, the value for total glycidol in the treated oil was below the limits of detection.

Table 1. Reference Reaction 1 Results

Reaction Time	**Total Glycidol (ppm)**	**1st Order Reaction Rate Constant 1/min**
Initial Spiked Soybean Oil	6.90	-
1 min	3.12	39.6
5 minutes	0.41	20.4
10 minutes	0.01	18.5
15 minutes	ND*	-

*Below detection limit

[0124] **Example 2 –Reference Reaction 2 – Refined Bleached Deodorized Palm Oil – Batch Reaction**

[0125] The general reaction procedure described above was followed in this example. Refined Bleached Deodorized (RBD) palm oil spiked with about 12 ppm of glycidyl oleate (100 g) was mixed and heated to an uppermost temperature of 90 °C under argon. Silica-zirconia catalyst (2 g) was added under agitation. The total glycidol concentration within the

reaction mixture was measured over a 30-minute period, as shown in Table 2 below. After 5 minutes, the total glycidol level was at or below 1 ppm, and after 15 minutes, the total glycidol level was below 0.5 ppm.

Table 2. Reference Reaction 2 –RBD Palm Oil – Batch Reaction

Reaction Time	Total Glycidol (ppm)	1st Order Reaction Rate Constant 1/min
RBD Palm Oil	11.8	-
5 minutes	1.03	24.4
10 minutes	0.60	14.9
15 minutes	0.37	11.5
30 minutes	0.41	5.6

[0126] **Example 3 –Reference Reaction 3 – Mixture of Monoglycerides and RBD SBO – Batch Reaction**

[0127] The general reaction procedure described above was followed in this example. A mixture (100 g) of 20% Monoglycerides and 80% RBD Soybean oil (SBO) with 1.85 ppm glycidyl oleate was mixed and heated to an uppermost temperature of 90 °C under argon. Silica-zirconia catalyst (2 g) was added under agitation. The total glycidol concentration within the reaction mixture was measured over a 60-minute period, as shown in Table 3 below. No appreciable reduction in total glycidol was observed over the one-hour reaction.

Table 3. Reference Reaction 3 – Monoglyceride/RBD SBO mixture – Batch Reaction

Reaction Time	Total Glycidol (ppm)	1st Order Reaction Rate Constant 1/min
Monoglyceride/RBD SBO	1.85	-

5 minutes	2.3	2.24
10 minutes	2.19	0.87
15 minutes	1.30	1.17
30 minutes	1.90	0.047
60 minutes	1.90	0.020

[0128] **Example 4 – Total Glycidol Reduction in DHA/EPA ethyl esters – Batch Reaction**

[0129] The general reaction procedure described above was followed in this example. A mixture (100 g) of DHA/EPA ethyl esters was mixed and heated to an uppermost temperature of 90 °C under argon. Silica-zirconia catalyst (2 g) was added under agitation. The total glycidol concentration within the reaction mixture was measured over a 30-minute period, as shown in Table 4 below. The total glycidol level was at or below 1 ppm after 5 minutes of reaction. UV absorbance at 233 nm was also measured over the 30-minute time period, and no increase in absorbance was observed, indicating no double bond rearrangement within the fatty acid chemical structure, and therefore no degradation of the DHA/EPA ethyl esters.

Table 4. Reference Reaction 2 – DHA/EPA Ethyl Esters – Batch Reaction

Reaction Time	**Total Glycidol (ppm)**	**1st Order Reaction Rate Constant 1/min**
Initial DHA/EPA	5.56	-
5 minutes	1.03	16.8
10 minutes	0.33	14.1
15 minutes	0.18	11.5
30 minutes	0.07	7.2

[0130] **FIG. 1** compares the reaction rate constants for the reactions described in Examples 1 – 4. The reaction rate constant for the reaction with the fatty acid ethyl esters is of the same order of magnitude as the rate constant for reaction with either RBD SBO or RBD PO, but one

to two orders of magnitude larger than the reaction rate constant for reaction with monoglyceride/RBD PO.

[0131] **Example 5 – Reaction Temperature and Its Effect On Total Glycidol Reduction in DHA/EPA ethyl esters**

[0132] The effect of temperature on the reaction with silica-zirconia catalyst was measured at four desired reaction temperatures: 50 °C, 70 °C, 80 °C, and 90 °C. For each desired temperature studied, the general reaction procedure described above was followed. A mixture (100 g) of DHA/EPA ethyl esters was mixed and heated to the desired final temperature under argon. Silica-zirconia catalyst (2 g) was added under agitation, and the desired temperature was maintained throughout the experiment. The total glycidol concentration within the reaction mixture was measured over a 30-minute period, as shown in Table 5 below. The experimental results indicate that the catalytic reaction proceeded at temperatures as low as 50 °C. Heating the mixture accelerated the reaction in true catalytic form; however, excessive heat could cause more glycidol/glycidyl oleate to form or the fatty acid esters to degrade. For example, it is previously known, in edible oil refining, that glycidyl esters form during the deodorization process at temperatures of 200 °C or greater.

Table 5. Total Glycidol Reduction at Various Temperatures in DHA/EPA Ethyl Esters

Reaction Temperature °C	**Reaction Time**	**Total Glycidol (ppm)**	**1st Order Reaction Rate Constant 1/min**
50	Initial DHA/EPA	5.57	-
	5 minutes	5.09	1.02
	10 minutes	4.91	0.70
	15 minutes	4.70	0.61
	30 minutes	3.52	0.79
70	Initial DHA/EPA	5.64	-
	5 minutes	4.01	3.42

	10 minutes	2.98	3.20
	15 minutes	2.21	3.13
	30 minutes	1.13	2.67
80	Initial DHA/EPA	5.1	-
	5 minutes	2.5	7.98
	10 minutes	1.7	5.94
	15 minutes	1.2	5.27
	30 minutes	0.5	4.19
90	Initial DHA/EPA	5.56	-
	5 minutes	1.03	17.0
	10 minutes	0.33	14.2
	15 minutes	0.18	11.5
	30 minutes	0.07	7.2

[0133] UV absorbance at 233 nm was also measured over the 30-minute time period, and no increase in absorbance was observed, indicating no degradation of the DHA/EPA ethyl esters (see Table 6).

Table 6. Comparison of UV absorbance before and after heating

Sample Description	Absorbance	EPA (%)	DHA (%)
50 °C, 0 min	0.99	24.2	48.4
50 °C, 30 min	0.91	24.5	49.1
70 °C, 0 min	1.00	24.2	48.1
70 °C, 30 min	0.89	24.5	49.0
90 °C, 0 min	1.53	24.2	48.3
90 °C, 30 min	1.17	23.8	47.2

[0134] **Example 6 – Total Glycidol Reduction in DHA/EPA ethyl esters versus in RBD Palm Oil**

[0135] A packed bed reactor was packed with glass wool (provided by Thermo Scientific, catalog number: 386062500), inert zirconia beads (Bio Spec Products, catalog number: NC0362415), and silica-zirconia catalyst (2 g). The catalyst bed was heated to 90 °C before

DHA/EPA ethyl esters or RBD palm oil was allowed to flow through the reactor at a rate of 3.4 g/min through the apparatus, corresponding to a gravimetric space velocity of 102 h^{-1}.

[0136] Total glycidol levels in the treated oil for both reactions were measured over time, and the first order rate constant was evaluated as a function of the amount of oil passed through the catalyst. Results for both oils are summarized in Table 7. **FIG. 2** shows that total glycidol reduction in the reaction with DHA/EPA ethyl esters proceeded at the same rate as the reaction with RBD palm oil.

Table 7. Total Glycidol Reduction in a Packed Bed Process

	DHA/EPA Ethyl Esters		**RBD Palm Oil**	
Amount of oil processed grams oil/grams of catalyst	**Total Glycidol (ppm)**	**1st Order Reaction Rate Constant 1/min**	**Total Glycidol (ppm)**	**1st Order Reaction Rate Constant 1/min**
Feed Oil	4.07		5.79	
250			0.27	5.26
350	0.40	3.72		
500			0.67	2.7
600	0.54	3.55		
850	0.73	3.18		
875			0.96	3.05
1000	0.76	3.19	1.10	2.82
1490			1.51	2.48

[0137] Surprisingly, the methods described herein reduce an amount of glycidol, glycidyl ester, or both glycidol and glycidyl ester within a composition containing fatty acid ethyl esters, thereby providing an effective, environmentally-friendly method without the shortcomings of previously known methods. Advantageously, the methods described herein require much lower processing temperatures, require shorter processing time, do not increase free fatty acid content of edible oils, do not result in any significant oxidation as measured by the p-anisidine

value and/or the peroxide value and/or the total oxidation value of the treated fatty acid ethyl ester-containing composition, and do not result in extensive double bond isomerization.

[0138] It should be understood that although the above-described silica-zirconia catalysts, methods and uses are described as "comprising" one or more components or steps, the above-described silica-zirconia catalysts, methods and uses may "comprise," "consists of," or "consist essentially of any of the above-described components or steps of the silica-zirconia catalysts, methods and uses. Consequently, where the present disclosure, or a portion thereof, has been described with an open-ended term such as "comprising," it should be readily understood that (unless otherwise stated) the description of the present disclosure, or the portion thereof, should also be interpreted to describe the present disclosure, or a portion thereof, using the terms "consisting essentially of" or "consisting of" or variations thereof as discussed below.

[0139] As used herein, the terms "comprises," "comprising," "includes," "including," "has," "having," "contains", "containing," "characterized by" or any other variation thereof, are intended to encompass a non-exclusive inclusion, subject to any limitation explicitly indicated otherwise, of the recited components. For example, a silica-zirconia catalyst, method and/or use that "comprises" a list of elements (e.g., components or steps) is not necessarily limited to only those elements (or components or steps), but may include other elements (or components or steps) not expressly listed or inherent to the silica-zirconia catalyst, method and/or use.

[0140] As used herein, the transitional phrases "consists of" and "consisting of" exclude any element, step, or component not specified. For example, "consists of" or "consisting of" used in a claim would limit the claim to the components, materials or steps specifically recited in the claim except for impurities ordinarily associated therewith (i.e., impurities within a given component). When the phrase "consists of" or "consisting of" appears in a clause of the body of a claim, rather than immediately following the preamble, the phrase "consists of or "consisting of" limits only the elements (or components or steps) set forth in that clause; other elements (or components) are not excluded from the claim as a whole.

[0141] As used herein, the transitional phrases "consists essentially of" and "consisting essentially of" are used to define silica-zirconia catalysts, methods and/or uses that include materials, steps, features, components, or elements, in addition to those literally disclosed, provided that these additional materials, steps, features, components, or elements do not materially affect the basic and novel characteristic(s) of the claimed invention. The term "consisting essentially of" occupies a middle ground between "comprising" and "consisting of."

[0142] While the invention has been described with a limited number of embodiments, these specific embodiments are not intended to limit the scope of the invention as otherwise described and claimed herein. It may be evident to those of ordinary skill in the art upon review of the exemplary embodiments herein that further modifications, equivalents, and variations are possible. All parts and percentages in the examples, as well as in the remainder of the specification, are by weight unless otherwise specified. Further, any range of numbers recited in the specification or claims, such as that representing a particular set of properties, units of measure, conditions, physical states or percentages, is intended to literally incorporate expressly herein by reference or otherwise, any number falling within such range, including any subset of numbers within any range so recited. For example, whenever a numerical range with a lower limit, R_L, and an upper limit R_u, is disclosed, any number R falling within the range is specifically disclosed. In particular, the following numbers R within the range are specifically disclosed: $R = R_L + k(R_u - R_L)$, where k may be from 1% to 100% with a 1% increment, *e.g.*, k is 1%, 2%, 3%, 4%, 5%. ... 50%, 51%, 52%. ... 95%, 96%, 97%, 98%, 99%, or 100%. Moreover, any numerical range represented by any two values of R, as calculated above is also specifically disclosed.

[0143] Any listed range can be easily recognized as sufficiently describing and enabling the same range being broken down into at least equal halves, thirds, quarters, fifths, tenths, etc. As a non-limiting example, each range discussed herein can be readily broken down into a lower third, middle third and upper third, etc. As will also be understood by one skilled in the art all language such as "up to," "at least," "greater than," "less than," and the like, include the number recited and refer to ranges which can be subsequently broken down into subranges as

discussed above. Finally, as will be understood by one skilled in the art, a range includes each individual member.

[0144] In addition, where features or aspects of the disclosure are described in terms of Markush groups, those skilled in the art will recognize that the disclosure is also thereby described in terms of any individual member or subgroup of members of the Markush group.

[0145] Any modifications of the technology described herein, in addition to those shown and described herein, will become apparent to those skilled in the art from the foregoing description and accompanying drawings. Such modifications are intended to fall within the scope of the appended claims.

[0146] All publications, patent applications, issued patents, and other documents referred to in this specification are herein incorporated by reference as if each individual publication, patent application, issued patent, or other document was specifically and individually indicated to be incorporated by reference in its entirety. Definitions that are contained in text incorporated by reference are excluded to the extent that they contradict definitions in this disclosure.

[0147] Other embodiments are set forth in the following claims.

WHAT IS CLAIMED IS

1. A method for reducing an amount of (i) glycidol, (ii) glycidyl ester, or (iii) both glycidol and glycidyl ester within a composition comprising a fatty acid ethyl ester, said method comprising:

contacting the composition comprising a fatty acid ethyl ester with an effective amount of a particulate silica-zirconia catalyst to reduce the amount of (i) glycidol, (ii) glycidyl ester, or (iii) both glycidol and glycidyl ester in the composition, the silica-zirconia catalyst comprising porous silica particles impregnated with zirconia,

wherein the amount of (i) glycidol, (ii) glycidyl ester, or (iii) both glycidol and glycidyl ester is reduced.

2. The method of claim 1, wherein the amount of (i) glycidol, (ii) glycidyl ester, or (iii) both glycidol and glycidyl ester is reduced without affecting other components of the composition comprising the fatty acid ethyl ester.

3. The method of claim 1 or claim 2, wherein the amount of (i) glycidol, (ii) glycidyl ester, or (iii) both glycidol and glycidyl ester is reduced without increasing a free fatty acid content of the fatty acid ethyl ester-containing composition, without any significant oxidation of the fatty acid ethyl ester-containing composition as measured by the p-anisidine value and/or the peroxide value and/or the total oxidation value of the treated fatty acid ethyl ester-containing composition, and without extensive double bond isomerization of the fatty acid ethyl ester.

4. The method of any one of claims 1 to 3, wherein the silica-zirconia catalyst comprises zirconia located on at least a portion of the surface of the porous silica particles.

5. The method of any one of claims 1 to 4, wherein the silica-zirconia catalyst comprises zirconia located in at least a portion of the pores of the porous silica particles.

6. The method of any one of claims 1 to 5, wherein the silica-zirconia catalyst comprises zirconia located substantially in the pores of the porous silica particles.

7. The method of any one of claims 1 to 6, wherein the silica-zirconia catalyst comprises particles having a median particle size of from about 0.1 micron (μm) to about 10,000 μm.

8. The method of any one of claims 1 to 7, wherein the silica-zirconia catalyst comprises particles having a median particle size of from about 80.0 μm to about 400 μm.

9. The method of any one of claims 1 to 8, wherein the silica-zirconia catalyst comprises particles having a pore volume of at least about 0.01 cubic centimeters/gram (cc/g) as determined by Barrett-Joyner-Halenda (BJH) method.

10. The method of any one of claims 1 to 9, wherein the silica-zirconia catalyst comprises particles having a pore volume of at least about 0.5 cc/g as determined by Barrett-Joyner-Halenda (BJH) method.

11. The method of any one of claims 1 to 10, wherein the silica-zirconia catalyst comprises particles having a pore volume of from about 0.5 cc/g to about 3.0 cc/g, or greater as determined by Barrett-Joyner-Halenda (BJH) method.

12. The method of any one of claims 1 to 11, wherein the silica-zirconia catalyst comprises particles having an average pore diameter of at least 0.1 nanometers (nm) up to about 1000 nm as determined by a mercury intrusion test procedure using an Autopore IV 9520 available from Micromeritics Instrument Corp.

13. The method of any one of claims 1 to 12, wherein the silica-zirconia catalyst comprises particles having an average pore diameter of from about 1.0 nm to about 100.0 nm.

14. The method of any one of claims 1 to 13, wherein the silica-zirconia catalyst comprises particles having an average pore diameter of from about 2.0 nm to about 50.0 nm.

15. The method of any one of claims 1 to 14, wherein the silica-zirconia catalyst comprises particles having a BET particle surface area of about 10 m^2/g up to about 2000 m^2/g, or greater.

16. The method of any one of claims 1 to 15, wherein the silica-zirconia catalyst comprises particles having a BET particle surface area of at least about 25.0 m^2/g.

17. The method of any one of claims 1 to 16, wherein the silica-zirconia catalyst comprises particles having a BET particle surface area of about 50.0 m^2/g up to about 800 m^2/g.

18. The method of any one of claims 1 to 17, wherein the porous silica particles comprise silica gel, precipitated silica, or fumed silica particles.

19. The method of any one of claims 1 to 18, wherein the silica-zirconia catalyst comprises particles comprising at least about 0.01 weight percent (wt%) of zirconia based on a total weight of the silica-zirconia catalyst.

20. The method of any one of claims 1 to 19, wherein the silica-zirconia catalyst comprises particles comprising from about 1.0 wt% to about 50.0 wt% of zirconia based on a total weight of the silica-zirconia catalyst.

21. The method of any one of claims 1 to 20, wherein the silica-zirconia catalyst comprises particles comprising from about 1.5 wt% to about 15.0 wt% of zirconia based on a total weight of the silica-zirconia catalyst.

22. The method of any one of claims 1 to 21, wherein the silica-zirconia catalyst comprises particles formed by:

impregnating porous silica particles with a soluble zirconium compound in water;

drying the impregnated porous silica particles at about 105 °C for about 2 hours; and

calcining the dried impregnated porous silica particles at about 500 °C for about 4 hours.

23. The method of claim 22, wherein said impregnating step allows contact between the porous silica particles and the soluble zirconium compound for about 30 minutes.

24. The method of claim 22 or 23, wherein said method further comprises:

after said impregnating step and before said drying step, allowing the impregnated porous silica particles to mill for about 60 minutes.

25. The method of any one of claims 1 to 24, further comprising:

mixing the composition comprising the fatty acid ethyl ester and the silica-zirconia catalyst.

26. The method of any one of claims 1 to 25, wherein said contacting step occurs at room temperature.

27. The method of claim 25 or 26, wherein said mixing step occurs at room temperature.

28. The method of any one of claims 1 to 27, further comprising:

heating the composition comprising the fatty acid ethyl ester and the silica-zirconia catalyst up to a temperature of at least about 40.0 °C.

29. The method of any one of claims 1 to 28, further comprising:

heating the composition comprising the fatty acid ethyl ester and the silica-zirconia catalyst up to a temperature of about 150.0 °C.

30. The method of claim 28 or 29, wherein said heating step comprises:

heating the composition comprising the fatty acid ethyl ester and the silica-zirconia catalyst up to an uppermost temperature; and

maintaining the uppermost temperature for at least about 10.0 minutes.

31. The method of any one of claims 28 to 30, wherein said heating step comprises:

heating the composition comprising the fatty acid ethyl ester and the silica-zirconia catalyst up to an uppermost temperature; and

maintaining the uppermost temperature for about 30.0 minutes.

32. The method of any one of claims 28 to 31, wherein said heating step and said mixing step occur simultaneously.

33. The method of any one of claims 1 to 32, wherein said contacting step comprises:

mixing the composition comprising the fatty acid ethyl ester and the silica-zirconia catalyst under an inert gas flow.

34. The method of claim 33, wherein the inert gas comprises nitrogen, argon, carbon dioxide, or any combination thereof.

35. The method of any one of claims 1 to 34, wherein said contacting step comprises:

mixing the composition comprising the fatty acid ethyl ester and the silica-zirconia catalyst under vacuum.

36. The method of any one of claims 1 to 35, wherein the amount of silica-zirconia catalyst comprises at least about 0.01 wt% of the silica-zirconia catalyst based on a total weight of the silica-zirconia catalyst and the composition comprising the fatty acid ethyl ester.

37. The method of any one of claims 1 to 36, wherein the amount of silica-zirconia catalyst comprises from about 0.5 wt% to about 10.0 wt% of the silica-zirconia catalyst based on a total weight of the silica-zirconia catalyst and the composition comprising the fatty acid ethyl ester.

38. The method of any one of claims 1 to 37, wherein the amount of silica-zirconia

catalyst comprises from about 1.0 wt% to about 3.0 wt% of the silica-zirconia catalyst based on a total weight of the silica-zirconia catalyst and the composition comprising the fatty acid ethyl ester.

39. The method of any one of claims 1 to 38, wherein the silica-zirconia catalyst exhibits a pH $\leq$ 9.

40. The method of any one of claims 1 to 39, wherein the silica-zirconia catalyst exhibits a pH of from about 1 to about 9.

41. The method of any one of claims 1 to 40, wherein the method reduces the amount of (i) glycidol, (ii) glycidyl ester, or (iii) both glycidol and glycidyl ester to a level of less than about 10.0 parts per million (ppm) of (i) glycidol, (ii) glycidyl ester, or (iii) both glycidol and glycidyl ester in the composition comprising the fatty acid ethyl ester.

42. The method of any one of claims 1 to 41, wherein the method reduces the amount of (i) glycidol, (ii) glycidyl ester, or (iii) both glycidol and glycidyl ester to a level of less than about 5.0 ppm of (i) glycidol, (ii) glycidyl ester, or (iii) both glycidol and glycidyl ester in the composition comprising the fatty acid ethyl ester.

43. The method of any one of claims 1 to 42, wherein the method reduces the amount of (i) glycidol, (ii) glycidyl ester, or (iii) both glycidol and glycidyl ester to a level of less than about 1.0 ppm of (i) glycidol, (ii) glycidyl ester, or (iii) both glycidol and glycidyl ester in the composition comprising the fatty acid ethyl ester.

44. The method of any one of claims 1 to 43, wherein the method reduces the amount of (i) glycidol, (ii) glycidyl ester, or (iii) both glycidol and glycidyl ester to a level of less than about 0.5 ppm of (i) glycidol, (ii) glycidyl ester, or (iii) both glycidol and glycidyl ester in the composition comprising the fatty acid ethyl ester.

45. The method of any one of claims 1 to 44, wherein the method reduces the amount of

(i) glycidol, (ii) glycidyl ester, or (iii) both glycidol and glycidyl ester to a level of less than about 0.2 ppm of (i) glycidol, (ii) glycidyl ester, or (iii) both glycidol and glycidyl ester in the composition comprising the fatty acid ethyl ester.

46. The method of any one of claims 1 to 45, wherein the method reduces the amount of (i) glycidol, (ii) glycidyl ester, or (iii) both glycidol and glycidyl ester within the composition comprising the fatty acid ethyl ester by at least about 50 weight percent (wt%).

47. The method of any one of claims 1 to 46, wherein the method reduces the amount of (i) glycidol, (ii) glycidyl ester, or (iii) both glycidol and glycidyl ester within the composition comprising the fatty acid ethyl ester by at least about 80.00 wt%.

48. The method of any one of claims 1 to 47, wherein the method reduces the amount of (i) glycidol, (ii) glycidyl ester, or (iii) both glycidol and glycidyl ester within the composition comprising the fatty acid ethyl ester by up to 99.99 wt%.

49. The method of any one of claims 1 to 48, wherein the composition comprising the fatty acid ethyl ester comprises (i) an oil or (ii) both an oil and an organic solvent.

50. The method of any one of claims 1 to 49, wherein the composition comprising the fatty acid ethyl ester comprises (i) a fatty acid ethyl ester-containing oil or (ii) both a fatty acid ethyl ester-containing oil and an organic solvent capable of dissolving fatty acid ethyl ester(s).

51. The method of claim 49 or claim 50, wherein the oil comprises an edible oil, wherein the edible oil is plant-derived oil, animal-derived oil, microbial-derived oil, or a combination thereof.

52. The method of any one of claims 49 to 51, wherein the organic solvent comprises heptane, hexane, toluene, diethyl ether, an alcohol, or any combination thereof.

53. The method of any one of claims 1 to 52, wherein the composition comprising the fatty acid ethyl ester comprises one or more of omega-3 fatty acid ethyl esters and/or omega-6 fatty acid ethyl esters.

54. The method of claim 53, wherein the omega-3 fatty acid ethyl esters are selected from the group consisting of α-linolenic acid ethyl ester, stearidonic acid ethyl ester, docosapentaenoic acid ethyl ester, docosahexaenoic acid ethyl ester, and eicosapentaenoic acid ethyl ester; and the omega-6 fatty acid ethyl esters are selected from the group consisting of linoleic acid and arachidonic acid.

55. The method of any one of claims 1 to 54, wherein the contacting step is performed in a continuous reactor.

56. The method of claim 55, wherein the continuous reactor is a packed bed reactor, a rotating bed reactor, a continuous stirred tank reactor (CSTR), a plug flow reactor, or a fluidized bed reactor.

57. The method of claim 55 or claim 56, wherein the continuous reactor is a packed bed reactor or CSTR.

58. The method of any one of claims 55 to 57, wherein the contacting step occurs at a gravimetric space velocity of about 1 hr^{-1} to about 500 hr^{-1}.

59. The method of any one of claims 55 to 58, wherein the silica-zirconia catalyst is present in the continuous reactor at a weight percent relative to the amount of the treated composition of less than about 2%.

60. A method of producing a purified fatty acid ethyl ester-containing edible oil, said method comprising performing the method of any one of claims 51 to 59 on an initial composition comprising a fatty acid ethyl ester to provide the purified fatty acid ethyl ester-containing edible oil.

61. The method of claim 60, further comprising subjecting an initial oil to a refined-bleached-deodorized (RBD) treatment to provide an intermediate oil prior to contact with the silica-zirconia catalyst as described in the method of any one of claims 51 to 59.

62. The method of claim 61, further comprising subjecting the intermediate oil to ethanolysis to provide the initial composition comprising a fatty acid ethyl ester.

63. The method of any one of claims 60 to 62, wherein the initial composition comprising a fatty acid ethyl ester has an initial free fatty acid content as measured as a content of oleic acid, and said method changes the initial free fatty acid content, as measured by AOCS Official Method Ca 5a-40, by less than about 20%.

64. The method of any one of claims 60 to 63, wherein the initial composition comprising a fatty acid ethyl ester has an initial free fatty acid content as measured as a content of oleic acid, and said method changes the initial free fatty acid content, as measured by AOCS Official Method Ca 5a-40, by less than about 10%.

65. The method of any one of claims 60 to 64, wherein the initial composition comprising a fatty acid ethyl ester has an initial p-anisidine value (AV), and said method changes the initial p-anisidine value (AV) by less than 10 units, as measured by AOCS Official Method Cd 18-90.

66. The method of any one of claims 60 to 65, wherein the initial composition comprising a fatty acid ethyl ester has an initial peroxide value (PV), and said method changes the initial peroxide value by less than 10 units, as measured by AOCS Official Method Cd 8-53.

67. The method of any one of claims 60 to 66, wherein the purified fatty acid ethyl ester-containing edible oil has a total oxidation value of less than 10 units.

68. The method of any one of claims 60 to 67, wherein the purified fatty acid ethyl ester-

containing edible oil demonstrates substantially no degradation as measured by UV absorbance at 233 nm compared to the initial composition comprising a fatty acid ethyl ester.