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(71) Applicant: **NOVITA NUTRITION, LLC** [US/US]; 2301 Research Park Way, Suite 226, Brookings, SD 57006 (US).

(72) Inventors: **ENDRES, Donald**; c/o Novita Nutrition, LLC, 2301 Research Park Way, Suite 226, Brookings, SD 57006 (US). **FURCICH, Steven, J.**; 4 Turtle Pointe, Monticello, IL 61856 (US).

(74) Agent: **STENDER, Brian, L.** et al.; Dewitt LLP, 901 Marquette Avenue, Suite 2100, Minneapolis, MN 55402 (US).

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(54) Title: EXTRACTION OF OIL FROM HIGH-OIL CONTENT CORN DISTILLERS DRIED GRAINS AND RELATED METHODS OF USE

(57) Abstract: The extraction of oil from a co-product of a dry ethanol process using a corn feedstock comprising at least a portion of high-oil content corn, such that the extracted corn oil and/or the resultant distillers meal having at least one signature marker relating to the high-oil content corn, which is not present in low-oil content corn. The resultant extracted corn oil suitable for consumer use, renewable diesel production, green diesel production and/or renewable oleochemical production. The resultant distillers meal suitable for an animal feed and/or animal feed supplement. The USPTO has already been reminded by the International Bureau (IB) about that concern. Unfortunately, the IB is not competent to solve the issue and is still waiting for their reply.

EXTRACTION OF OIL FROM HIGH-OIL CONTENT CORN DISTILLERS DRIED GRAINS AND RELATED METHODS OF USE

CROSS-REFERENCE TO RELATED APPLICATION

5 This PCT application claims benefit of U.S. Provisional Application No. 63/513,234 filed July 12, 2023 which is hereby incorporated herein its entirety by reference.

FIELD OF THE INVENTION

10 The present invention relates generally to the extraction of oil from a corn feedstock comprising at least a portion of high-oil content corn, particularly to the extraction of oil from a by-product of ethanol production, such as distillers dried grains with solubles, distillers dried grains and/or distillers corn oil, whereby the corn feedstock to the ethanol production comprises at least a portion of high-oil content corn, methods of using the oil extracted, and method of using the resulting distillers meal. More particularly, the extracted corn oil and/or
15 the resultant distillers meal having at least one signature marker relating to the high-oil content corn feedstock, which is not present in low-oil corn, and the resultant extracted corn oil suitable for consumer use, renewable diesel production, green diesel production and/or renewable oleochemical production.

20 BACKGROUND OF THE INVENTION

Corn (*Zea mays L.*), also called maize, is the most valuable crop grown in the United States. The United States accounts for approximately 32% of world production of corn. Three major types of corn are grown in the United States: 1) grain or field corn; 2) sweet corn; and 3) popcorn. According to the U.S. Department of Agriculture, 89.7 million acres of
25 corn was planted in the U.S. in 2019, with an estimated 81.5 million acres harvested for grain and 6.59 million acres harvested for silage. Most of the corn grown in the United States is No. 2 yellow corn, also known as field corn, grain corn or dent corn.

There are several reasons for wanting to develop corn that is high in oil content. First, corn oil is a premium oil and regularly more valuable than starch, the other major component
30 of corn kernels. Second, high oil corn possesses a higher available energy content than ordinary corn, and thus is a more valuable feed for poultry and livestock. In animal feeding trials it has been found that less high oil corn is required per unit of gain than is required with ordinary corn. In addition, high oil corn requires substantially less soybean meal to balance a typical animal diet and may be used to replace oil containing additives in animal feed.

Ethanol can be produced using grains, such as corn, or other biomass, which are renewable resources. Presently, the majority of ethanol-producing biorefineries in the United States are dry-grind corn biorefineries, and it is estimated that the present ethanol production capacity of such biorefineries runs into the billions of gallons each year. Other alcohols, such as C3-C6 alcohols, can also be produced by the fermentation process of fermentable sugars from grains and other biomass. By-products or co-products of the fermentation process using corn as the feedstock in a corn ethanol biorefining process are distillers corn oil (DCO), distillers dried grains (DDG) and distillers dried grains with solubles (DDGS). Based on recent production rates of ethanol from dry-grind ethanol plants, approximately 44 million metric tons of DDGS are produced in the United States annually. The fermentation process to produce other C3-C6 alcohols from fermentable sugars from biomass also produces similar distillers oil.

Over the past few decades, achieving an ethanol product from grain-based biorefineries that is both commercial viable and truly renewable has proven challenging. Two of the more significant hurdles are: 1) the cost of grain-based ethanol production; and 2) the energy input to output ratio of grain-based ethanol production processes. As is easily appreciated, these two problems are intertwined. Grain-based ethanol production has historically required significant and costly input of fossil fuels (e.g., natural gas) to drive the biorefining process. Moreover, the amount of fossil fuel that has been historically required to drive grain-based ethanol production is costly, particularly so as the cost of natural gas and other fossil fuels increases.

One of the ways by which the effective cost of grain-based ethanol production can be reduced is the sale of commercially valuable co-products of the biorefining process. DDGS are co-products of grain-based ethanol production processes that have recognized commercial value. In particular, DDGS are sold as a livestock feed supplement. Because it is primarily the starch of the grain that is consumed in the production of ethanol, the DDGS remaining after fermentation and distillation contain nutritionally valuable fiber, protein and fat. Relative to raw grain, DDGS may even be considered a superior feed, as they contain concentrated amounts of fiber, protein and fat, together with a significantly reduced amount of starch. In addition, DDGS are considerably less expensive than some feeds of comparable nutritional value.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 provides a flow-chart schematic representation of a process by which crude corn oil is solvent extracted from DDGS, DDG or a combination thereof, which also

produces a de-oiled product, according to certain aspects of the present invention.

FIG. 2 provides a flow-chart schematic representation of a process by which glycerin and/or biodiesel are produced from one or more renewable oil sources, according to certain aspects of the present invention. In some preferred aspects, the one or more renewable oil sources comprises crude corn oil produced according to the solvent extraction process of FIG. 1.

FIG. 3 provides a flow-chart schematic representation of a reduction of FFAs from a feedstock by a glycerolysis process in the presence of a molar excess of glycerin to provide a feedstock mixture having a reduced FFA level compared to the feedstock FFA level, according to certain aspects of the present invention. In some preferred aspects, the feedstock comprises crude corn oil produced according to the solvent extraction process of FIG. 1 and/or the glycerin source is provided according to the process of FIG. 2.

FIG. 4 provides a flow-chart representation of the renewable diesel production process using renewable oil according to certain aspects of the present invention.

FIGS. 5A-5D provide a flow-chart representation of the oleochemical production processing using renewable oil according to certain aspects of the present invention.

While various embodiments are amenable to various modifications and alternative forms, specifics thereof have been shown by way of example in the drawings and will be described in detail. It should be understood, however, that the intention is not to limit the claimed inventions to the particular embodiments described. On the contrary, the intention is to cover all modifications, equivalents, and alternatives falling within the spirit and scope of the subject matter as defined by the claims.

DESCRIPTION

The terms “distillers oil” or “DO” referred to herein shall mean a co-product of a bio-fermentation process using biomass for fermentation that is extracted from the thin stillage.

The terms “distillers corn oil” or “DCO” referred to herein shall mean a coproduct of dry-milled corn C2-C6 alcohol production that is extracted from the thin stillage.

The terms “distiller’s dried grains with solubles” or “DDGS” referred to herein shall mean a co-product of alcohol production having the AAFCO definition, which is the product obtained after the removal of ethyl alcohol by distillation from the yeast fermentation of corn, grain or a grain mixture by condensing and drying at least three-quarters of the solids of the resultant whole stillage by methods employed in the grain distilling industry, wherein the predominating grain can precede the terms (e.g., corn DDGS, barley DDGS, wheat DDGS,

etc.).

The terms “dried distiller’s grains” or “distiller’s dried grains” or “DDG” referred to herein shall mean a co-product of dry-milled ethanol production having the AAFCO definition, which is the product obtained after the removal of ethyl alcohol by distillation from the yeast fermentation of corn, grain or a grain mixture by separating the resulting coarse grain fraction of the whole stillage and drying it by methods employed in the grain distilling industry, wherein the predominating grain can precede the terms (e.g., corn DDG, barley DDG, wheat DDG, etc.).

The term “distillers meal” referred to herein shall mean the product or co-product resulting from solvent extraction of DDGS, DDG or a combination thereof, that has been dried of excess water, including the instance of the resultant product or co-product retaining substantially all the crude protein and fiber content of the respective DDGS, DDG or a combination thereof, prior to solvent extraction, and also including the instance of the resultant product or co-product having a portion of the fiber and/or soluble fractions reduced by any further processes such that the resultant product or co-product has a higher protein content compared to the DDGS, DDG or a combination thereof prior to solvent extraction.

The terms “high free fatty acid level” or “high free fatty acid content” referred to herein shall mean a free fatty acid content greater than 1.0%, in some aspects about 2% to about 15%, by mass of total oil or fat as measured by ASTM D5555-95 (2017) in a renewable oil source or a renewable oil feedstock, including a renewable plant-based oil, a renewable animal-based fat or oil, distillers corn oil from a dry-grind ethanol process, oil extracted from DDGS and/or DDG, corn oil extracted from DDGS and/or DDG from a dry-grind ethanol process, oil solvent extracted from DDGS and/or DDG from a dry-grind ethanol process, and/or corn oil solvent extracted from DDGS and/or DDG from a dry-grind ethanol process.

The term “low free fatty acid level” or “low free fatty acid content” referred to herein shall mean a free fatty acid content of 1.0% or less, in some aspects between about 0.25% to less than 1.0%, by mass of total oil or fat as measured by ASTM D5555-95 (2017) in a renewable oil source or a renewable oil feedstock, including a renewable plant-based oil, a renewable animal-based fat or oil, distillers corn oil from a dry-grind ethanol process, oil extracted from DDGS and/or DDG, corn oil extracted from DDGS and/or DDG from a dry-grind ethanol process, oil solvent extracted from DDGS and/or DDG from a dry-grind ethanol process, and/or corn oil solvent extracted from DDGS and/or DDG from a dry-grind ethanol process.

The term “high-oil” or “high-oil content” in relation to corn means the kernels of corn

containing elevated levels of oil on a percent dry weight basis when compared to #2 yellow dent corn.

The term “low-oil” or “low-oil content” in relation to corn means the kernels of corn containing levels of oil on a percent dry weight basis consistent with that of #2 yellow dent corn, which typically has an oil content of about 3.5% to about 4.0%.

The term “oil content” refers to the oil concentration of a corn kernel expressed on a dry weight basis.

It will be readily understood that the methods and materials as they are generally described and illustrated in the figures herein could be arranged and designed in a wide variety of different configurations. Thus, the following more detailed description of various embodiments of the methods and materials provided herein is not intended to limit the scope of the claims, but merely provides representative examples of various embodiments of the subject matter recited in the appended claims.

For example, though DDGS are referenced herein with respect to the methods and materials described, it is to be understood that DDG could also be utilized instead of or in addition to the DDGS. In particular, DDG retain significant oil content, and in embodiments of the processes and methods described herein DDG may be used in place of DDGS or in combination with DDGS. Also, while every ethanol plant is configured differently, each ethanol plants handles recycle streams differently, including recycling different process streams of solubles to the distilled dried grains. Additionally, ethanol plants may also contain a commercial production of other biobased alcohols, such as isobutanol, alongside ethanol. Still further, biobased alcohol production can relate any of the C2-C6 organic alcohol productions. Thus, the following description specific to DDGS should also be understood to be applicable to DDG or a combination of DDGS and DDG as it relates to the various grain and/or biomass feedstocks. Thus, the following description specific to DDGS should also be understood to be applicable to DDG or a combination of DDGS and DDG.

The commercial value of oil extracted from a co-product of the grain-based ethanol production process can be further enhanced. In particular, commercially valuable amounts of oil can be extracted from the DDG and DDGS using a solvent extraction process. Commercially valuable amounts of oil can also be extracted from the thin stillage.

The extracted oil can then be further processed to provide, for example, food grade oil, such as food grade corn oil where the co-product is derived from an ethanol biorefinery that utilizes corn grain as biomass. Alternatively, the oil extracted can be subjected to a transesterification process, sometimes in conjunction with an esterification process, to yield

biodiesel and glycerine. Alternatively, the oil extracted can be subjected to a hydro-treating process to yield a renewable green diesel fuel.

Still alternatively, the oil extracted can be subjected to other oleochemical processing, such as fat splitting (or hydrolysis) of the glycerides (e.g., triglyceride, diglyceride and monoglyceride) into different oleochemical fractions to produce crude fatty acids and glycerine. After the splitting process, the crude fatty acids may be subjected to additional processing, such as distillation, fractionation, and other methods of separation to produce crude, distilled and fractionated fatty acids. Likewise, the crude glycerine may be subjected to additional processing, such as adsorptive filtration using adsorptive materials, such as activated carbon, and distillation to produce refined glycerine. The fatty acids and/or glycerine may be subjected to further chemical and enzymatic reactions to yield desired oleochemicals for personal care products and home care products.

In some aspects, the renewable oil feedstock is derived from standard #2 yellow dent corn typically having about 3% up to about 5% oil, which represents about 99% of corn grown in the U.S. and currently used for animal feed and industrial uses. In some aspects, the renewable oil feedstock is derived from at least 50%, in some aspects at least 55%, in some aspects at least 60%, in some aspects at least 65%, in some aspects at least 70%, in some aspects at least 75%, in some aspects at least 80%, in some aspects at least 85%, in some aspects at least 90%, in some aspects at least 95%, in some aspects at least 99%, and in some aspects 100%, standard #2 yellow dent corn.

In some other aspects, the renewable oil feedstock is derived from high-oil content corn, which is genetically altered to have an oil content greater than standard #2 yellow dent corn. High-oil corn grain can also include water, starch, protein, enzymes, pigments, amino acids, nutraceuticals and antioxidants.

High-oil content corn grain can be harvested from any of several different types of corn plants. For example, the corn plants giving rise to high-oil content corn grain includes hybrids, inbreds, transgenic plants, genetically-modified plants or a specific population of plants.

High-oil content corn grain is commercially available under the tradename Value Plus™ high oil corn from Brownseed Genetics, LLC, Bay City, Wis. Exemplary high oil corn grain is also described in U.S. Pat. No. 7,528,303 (Pylman et al.); U.S. Pat. No. 7,371,941 (Pylman et al.); and U.S. Pat. No. 7,378,579 (Pylman et al.); the entireties of which patents are incorporated herein by reference for all purposes. Methods for developing corn inbreds, hybrids, transgenic species and populations that generate corn plants producing grain having

elevated oil concentrations are known and described in Lambert (Specialty Corn, CRC Press Inc., Boca Raton, Fla., pp. 123-145 (1994).

Corn grain having an elevated total corn oil content can be identified by any of a number of methods known to those of ordinary skill in the art. For example, the oil content of grain can be determined using American Oil and Chemical Society Official Method, 5th edition, March 1998, ("AOCS method Ba 3-38"). AOCS method Ba 3-38 quantifies substances that are extracted by petroleum ether under conditions of the test. The oil content or concentration is the weight percentage of the oil with respect to the total weight of the grain sample. Oil content may be normalized and reported at any desired moisture basis. Another suitable method for identifying high oil corn grain involves using a near infrared (NIR) oil detector.

In some preferred aspects, the high-oil content corn has an oil content of more than 5%, in some aspects at least 6%, in some aspects up to 30%, in some aspects up to 20%, in some aspects up to 10%, in some aspects up to 9.5%, and in some aspects up to 9.0%, on a dry weight basis of the corn grain. In some preferred aspects, the renewable oil feedstock is derived from high-oil content corn having an oil content between 6% and 30%, in some aspects between 6% and 20%, in some aspects between 6% and 10%, in some aspects between 6.0% and 9.5%, in some aspects between 6.1% and 9.5%, in some aspects between 6.2% and 9.5%, in some aspects between 6.3% and 9.5%, in some aspects between 6.4% and 9.5%, in some aspects between 6.5% and 9.5%, in some aspects between 6.5% and 9.4%, in some aspects between 6.5% and 9.3%, in some aspects between 6.5% and 9.2%, in some aspects between 6.5% and 9.1%, in some aspects between 6.5% and 9.0%, on a dry weight basis of the corn grain.

In some aspects, the high-oil content corn has a relatively lower starch content as compared to #2 yellow dent corn. In some aspects, the high-oil content corn has a starch content of 70% or less, in some aspects 68% or less, and in some aspects 65% or less, on a dry weight basis of the corn grain. In some aspects, high-oil corn includes corn grain having a starch content from 58% to 65% on a dry weight basis of the corn grain.

In some aspects, the renewable oil feedstock is derived from a feedstock having at least 1%, in some aspects at least 2%, in some aspects at least 3%, in some aspects at least 4%, in some aspects at least 5%, in some aspects at least 6%, in some aspects at least 7%, in some aspects at least 8%, in some aspects at least 9%, in some aspects at least 10%, high-oil content corn.

In some aspects, the renewable oil feedstock is derived from corn grain blend of high-

oil content corn and low-oil content corn, such as to permit optimal processing, including milling, saccharification, fermentation and subsequent co-product oil extraction.

For example, the corn grain blend can include a first portion of #2 yellow dent corn grain having an oil content having an average oil content less than 5% on a dry weight basis of the corn grain and a second portion of high-oil content corn grain having an oil content having an average oil content of at least 6% on a dry weight basis of the corn grain. In some aspects, the first and second portions are provided such that the corn grain blend has an average oil content greater than 5%, in some aspects between 5% and 25%, in some aspects between 5% and 20%, and in some other aspects between 6% and 15%, on a dry weight basis of the corn grain.

In some preferred aspects, the renewable oil feedstock is derived from a corn grain blend of high-oil content corn and low-oil content corn having a high-oil content corn to low-oil content corn ratio (high-oil:low-oil) of at least 1:20, in some aspects at least 3:50, in some aspects at least 7:100, in some aspects at least 4:25, in some aspects at least 9:100, and in some aspects at least 1:10. In some preferred aspects, the renewable oil feedstock is derived from a corn grain blend of high-oil content corn and low-oil content corn having a high-oil content corn to low-oil content corn ratio (high-oil:low-oil) up to 1:1, in some aspects up to 2:5, in some aspects up to 3:10, in some aspects up to 1:4, and in some aspects up to 1:5. In some preferred aspects, the high-oil content corn to low-oil content corn ratio (high-oil:low-oil) is between 1:100 and 1:1, in some aspects between 1:50 and 2:5, in some aspects between 1:20 and 3:10, in some aspects between 1:20 and 1:4, in some aspects between 1:20 and 1:5, and in some preferred aspects between 1:10 and 1:5.

A corn grain blend can be provided by various techniques, such as those disclosed in U.S. Patent 10,889,837, the contents of which are incorporated-by-reference in its entirety herein.

For example, a corn blend can be provided by planting a mix of different corn seeds in a field, harvesting the mix of corn grains, and then milling the mix of corn grains. An example of planting a mix of different corn seeds includes mixing in the field a high-oil content corn grain and a low-oil content corn grain, wherein the high-oil content corn grain comprises at least 5% and up to 25% by weight of corn grain and the low-oil content corn grain comprises at least 75% by weight of corn grain, such as #2 yellow dent commodity corn, to form a corn grain blend that is then planted, harvested, and milled. This technique is known as Sidekick™ planting method by Brownseed Genetics, LLC, Bay City, Wis.

Another example of planting a mix of different corn seeds includes providing bags or

containers of a corn seed blend that includes a first portion of high-oil content corn grain and second portion of low-oil content corn grain, wherein the high-oil content corn grain comprises at least 5% and up to 25% by weight of corn grain and the low-oil content corn grain comprises at least 75% by weight of corn grain, such as #2 yellow dent commodity corn, to form the corn grain blend in a bag or container. The bags or containers can be emptied into a planting device and planted in a field. The corn plants produced can be harvested so as to provide a corresponding corn grain blend.

Another technique for providing a corn grain blend involves blending different corn grains at the mill from separate sources. For example, a first source high-oil content corn grain and a second source of low-oil content corn grain, such as #2 yellow dent corn grain, can be mixed at the mill to form a corn grain blend. The mixing at the mill can be done prior to grinding or the ground corn grain can be mixed to provide the corn grain blend.

The oil extracted from the co-product of ethanol processing, including DCO extracted from thin stillage and oil mechanically or solvent extracted from DDGS, DDG or a combination thereof, preferably has one or more signature traits that are not available in standard #2 yellow dent corn, such that the resultant oil from high-oil content corn can be determined.

In some preferred aspects, the resultant DCO has an oil content derived from a corn grain blend of low-oil content corn and high-oil content corn, wherein the corn grain blend having at least 5% high-oil content corn that can be determined by one or more signature protein traits expressed in high-oil corn that are not available in standard #2 yellow dent corn.

In some preferred aspects, the oil solvent extracted from DDGS, DDG, or a combination thereof, has an oil content derived from a corn grain blend of low-oil content corn and high-oil content corn, wherein the corn grain blend having at least 5% high-oil content corn can be determined by one or more signature protein traits expressed in high-oil corn that are not available in standard #2 yellow dent corn.

The one or more signature traits expressed in high-oil corn can be identified by any of a number of methods known to those of ordinary skill in the art. In some preferred aspects, the one or more signature traits comprises a protein signature trait that can be identified by any of a number of methods known to those of ordinary skill in the art. Preferably, the signature trait is present in the oil extracted from the co-product. For instance, the signature trait is present in the oil solvent extracted from DDGS, DDG, or a combination thereof.

In some aspects, DDGS and/or DDG have a signature trait prior to solvent extraction that comprises an average oil content at an increased level that is not available in DDGS

and/or DDG derived from standard #2 yellow dent corn alone.

In some aspects, feedstocks of renewable oil may have a FFA content that is higher than desired. According to certain aspects of the present disclosure, the FFA content of the renewable oil feedstock derived from at least a portion of high-oil content corn is reduced to a
5 desirable level prior to being utilized in a renewable fuel process, renewable diesel process, biofuel process and/or biodiesel process.

In some preferred aspects, the feedstock is extracted from a byproduct of a dry-grind fermentation process to produce alcohol, including C2-C6 organic alcohols, such as ethanol, isopropanol, n-propanol, isobutanol, n-butanol, isopentanol, n-pentanol, isohexanol and n-
10 hexanol and the like, produced from the starch or sugars of plants, including grains and biomass, such as corn. For instance, commercially valuable amounts of corn oil can be extracted from the DDG and/or DDGS, such as by a solvent extraction process. The corn oil extracted from DDG and DDGS can then be subjected to a transesterification process, sometimes in conjunction with an esterification process, to yield biodiesel and glycerin.
15 Alternatively, the oil extracted from DDG and DDGS can be subjected to a hydro-treating process to yield a renewable green diesel fuel.

In some preferred aspects, one or more feedstocks of renewable oil can be subjected to other oleochemical processing, such as fat splitting (or hydrolysis) of the glycerides (e.g., triglyceride, diglyceride and monoglyceride) into different oleochemical fractions to produce
20 crude fatty acids and glycerin. After the splitting process, the crude fatty acids may be subjected to additional processing, such as distillation, fractionation, and other methods of separation to produce crude, distilled and fractionated fatty acids. Similarly, the crude glycerin may be subjected to additional processing, such as adsorptive filtration using adsorptive materials, such as activated carbon, and distillation to produce refined glycerine.
25 The fatty acids and/or glycerine may be subjected to further chemical and enzymatic reactions to yield desired oleochemicals to be utilized in renewable green diesel fuel production and/or biodiesel production.

In some aspects, the crude fatty acids are subjected to fractionation processing to yield C12, C14, C16 and/or C18 fractionated fatty acids.

The distillers meal resulting from solvent extraction as described herein is still
30 suitable for use as an animal feed ingredient, such as, for example, a feed supplement or constituent for domestic pets, livestock (such as beef cattle, dairy cattle, equine, sheep and/or swine), aquaculture or poultry, including chickens, geese and/or turkey. Therefore, solvent extraction of DDG and DDGS according to the methods described herein may facilitate a

reduction in the effective costs of producing ethanol from a grain-based biorefinery, as it allows for production of multiple, commercially-valuable products from DDG and DDGS.

In one embodiment, ethanol production, solvent extraction of DDGS, and refining of the crude oil removed from the DDGS and/or DDG can occur in a single facility. For example, in such an embodiment, a grain-based ethanol biorefinery may further include facilities for solvent extraction of the DDGS and/or DDG produced at the biorefinery. In another such embodiment, a grain-based ethanol biorefinery may further include facilities for solvent extraction of the DDGS and/or DDG produced at the biorefinery and facilities for processing the crude oil extracted from the DDGS and/or DDG to produce glycerin, biodiesel and renewable diesel. In yet another embodiment, a grain-based ethanol biorefinery may further include facilities for solvent extraction of the DDGS and/or DDG produced at the biorefinery and facilities for processing and refining the crude oil extracted from the DDGS and/or DDG to produce renewable biodiesel and/or renewable diesel. In yet another embodiment, a grain-based ethanol biorefinery may further include facilities for solvent extraction of the DDGS and/or DDG produced at the biorefinery and facilities for processing and refining the crude oil extracted from the DDGS and/or DDG to provide a desirable feedstock by a glycerolysis reaction in order to produce biodiesel and/or renewable diesel. By integrating these operations within a single facility, process efficiencies may be gained and costs of solvent extracting the DDGS and/or DDG and processing or refining the extracted oil may be reduced.

In another embodiment, a biorefinery or facility may process a renewable oil source at least partially derived from high-oil content corn, wherein the renewable oil source having higher than desired levels of free fatty acids by performing either thermodynamic or enzymatic glycerolysis of the renewable oil source having higher than desired levels of free fatty acids in the presence of glycerin to provide a feedstock having a lowered free fatty acid level compared to the renewable oil source. In some preferred aspects, the renewable oil source has free fatty acids and/or triglycerides converted to monoglycerides and/or diglycerides in the glycerolysis process. In some preferred aspects, the glycerolysis process is conducted under a molar excess of glycerin to the fatty acids in the renewable oil source. In some preferred aspects, the glycerolysis process provides a result feedstock mixture of renewable oil having a resultant composition containing at least 15% monoglycerides, diglycerides, or a combination thereof.

In some aspects, the free fatty acid content of the renewable oil source contains between about 75% and about 95% triacylglycerides, between about 5% and about 12%

diacylglycerides and less than about 5%, in some aspects less than about 4%, in some aspects less than about 3%, and in some aspects less than about 2% monoacylglycerides, such that the total content of the diacylglycerides and monoacylglycerides in the renewable oil source is less than 15%.

5 In some aspects, at least 80% and up to 99% of the free fatty acid content is converted to a mixture of monoglycerides and diglycerides by the glycerolysis process.

In some preferred aspects, the renewable oil source is crude oil from DDGS and/or DDG. In some preferred aspects, the crude oil from DDGS and/or DDG is solvent extracted. In some more preferred aspects, the DDGS and/or DDG is derived from a corn grain blend
10 having a first portion of low-oil corn grain having an oil content having an average oil content less than 5% on a dry weight basis of the corn grain and a second portion of high-oil content corn grain having an oil content having an average oil content of at least 6% on a dry weight basis of the corn grain.

15 Solvent Extraction of Crude Oil from DDGS and/or DDG

While the following disclosure is in reference to DDGS, it is to be understood that DDG could also be utilized instead of or in addition to the DDGS. In particular, DDG retain significant oil content, and in embodiments of the processes and methods described herein DDG may be used in place of DDGS or in combination with DDGS, such that use of the term
20 DDGS herein shall be understood to mean DDGS, DDG or a combination thereof.

Using solvent extraction processes, commercially significant amounts of crude plant oils can be isolated from DDGS, while maintaining the value of DDGS as a feed supplement. In one embodiment, the DDGS used in a solvent extraction process as described herein are selected from DDGS generated in alcohol production processes that utilize corn, barley, rye,
25 sorghum, or soybean grain, such as ethanol, isobutanol or other C2-C6 organic alcohol productions. In another embodiment, the DDGS used in a solvent extraction process are corn DDGS generated from a dry-grind corn alcohol biorefinery, in some aspects preferably an ethanol biorefinery. In some more preferred aspects, the DDGS is derived from a corn grain blend having a first portion of low-oil content corn grain having an oil content having an
30 average oil content less than 5% on a dry weight basis of the corn grain and a second portion of high-oil content corn grain having an oil content having an average oil content of at least 6% on a dry weight basis of the corn grain.

In certain aspects, the corn DDGS and/or DDG is derived from a corn feedstock, such that the DDGS and/or DDG prior to solvent extraction of crude oil has an average oil content

that is greater than DDGS and/or DDG derived from #2 yellow dent commodity corn.

In some aspects, the corn DDGS and/or DDG is derived from a corn grain blend having a first portion of low-oil content corn grain having an oil content having an average oil content less than 5% on a dry weight basis of the corn grain and a second portion of high-oil content corn grain having an oil content having an average oil content of at least 6% on a dry weight basis of the corn grain, such that the DDGS and/or DDG prior to solvent extraction of crude oil has an average oil content that is greater than if the DDGS and/or DDG were derived from the first portion of low-oil content corn grain alone.

In some preferred aspects, the corn DDGS and/or DDG is derived from a corn grain blend having a first portion of low-oil content corn grain having an oil content having an average oil content less than 5% on a dry weight basis of the corn grain and a second portion of high-oil content corn grain having an oil content having an average oil content of at least 6% on a dry weight basis of the corn grain, such that the DDGS and/or DDG prior to solvent extraction of crude oil has an average oil content greater than 10%, in some aspects greater than 11%, and in some aspects greater than 12%. In some aspects, the average oil content of the the DDGS and/or DDG prior to solvent extraction of crude oil has an average oil content between 10% and 25%, in some aspects between 11% and 22%, in some other aspects between 12% and 20%, in some other aspects between 13% and 19%, and in some aspects between 14% and 17%, on a dry weight basis of the corn grain.

Solvent extraction processes suitable for extraction of crude oil from DDGS include processes that utilize ethanol, hexane, iso-hexane, petroleum distillate, mixtures thereof, or one or more other suitable solvents, as known in the art, for oil extraction of DDGS. In one preferred aspect, solvent extraction processes suitable for extraction of crude oil from DDGS include processes that utilize one or more renewable solvents. In some preferred aspects, the one or more renewable solvents comprises 2-methyloxolane. One of ordinary skill in the art will appreciate that such solvents may be commercial grade or reagent grade solvents. In some aspects, solvent extraction processes suitable for extraction of crude oil from DDGS or crude corn oil form corn DDGS include processes that utilize suitable non-polar solvents that have a high solvent power for lipids, are commercially available, are acceptable regulatory-recognized solvents and/or can be readily removed from the resulting product by commonly accepted methods such as distillation, washing and/or evaporation.

In some aspects, suitable non-polar solvents comprise saturated hydrocarbons, such as one or more C5-C7-alkanes, including one or more isomers, one or more enantiomers, and mixtures thereof. In some aspects, the isomers, enantiomers and mixtures of C5-C7-alkanes

includes one or more of n-pentane, n-hexane and n-heptane, as well as the structural isomers thereof (i.e., isopentane, neopentane, isohexane, 2-methylpentane, 2,3-dimethylbutane, neohexane, isohexane, 2-methylhexane, 2,2-dimethylpentane, 2,3-dimethylpentane, 2,4-dimethylpentane, 3-ethylpentane, and 2,2,3-trimethylbutane) and petroleum ether. In some aspects, suitable solvents are renewable solvents, such as 2-methyloxolane alone or in combination with one or more suitable non-polar solvents.

In some aspects, suitable non-polar solvents or mixtures thereof have a boiling point in the range from about 36°C to about 99°C. In some aspects, the non-polar solvents may be purified or commercial grade. For example, in some aspects, a suitable non-polar solvent includes commercial grade hexane, which one of ordinary skill in the art will appreciate comprises a mixture of n-hexane, other isomers of hexane and small amounts of other miscellaneous hydrocarbons (i.e., acetone, methyl ethyl ketone, dichloromethane, and trichloroethylene, aromatics such as toluene and/or other types of petroleum hydrocarbons).

In some aspects, suitable solvents comprise mixtures of solvents containing alkanes or blends of polar and non-polar solvents that form azeotropes. For example, suitable blends of polar and non-polar solvents may include hexane:ethanol or hexane:isopropanol. Such solvents may also include ketones such as acetone. In some aspects, the azeotrope comprises a blend of polar and non-polar solvents, such that the blend is a positive azeotrope, which has a boiling point at a lower temperature than any other ratio of its constituents.

In some other preferred aspects, suitable solvents comprise mixtures of solvents containing alkanes or blends of renewable solvents and non-polar solvents, polar solvents, or a mixture thereof. For example, suitable blends of renewable and non-polar solvents may include 2-methyloxolane:hexane, suitable blends of renewable and polar solvents may include 2-methyloxolane:ethanol or 2-methyloxolane:isopropanol, and suitable blends of renewable, non-polar and polar solvents may include 2-methyloxolane:hexane:ethanol or 2-methyloxolane:hexane:isopropanol. Such solvents may also include ketones such as acetone. In some aspects, the suitable blends forms an azeotrope, which comprises a blend of polar and non-polar solvents, such that the blend is a positive azeotrope, which has a boiling point at a lower temperature than any other ratio of its constituents.

In one embodiment, the solvent extraction process utilizes a solvent, such as, for example, hexane and/or 2-methyloxolane that serves to remove oil from the DDGS without substantially altering the protein or fiber content of the DDGS. Oil extraction of the DDGS as described herein yields a distillers meal. In one embodiment, the solvent extraction process removes about 60% or more, about 65% or more, about 70% or more, about 75% or more,

about 80% or more, or about 90% or more of the oil present in the DDGS.

In another embodiment, the solvent extraction process is a hexane extraction process that removes about 60% or more, about 65% or more, about 70% or more, about 75% or more, about 80% or more, or about 90% or more of the oil present in the DDGS. In yet
5 another embodiment, the solvent extraction process is a hexane extraction process that removes about 75% or more, about 80% or more, or about 90% or more of the oil present in corn DDGS.

In another embodiment, the solvent extraction process is a 2-methyloxolane extraction process that removes about 60% or more, about 65% or more, about 70% or more, about 75%
10 or more, about 80% or more, or about 90% or more of the oil present in the DDGS. In yet another embodiment, the solvent extraction process is a 2-methyloxolane extraction process that removes about 75% or more, about 80% or more, or about 90% or more of the oil present in corn DDGS.

In yet another embodiment, the solvent extraction process is an extraction process
15 using a mixture of non-polar solvents having a boiling point range between about 36°C to about 99°C that removes about 60% or more, about 65% or more, about 70% or more, about 75% or more, about 80% or more, or about 90% or more of the oil present in DDGS, and in some aspects corn DDGS.

In yet another embodiment, the solvent extraction process is an extraction process
20 using an azeotrope of a polar solvent and an alkane solvent that removes about 75% or more, about 80% or more, or about 90% or more of the oil present in DDGS, and in some aspects corn DDGS.

In yet another embodiment, the solvent extraction process is a hexane extraction process that removes about 60% or more, about 65% or more, about 70% or more, about 75%
25 or more, about 80% or more, or about 90% or more of the oil present in DDGS produced at a dry-grind corn ethanol biorefinery. Corn DDGS typically include about 5% up to about 15% by weight oil content, and in one embodiment, the solvent extraction process is a hexane extraction process that results in a corn distillers meal having a residual oil content of approximately 0.25-5% by weight, in some other aspects approximately 0.5-4% by weight, in
30 some other aspects approximately 2-3% by weight, and in still some other aspects approximately 0.25-3% by weight. In another embodiment, corn DDGS are subjected to a hexane extraction process that results in a corn distillers meal having a residual oil content of no more than 3.0% by weight, in some aspects no more than 2.5% by weight.

In another embodiment, the solvent extraction process is a 2-methyloxolane extraction

process that results in a corn distillers meal having a residual oil content of approximately 0.25-5% by weight, in some other aspects approximately 0.5-4% by weight, in some other aspects approximately 2-3% by weight, and in still some other aspects approximately 0.25-3% by weight. In another embodiment, corn DDGS are subjected to a 2-methyloxolane
5 extraction process that results in a corn distillers meal having a residual oil content of no more than 3.0% by weight, in some aspects no more than 2.5% by weight.

In yet another embodiment, the solvent extraction process utilizes a solvent extraction process that results in a corn distillers meal having a residual oil content of approximately 2-3% by weight, in some other aspects approximately 0.25-5% by weight, in some other
10 aspects approximately 1-4% by weight, and in still some other aspects approximately 0.25-3% by weight. In another embodiment, corn DDGS are subjected to a solvent extraction process that results in a corn distillers meal having a residual oil content of no more than 3.0% by weight, in some aspects no more than 2.5% by weight.

Where the DDGS are produced at a dry-grind corn ethanol biorefinery, a flow-chart
15 representation of a suitable solvent extraction process, such as hexane solvent extraction, is shown in FIG. 1. In a typical dry-grind process for ethanol production from corn, the DDGS are a by-product or co-product derived from the corn mash after the starch has been converted to ethanol and the ethanol has been removed by distillation. The stillage is typically subjected to centrifugation, evaporation and drying to remove residual liquid
20 content, resulting in DDGS. Methods of extracting crude corn oil from corn DDGS are discussed in Sing et. al., "Extraction of Oil From Corn Distillers Dried Grains with Solubles", Transactions of the ASAE 41 (6), 1775-1777 (1998), the teachings of which are incorporated by reference herein. In addition, solvent extraction technologies and equipment are available from, for example, Crown Iron Works Company of Minneapolis, Minn., U.S.A. Moreover,
25 technology directed to removal of the oil from vegetable particles, removal of residual solvent from solvent extracted materials, and recovery of solvents used in solvent extraction processes are described in, for example, U.S. Pat. No. 6,996,917, U.S. Patent No. 6,766,595, U.S. Patent No. 6,732,454, and U.S. Patent No. 6,509,051. These patents are assigned to Crown Iron Works Company, and the teachings of each of these patents are incorporated by
30 reference herein. Still further, the solvent extraction technologies relating to DDGS are disclosed in U.S. Patent Nos. 8,227,015 and 9,113,645, the teachings of each of these patents being incorporated by reference herein.

Referring again to FIG. 1, which illustrates an embodiment of a solvent extraction process that may be applied to DDGS, as a first step, DDGS meal is fed into an extractor. In

some aspects, the DDGS meal may optionally be ground before being fed into an extractor to reduce the particle size of the DDGS meal. In some aspects, the DDGS meal is ground such that about 80%, in some aspects about 85%, in some aspects about 90%, in some aspects about 95%, in some aspects about 99%, and in some aspects about 100% of the DDGS meal

5 has a particle size less than about 1 millimeter. In some aspects about 90% of the ground DDGS meal has a particle size less than about 1 millimeter to about 150 microns, in some aspects less than about 840 microns to about 150 microns, in some aspects less than about 710 microns to about 150 microns, in some aspects less than about 595 microns to about 150 microns, and in some other aspects less than about 525 microns to about 150 microns. In

10 other aspects, the DDGS meal is ground such that at least 95% of the DDGS meal has a particle size less than about 1 millimeter to about 150 microns, in some aspects less than about 840 microns to about 150 microns, in some aspects less than about 710 microns to about 150 microns, in some aspects less than about 595 microns to about 150 microns, and in some other aspects less than about 525 microns to about 150 microns. In some other aspects,

15 the DDGS meal is ground such that about 99% of the DDGS meal has a particle size less than about 1 millimeter to about 150 microns, in some aspects less than about 840 microns to about 150 microns, in some aspects less than about 710 microns to about 150 microns, in some aspects less than about 595 microns to about 150 microns, and in some other aspects less than about 525 microns to about 150 microns.

20 In the extractor, the DDGS meal is washed with solvent, and in one embodiment, the DDGS meal is turned at least once in order to ensure that all DDGS particles are contacted as equally as practicable with solvent. After washing, the resulting mixture of oil and solvent, called miscella, is collected for separation of the extracted oil from the solvent. During the extraction process, as the solvent washes over the DDGS flakes, the solvent not only brings

25 oil into solution, but may collect fine, solid DDGS particles. These "fines" are generally undesirable impurities in the miscella, and in one embodiment, the miscella is discharged from the separator through a device that separates or scrubs the fines from the miscella as the miscella is collected for separation of the oil from the solvent.

In some alternative aspects, one or more enzymes may be added to the miscella to

30 reduce the free fatty acid content. In some aspects, the enzyme can be a commercially available enzyme, such as an immobilized lipase.

In order to separate the oil and the solvent contained in the miscella, the miscella may be subjected to a distillation step. In this step, the miscella can, for example, be processed through an evaporator, which heats the miscella to a temperature that is high enough to cause

vaporization of the solvent, but is not sufficiently high to adversely affect or vaporize the extracted oil. The oil may be further stripped of solvent in an oil stripper to further reduce residual solvent levels. As the solvent evaporates, it may be collected, for example, in a condenser, and recycled for future use. Separation of the solvent from the miscella results in a stock of renewable crude oil, which may be further processed to provide, for example, food grade oil for ultimately consumer uses or an oil product suitable for use in a renewable diesel process by hydro-treating the oil to produce green renewable diesel or a transesterification process that yields fatty acid methyl esters for use in biodiesel and/or for ultimate use in the production of oleochemicals, as well as glycerin which may be produced as a consequent of processing the oil. The renewable crude oil may also undergo other processes prior to being produced into renewable diesel, biodiesel, glycerin and/or oleochemicals.

After extraction of the oil, the wet, de-oiled DDGS may be conveyed out of the extractor and subjected to a drying process that removes residual solvent. Removal of residual solvent is important to production of distillers meal suitable for use as an animal feed ingredient. In one embodiment, the wet meal can be conveyed in a vapor tight environment to preserve and collect solvent that transiently evaporates from the wet meal as it is conveyed into the desolventizer. As the meal enters the desolventizer, it may be heated to vaporize and remove the residual solvent. In order to heat the meal, the desolventizer may include a mechanism for distributing the meal over one or more trays, and the meal may be heated directly, such as through direct contact with heated air or steam, or indirectly, such as by heating the tray carrying the meal, or both. The desolventizer may further include multiple different trays for carrying the meal through different processing steps within the desolventizer. In order to facilitate transfer of the meal from one tray to another, the trays carrying the meal may include openings between trays that allow the meal to pass from one tray to the next.

Where the desolventizer utilizes multiple process steps to remove residual solvent from the wet, de-oiled DDGS to produce distillers meal, the wet, de-oiled DDGS may be loaded and transferred through various trays to facilitate heating and solvent removal in multiple process steps. For example, in one embodiment, as the meal enters the desolventizer, it may be loaded on a first group of heated trays where the meal is evenly distributed and solvent vapor is flashed from the meal. From this first set of trays, the meal may be transferred onto a second group of trays, where it is again evenly distributed. The second set of trays may be heated indirectly by steam. The trays may be designed to allow venting of the solvent from one tray to the next and the meal contained in the second set of trays travels

counter current to the solvent vapors. A third tray or set of trays may be provided to allow direct steam injection into the meal, which works to strip remaining solvent. Where the desolventizer includes multiple trays and utilizes multiple desolventizing processes, the quantity of trays and their positions may be designed to allow maximum contact between vapors and meal.

From the desolventizer, the meal may be conveyed to a dryer where the meal is dried of residual excess water and cooled to provide a finished distillers meal. As it is conveyed into the dryer, the meal may be deposited into drying trays and it is warmed by heated air. As the meal is heated, residual water is vaporized. After drying, the meal may be cooled using ambient air. The desolventized, dried and cooled distillers meal may be stored, further processed, such as pelletizing to increase densification, or prepared for sale or distribution.

In some aspects, at least about 80%, in some aspects about 85%, in some aspects about 90%, in some aspects about 95%, in some aspects about 99%, and in some aspects about 100% of the distillers meal has a particle size less than about 1 millimeter. In some aspects about 90% of the distillers meal has a particle size less than about 1 millimeter to about 150 microns, in some aspects less than about 840 microns to about 150 microns, in some aspects less than about 710 microns to about 150 microns, in some aspects less than about 595 microns to about 150 microns, and in some other aspects less than about 525 microns to about 150 microns. In other aspects, about 95% of the distillers meal has a particle size less than about 1 millimeter to about 150 microns, in some aspects less than about 840 microns to about 150 microns, in some aspects less than about 710 microns to about 150 microns, in some aspects less than about 595 microns to about 150 microns, and in some other aspects less than about 525 microns to about 150 microns. In some other aspects, about 99% of the distillers meal has a particle size less than about 1 millimeter to about 150 microns, in some aspects less than about 840 microns to about 150 microns, in some aspects less than about 710 microns to about 150 microns, in some aspects less than about 595 microns to about 150 microns, and in some other aspects less than about 525 microns to about 150 microns.

In some aspects, the distillers meal has an average particle size of about 105 microns to about 625 microns, in some aspects about 150 microns to about 600 microns, in some aspects about 175 microns to about 575 microns, in some aspects about 200 microns to about 525 microns, and in some aspects about 250 microns to about 500 microns.

In some aspects, the distillers meal may comprise a residual level of solvent utilized in the solvent extraction process in an amount less than about 2000 ppm, less than about 1500

ppm, less than about 1000 ppm, less than about 500 ppm, less than about 400 ppm, and in some aspects less than about 350 ppm.

In some aspects, the distillers meal may comprise a residual level of solvent utilized in the solvent extraction process in an amount of about 10 ppm to about 2000 ppm, in other
5 aspects about 20 ppm to about 1000 ppm, in some aspects about 50 ppm to about 800 ppm, in other aspects about 100 ppm to about 500 ppm, in some other aspects about 200 ppm to about 400 ppm, and still in some other aspects about 300 ppm to about 350 ppm.

In some aspects, the distillers meal may comprise a residual level of hexane solvent utilized in the solvent extraction process in an amount less than about 2000 ppm, less than
10 about 1500 ppm, less than about 1000 ppm, less than about 500 ppm, less than about 400 ppm and in some aspects less than about 350 ppm.

In some aspects, a residual level of hexane solvent is present in the distillers meal in an amount of about 10 ppm to about 2000 ppm, in other aspects about 20 ppm to about 1000 ppm, in some aspects about 50 ppm to about 800 ppm, in other aspects about 100 ppm to
15 about 500 ppm, in some other aspects about 200 ppm to about 400 ppm, and still in some other aspects about 300 ppm to about 350 ppm.

In some aspects, the distillers meal may comprise a residual level of 2-methyloxolane solvent utilized in the solvent extraction process in an amount less than about 2000 ppm, less than about 1500 ppm, less than about 1000 ppm, less than about 500 ppm, less than about 400
20 ppm, and in some aspects less than about 350 ppm.

In some aspects, a residual level of hexane solvent and 2-methyloxolane solvent is present in the distillers meal in an amount of about 10 ppm to about 2000 ppm, in other aspects about 20 ppm to about 1000 ppm, in some aspects about 50 ppm to about 800 ppm, in other aspects about 100 ppm to about 500 ppm, in some other aspects about 200 ppm to about
25 400 ppm, and still in some other aspects about 300 ppm to about 350 ppm.

In some aspects, the distillers meal may comprise a total residual level of hexane solvent and 2-methyloxolane solvent utilized in the solvent extraction process in an amount less than about 2000 ppm, less than about 1500 ppm, less than about 1000 ppm, less than about 500 ppm, less than about 400 ppm, and in some aspects less than about 350 ppm.

In some aspects, a total residual level of hexane solvent and 2-methyloxolane solvent is present in the corn distillers meal in an amount of about 10 ppm to about 2000 ppm, in other aspects about 20 ppm to about 1000 ppm, in some aspects about 50 ppm to about 800 ppm, in other aspects about 100 ppm to about 500 ppm, in some other aspects about 200 ppm to about 400 ppm, and still in some other aspects about 300 ppm to about 350 ppm. In some

aspects, the distillers meal may comprise a residual moisture content of about 3% to about 15%, in some aspects about 4% to about 13%, and still in other aspects about 7% to about 11%.

The biorefining and solvent extraction processes may be tailored to provide extracted oil exhibiting specific qualities. For example, where the DDGS are corn DDGS and the solvent extraction process is a hexane extraction process, the biorefining and solvent extraction process may be controlled to provide an extracted crude corn oil exhibiting no more than about 15% by weight free fatty acids, such as oleic acid, no more than about 1% by weight crude protein, about 0.5% by weight total nitrogen, 0.2% by weight ash, about 0.05% phosphorus, about 0.01% by weight potassium, about 0.005% sodium, or about 0.05% by weight sulfur, or any combination of one or more such qualities. In one such embodiment, the crude corn oil includes no more than about 0.6%, 0.7%, 0.8% or 0.9% by weight crude protein. In another such embodiment, the crude corn oil contains no more than about 10%, 11%, 12%, 13%, 14%, or 15% by weight free fatty acids. In another such embodiment, the crude corn oil contains free fatty acids in an amount between about 1% to about 15%, in some aspects between about 1% and about 14%, in some aspects between about 1% and about 13%, in some aspects between about 1% and about 12%, in some aspects between about 1% and about 11%, in some aspects between about 1% and about 10%, in some aspects between about 1% and about 9%, in some aspects about 1% and about 8%, in some aspects about 3% to about 15%, by weight of the crude corn oil, with other ranges and subranges of the foregoing ranges contemplated. In another such embodiment, the crude corn oil contains no more than about 0.09%, 0.1%, 0.2%, 0.25%, 0.3%, or 0.4% by weight total nitrogen. In yet another such embodiment, the crude corn oil contains no more than about 0.08%, 0.09%, 0.1%, or 0.15% by weight ash. In another such embodiment, the crude corn oil contains no more than about 0.02%, 0.03%, or 0.04% by weight phosphorus. In yet another such embodiment, the crude corn oil contains no more than about 0.02%, 0.03%, or 0.04% by weight potassium. In yet another such embodiment, the crude corn oil contains no more than about 0.003% or 0.004% by weight sodium. In yet another such embodiment, the crude corn oil contains no more than about 0.02%, 0.03%, or 0.04% by weight sulfur.

It is contemplated that where the DDGS is corn DDGS and the solvent extraction process utilizes other solvents or mixtures of solvents containing alkanes, the biorefining and solvent extraction process may be controlled to provide an extracted crude oil exhibiting no more than about 15% by weight free fatty acids, such as oleic acid, no more than about 1% by weight crude protein, 0.5% by weight total nitrogen, 0.2% by weight ash, 0.05% phosphorus,

0.01% by weight potassium, 0.005% sodium, or 0.05% by weight sulfur, or any combination of one or more such qualities. In one such embodiment, the crude corn oil includes no more than about 0.6%, 0.7%, 0.8% or 0.9% by weight crude protein. In another such embodiment, the crude oil contains no more than about 10%, 11%, 12%, 13%, 14%, or 15% by weight free fatty acids. In another such embodiment, the crude corn oil contains free fatty acids in an amount between about 1% to about 15%, in some aspects between about 1% and about 14%, in some aspects between about 1% and about 13%, in some aspects between about 1% and about 12%, in some aspects between about 1% and about 11%, in some aspects between about 1% and about 10%, in some aspects between about 1% and about 9%, in some aspects about 1% and about 8%, in some aspects about 3% to about 15%, by weight of the crude corn oil, with other ranges and subranges of the foregoing ranges contemplated. In another such embodiment, the crude corn oil contains no more than about 0.09%, 0.1%, 0.2%, 0.25%, 0.3%, or 0.4% by weight total nitrogen. In yet another such embodiment, the crude corn oil contains no more than about 0.08%, 0.09%, 0.1%, or 0.15% by weight ash. In another such embodiment, the crude corn oil contains no more than about 0.02%, 0.03%, or 0.04% by weight phosphorus. In yet another such embodiment, the crude corn oil contains no more than about 0.01%, 0.02%, 0.03%, or 0.04% by weight potassium. In yet another such embodiment, the crude corn oil contains no more than about 0.003% or 0.004% by weight sodium. In yet another such embodiment, the crude corn oil contains no more than about 0.02%, 0.03%, or 0.04% by weight sulfur.

In some aspects, the crude oil extracted utilizing a solvent extraction process on DDGS comprises a residual level of solvent utilized in the solvent extraction process in an amount of about 1 ppm to about 500 ppm, in other aspects about 1 ppm to about 400 ppm, in other aspects about 5 ppm to about 100 ppm, in some aspects about 10 ppm to about 50 ppm, in some aspects about 15 ppm to about 40 ppm, and still in some other aspects about 20 ppm to about 30 ppm. In some aspects, a residual level of solvent is present in the crude corn oil extracted from corn DDGS, the residual level of hexane present in the crude oil present in an amount of about 1 ppm to about 500 ppm, in other aspects about 1 ppm to about 400 ppm, in other aspects about 5 ppm to about 100 ppm, in some aspects about 10 ppm to about 50 ppm, in some aspects about 15 ppm to about 40 ppm, and still in some other aspects about 20 ppm to about 30 ppm. In some aspects, a residual level of hexane solvent is present in the crude oil extracted from DDGS, the residual level of hexane present in the crude oil present in an amount of about 1 ppm to about 500 ppm, in other aspects about 1 ppm to about 400 ppm, in other aspects about 5 ppm to about 100 ppm, in some aspects about 10 ppm to about 50 ppm,

in some aspects about 15 ppm to about 40 ppm, and still in some other aspects about 20 ppm to about 30 ppm. In some aspects, a residual level of hexane solvent is present in the crude corn oil extracted from corn DDGS, the residual level of hexane present in the crude oil present in an amount of about 1 ppm to about 500 ppm, in other aspects about 1 ppm to about 400 ppm, in other aspects about 5 ppm to about 100 ppm, in some aspects about 10 ppm to about 50 ppm, in some aspects about 15 ppm to about 40 ppm, and still in some other aspects about 20 ppm to about 30 ppm. In some aspects, a residual level of 2-methyloxolane solvent is present in the crude oil extracted from DDGS, the residual level of 2-methyloxolane present in the crude oil present in an amount of about 1 ppm to about 500 ppm, in other aspects about 1 ppm to about 400 ppm, in other aspects about 5 ppm to about 100 ppm, in some aspects about 10 ppm to about 50 ppm, in some aspects about 15 ppm to about 40 ppm, and still in some other aspects about 20 ppm to about 30 ppm. In some aspects, a residual level of 2-methyloxolane solvent is present in the crude corn oil extracted from corn DDGS, the residual level of 2-methyloxolane present in the crude oil present in an amount of about 1 ppm to about 500 ppm, in other aspects about 1 ppm to about 400 ppm, in other aspects about 5 ppm to about 100 ppm, in some aspects about 10 ppm to about 50 ppm, in some aspects about 15 ppm to about 40 ppm, and still in some other aspects about 20 ppm to about 30 ppm.

In comparing the contents of corn stillage oil (CSO), which is corn oil extracted from the stillage of an ethanol process, to that of crude corn oil extracted utilizing a solvent extraction process on corn DDGS, the content of phosphorous and phosphorous containing compounds in CSO is more than about 100 ppm, and in some instances more than about 105 ppm, which is higher than solvent extracted crude corn oil, which in some aspects can have phosphorous and phosphorous containing compounds in an amount of about 1 ppm to about 50 ppm. Without wishing to be bound by theory, while corn contains some native phosphorus content, which is primarily in the form of phospholipids or phosphatides, the majority of phosphorous is contributed by chemical addition during the ethanol process. The chemical forms of phosphorous, including phosphates, have a relatively high degree of solubility in water. Thus, in the process of recovering CSO, it is expected the various phosphorous forms would be partially washed out with the CSO, and some residual phosphorous content would remain in the CSO. Conversely, these same water soluble phosphorous compounds are not easily extracted with non-polar solvents, such as hexane. Consequently, crude corn oil extracted by a solvent extraction process from corn DDGS contain initial levels of phosphorous and phosphorous containing compounds in an amount of about 1 ppm to about 50 ppm, in some other aspects about 1 ppm to about 20 ppm, in some

other aspects about 1 ppm to about 10 ppm, and in still other aspects about 1 ppm to about 5 ppm.

In comparing the contents of CSO to that of crude corn oil extracted utilizing a solvent extraction process on corn DDGS, the content of sulfur and sulfur containing compounds in CSO is more than about 30 ppm, and in some instances about 34 ppm, which is higher than solvent extracted crude corn oil, which in some aspects can have sulfur and sulfur containing compounds in an amount of about 1 ppm to about 20 ppm. While corn contains some native sulfur content, primarily bound in the form of amino acids such as methionine, the majority of sulfur is contributed by chemical addition during the ethanol process. Both the amino acid form and the chemical forms, such as sulfates and sulfites, have a relatively high degree of solubility in water. Thus, in the process of recovering CSO, it is expected the various sulfur forms would be partially washed out with the CSO, and some residual sulfur content would remain in the CSO. Conversely these same water soluble sulfur compounds would not be easily extracted with non-polar solvents, such as hexane. Consequently, crude corn oil extracted by a solvent extraction process from corn DDG contain initial levels of sulfur and sulfur containing compounds in an amount of about 1 ppm to about 20 ppm, in some aspects less than about 15 ppm, in some aspects less than about 12 ppm, in some other aspects about 1 ppm to about 10 ppm, and in still other aspects about 1 ppm to about 5 ppm.

The CSO recovery process in ethanol plants relies on the concept of using an emulsifier to emulsify some of the free oil in water in order to help wash out additional oil from the stillage. An emulsion breaker such as flocculent may be used to separate the lipid and aqueous components into distinct phases in order to fully recover the CSO. Crude oil solvent extracted from DDGS, including crude corn oil solvent extracted from corn DDGS, have reduced contents of non-native emulsifiers and also flocculants (i.e., those used in the Nalco process). In some aspects, the crude oil solvent extracted from DDGS, including crude corn oil solvent extracted from corn DDGS, are substantially free of non-native emulsifiers and also flocculants. Crude oil solvent extracted from DDGS, including crude corn oil solvent extracted from corn DDGS, may also have a reduced content of acids and/or reaction products resulting from the classic method of decreasing pH to break an emulsion. In some aspects, crude oil solvent extracted from DDGS, including crude corn oil solvent extracted from corn DDGS, is substantially free of acids and/or reaction products resulting from the classic method of decreasing pH to break an emulsion. In some aspects, the distillers meal of the present invention has a reduced residual content of any chemicals used for enhanced

recovery of oil from stillage including one or more emulsifiers and/or flocculants, which are soluble in solvent and/or oil. In some aspects, a non-polar solvent extraction reduces residual levels of such chemicals to levels of about 50% less than DDGS, in some aspects about 75% less, and in some aspects about 90% less, than DDGS that has not been solvent extracted but
5 has been subjected to CSO recovery using such chemicals. During the CSO recovery process, an emulsifier may be used to help enhance the removal of oil from spent grains, and a flocculent may be used to further help recover oil from thin stillage after mechanical separation.

Crude oil that is solvent extracted from DDGS, including crude corn oil that is solvent
10 extracted from corn DDGS, may also be substantially free of non-native emulsifiers and also flocculants (i.e., Nalco process). Crude oil solvent extracted from DDGS, including crude corn oil solvent extracted from corn DDGS, are also substantially free of acids and/or reaction products resulting from the classic method of decreasing pH to break an emulsion. In comparison, the CSO recovery process in ethanol plants relies on the concept of using an
15 emulsifier to emulsify some of the free oil in water in order to help wash out additional oil from the stillage.

Crude corn oil that is solvent extracted from DDGS that is the result of high-oil content corn may contain one or more signature protein traits that are not available in standard #2 yellow dent corn.

In some preferred aspects, the crude corn oil that is solvent extracted from DDGS has
20 an oil content derived from a corn grain blend of low-oil content corn and high-oil content corn, wherein the corn grain blend having at least 5% high-oil content corn, wherein a portion of the crude corn oil derived from the high-oil content corn can be determined by one or more signature protein traits expressed in the high-oil content corn that are not available in standard
25 #2 yellow dent corn.

Processing of Renewable Oil Sources – Transesterification to Biofuels and/or Glycerin

According to certain aspects, crude oil from renewable oil sources may be used to produce other oleochemicals, particularly oleochemicals for the production of renewable
30 fuels and/or biofuels. In some aspects, the crude oil from one or more renewable oil sources, such as crude oil extracted from DDGS, may be used to produce various oleochemicals after the crude oil undergoes a splitting (or hydrolysis) process of the triglycerides into crude fatty acids and glycerol/glycerin. After the splitting process, additional processing may be utilized, including evaporation, purification and/or bleaching to produce glycerol/glycerin

and crude fatty acids. The crude fatty acids and/or glycerin can be subjected to further chemical and enzymatic reactions to produce desired oleochemicals for the production of renewable fuels and/or biofuels.

Referring now to the flow-chart representation of a process for refining biodiesel and glycerin in FIG. 2, one or more renewable oil sources, such as DCO, CSO or crude oil extracted from DDGS, may be used to produce biodiesel and/or glycerin. There are several processes that may be used to produce biodiesel from oils and fats, including base catalyzed transesterification, direct acid catalyzed transesterification and/or esterification, enzyme catalyzed transesterification and/or esterification, high pressure transesterification (i.e. Henkel process), and/or a combination of same for conversion of the oil to biodiesel. Biodiesel production technologies and equipment are commercially available from, for example, Crown Iron Works Company of Minneapolis, Minn., U.S.A., and from Lurgi AG of Frankfurt, Germany. To produce biodiesel and/or glycerin from one or more renewable oil sources, such as the crude oil extracted from the DDGS, an acid catalyzed esterification or caustic neutralization, followed by a transesterification process may be used.

In one preferred aspect of the refining process outlined in FIG. 2, the renewable oil source is a crude extracted oil, such as crude corn oil that has been solvent extracted from DDGS. Before the crude corn oil is subjected to a transesterification process, it may be pretreated. Pretreatment of the crude corn oil may be carried out, for example, to remove gums included in the oil or to remove or neutralize free fatty acids. As part of a degumming process, an acid, such as phosphoric acid, may be added to the crude corn oil and the crude oil may be heated, for example, using steam. In such a process, the acid and steam work to hydrate the gums so that the gums can be separated from the crude corn oil, such as by centrifugation or another suitable separation technique.

Free fatty acids in the crude corn oil are generally undesirable because they form soaps within the oil as they react with the base catalyst used to drive the transesterification reaction. If the crude corn oil is also pretreated with a degumming step, the addition of the strong base intended to neutralize the free fatty acids may occur after addition of the acid in the degumming step. In this manner, the base added to neutralize the free fatty acids can also work to neutralize the acid used in the degumming step. The soap stock that results from degumming and neutralization of the crude corn oil may be separated from the corn oil using standard equipment, such as a centrifugal separator. Alternatively, the free fatty acids can be removed and acid esterified to form biodiesel, or combined with glycerin to form triglycerides, which are then transesterified to form biodiesel.

Treatment of the crude corn oil may also include one or more bleaching steps, such as one or more heat bleaching or clay bleaching steps to remove residual color or other impurities from the corn oil.

Where pretreatment of the crude corn oil includes degumming and neutralization of free fatty acids, prior to a transesterification process, the degummed and neutralized oil is typically washed prior to transesterification. Washing may include, for example, mixing the pretreated corn oil with warm wash water. After washing, the oil and wash water are separated, and the pretreated corn oil is dried, such as by a vacuum-dryer, to a desired water content.

In one embodiment, the pretreated corn oil can be subjected to a transesterification reaction to provide biodiesel and/or glycerin. The transesterification reaction is based on the chemical reaction of triglycerides contained in the crude corn oil with an alcohol in the presence of an alkaline catalyst. The alkaline catalyst used in the transesterification reaction may be selected from several different alkaline materials. Suitable catalysts are strong bases and include, for example, NaOH (caustic soda), KOH (potash), and CH_3NaO (sodium methylate). The alcohol used in the transesterification reaction may be selected from, for example, methanol or ethanol.

As the transesterification reaction is carried out, the alcohol and catalyst may be delivered into the corn oil in parallel, as separate reaction components, or the alcohol and catalyst can be delivered to the crude corn oil as a mixture. When delivered as a mixture, the catalyst may be dissolved in the alcohol by any suitable means prior to charging the mixture into the corn oil. Alternatively, the catalyst may be provided as a liquid and mixed with the alcohol, limiting the need for dissolution of the catalyst in the alcohol prior to mixing the alcohol and catalyst with the corn oil. Where the catalyst is mixed with the alcohol as a liquid, the catalyst may be added to the alcohol by, for example, one or more metering pumps. In addition, because an alkaline catalyst might be sensitive to water, the catalyst may be stored in a pump tank protected with a nitrogen layer.

In carrying out the transesterification reaction, the alcohol, catalyst and corn oil may be charged into a closed reaction vessel. The reaction system can be closed to the atmosphere to prevent loss of the alcohol used in the transesterification reaction. As the reaction components are mixed, the mixture may be kept just below the boiling point of the alcohol to speed the reaction time. In addition, an excess amount of alcohol is typically used to ensure total conversion of the corn oil triglycerides into the desired ester product. The transesterification reaction produces a two-phase reaction product that includes an ester-rich

phase (crude biodiesel) and a glycerin-rich phase (crude glycerin). The crude glycerin is much more dense than the crude biodiesel and the two phases can be easily separated by gravity separation or, if needed or desired, centrifugation.

In one embodiment, transesterification of the corn oil takes place in one or more mixer-settler units. In such units, the transesterification reaction occurs in a mixer or reactor included in the mixer-settler units. The crude biodiesel and crude glycerin resulting from the transesterification reaction form two distinct phases that can be separated in the settlers. If two or more mixer-settler units are used as the reaction vessels, the feedstock and the intermediate product, respectively, may flow successively through the two or more mixer-settler units. Each mixer-settler unit can be supplied with the desired alcohol and catalyst in parallel. The reactors included in the mixer-settler units can be multi-stage in design, comprising various reaction chambers in order to achieve maximum conversion efficiency to the ester product. The settlers allow phase separation to approach the limit of solubility, which eases downstream purification of the biodiesel and glycerin products.

At the transesterification stage, vapors vented from the reaction vessel, such as the one or more mixer-settlers, may be routed to a condenser where they are partly or completely condensed and returned to the reaction process. The same may be done with the vessel used to store or deliver the alcohol used in the transesterification reaction. Even further, where the catalyst is provided in liquid form, it too may be stored and delivered from a storage vessel, and any vapors vented from the catalyst storage vessel may also be captured, partly or completely condensed, and returned to the reaction process in liquid form.

Once the transesterification reaction is complete, two major products exist: glycerin and biodiesel. The glycerin is included in the crude glycerin phase and the biodiesel is incorporated in the crude biodiesel phase. Each of these crude phases may include a substantial excess of the alcohol used in the reaction. Moreover, the crude reaction products may include other impurities such as excess catalyst, soaps and high boiling impurities. If desired, some of these impurities may be treated or removed from the crude reaction products before the crude biodiesel and the crude glycerin phases are separated. For example, a suitable acid may be added to and mixed with the reaction products to neutralize excess catalyst and further help break any emulsions. Additionally, excess alcohol may be removed from the crude reaction products using standard distillation equipment and techniques.

After the crude biodiesel and crude glycerin are separated, they are typically subjected to further refining. For example, after separation, the crude biodiesel may contain residual alcohol, glycerin, small amounts of catalyst, and soaps. This may be the case even if the

crude reaction products are refined to remove or neutralize impurities prior to separation. If they have not already been refined to neutralize excess catalyst or remove excess alcohol, or if residual catalyst and excess alcohol still remain in the separated reaction products, the crude biodiesel and crude glycerin may be treated with a suitable acid to neutralize the residual catalyst and subjected to, for example, a flash evaporation process or distillation to remove the excess alcohol.

Even where steps are taken to neutralize residual catalyst and remove excess alcohol, the refined biodiesel may still include water soluble impurities. In order to remove such water-soluble substances, the refined biodiesel may be washed and dried. To avoid the formation of emulsions during washing, the biodiesel may be pH adjusted, for example, by the addition of an acid to the biodiesel to be washed. Dilute HCl, such as a 3.7% strength HCl, is suitable for such an application and can be prepared and added as necessary. The biodiesel wash process may simply include gentle mixing of the biodiesel with warm water, which will work to remove residual, water soluble impurities as they are taken up in the aqueous phase.

If the biodiesel is processed through such a washing step, the refined and washed biodiesel may contain excess water. Such excess water may be removed, for example, by subjecting the biodiesel to a drying step. The drying step may include, for example, vacuum drying the biodiesel to a desired water content in a dryer circuit. The dried biodiesel, which is ready for use, distribution or sale, is collected and stored. Though the biodiesel is serviceable at this point, if desired, it can be subjected to further distillation to remove any color bodies and other higher molecular weight impurities remaining to provide a colorless biodiesel.

The separated, crude glycerin phase may also be further refined after separation. In particular, the crude glycerin may be neutralized with a suitable acid, the excess alcohol may be removed by distillation or flash evaporation, and the crude glycerin may be dried to remove residual water. Even if the crude reaction products of the transesterification process are neutralized and the excess alcohol present in the crude reaction products is removed prior to separation, the separated, crude glycerin may still contain residual catalyst or alcohol. Where that is the case, the separated, crude glycerin may be subjected to additional neutralization, absorptive filtration, and/or distillation steps to neutralize any residual catalyst and remove any remaining alcohol. Once such neutralization, distillation and drying steps are complete, the crude product typically contains approximately 80-88% pure glycerin. This crude glycerin can be further refined to a purity of 99% or higher, as is known in the art, such that the glycerin product is suitable for use in cosmetic or pharmaceutical applications. In

some preferred aspects, as described in more detail herein, the glycerin can be used in a glycerolysis reaction to reduce the FFA content of a feedstock.

In order to minimize loss of the alcohol used in the transesterification reaction, all vessels which contain alcohol, whether in substantially pure form or as part of a crude reaction product, may be connected to a vent system to capture any alcohol vapors. Captured alcohol vapors may be fed into a condensing system that recovers the alcohol and recycles the alcohol back into the refining process.

In some aspects, the transesterification reaction is a batch process. In some other aspects, the transesterification reaction is a continuous process.

While the foregoing transesterification reaction has been discussed in relation to the renewable oil sources being DCO, CSO or crude oil extracted from DDGS to produce biodiesel and/or glycerin, the renewable oil source may be any other crude oil from one or more renewable oil sources, preferably one or more plant-based oils.

Reduction of FFA Content by Glycerolysis for Renewable Fuel Production

In some aspects, a renewable oil source may be a feedstock for production of biodiesel and/or renewable fuels. However, in some aspects, the renewable oil source may contain an undesirable level of free fatty acids, which may poison and thereby reduce the lifetime of catalysts for the production of biodiesel and/or renewable fuels, such as renewable diesel, or cause equipment problems due to the corrosive nature of free fatty acids, especially at higher weight-%, time and temperature during processing.

According to certain aspects of the present disclosure, conducting a glycerolysis process on the renewable oil source having a high level of free fatty acids will provide commercially significant amounts of a feedstock having a lowered free fatty acid level that is acceptable for biodiesel production and/or renewable diesel production, as illustrated in FIG. 3.

In some preferred aspects, the renewable oil source is one or more plant-based oils. Plant-based oils may include soy bean oil, palm oil, peanut oil, rice oil, flaxseed oil, sesame oil, grape seed oil, sunflower oil, rapeseed oil, olive oil, canola oil, coconut oil, almond oil, avocado seed oil, cottonseed oil, hemp oil, pumpkin seed oil, safflower seed oil, castor oil, nut oil and the like. In some preferred aspects, the plant-based oil comprises corn oil, which can be preferably produced from a dry solvent extraction process as discussed above in relation to FIG. 1. In some preferred aspects, the plant-based oil is corn oil produced from an ethanol production process, such as CSO, DCO, crude oil extracted from DDGS, such as

solvent extracted crude corn oil from DDGS, or a mixture thereof. In some aspects, the plant-based oil is produced from an ethanol production process that utilizes corn, barley, rye, sorghum, or soybean grain. In some preferred aspects, the plant-based oil is produced from a solvent extraction process of a by-product of the ethanol production process. In one preferred aspect, the plant-based oil comprises crude corn oil produced from a solvent extraction process from corn DDGS and/or DDG as discussed above in relation to FIG. 1. In some other aspects, the plant-based oil comprises distillers corn oil (DCO). In still other aspects, the plant-based oil can be the result of acidulation of soapstock from vegetable oil refining. In still some other aspects, the renewable oil source comprises a combination of any of the foregoing plant-based oils.

In some other preferred aspects, the renewable crude oil source is one or more animal-based fats or oils, whereby fatty acids can be derived from splitting animal fats or oils. Animal-based fats/oils are primarily extracted from rendered tissue fats from livestock animals, such as pigs, cows and chickens and the like. Accordingly, animal-based fats/oils may include or derived from choice white grease, tallow, suet, lard, schmaltz, poultry oil and the like.

In yet some other preferred aspects, the renewable crude oil source is a mixture of one or more plant-based oils and one or more animal-based fats or oils.

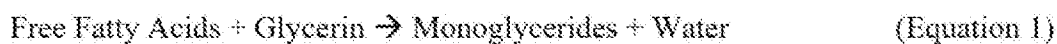
In some preferred aspects, the levels of free fatty acids in the renewable oil source as a feedstock may be reduced to a desirable level by conducting either thermodynamic or enzymatic glycerolysis of the feedstock in the presence of glycerin. Conducting glycerolysis converts triglycerides in the feedstock having a high level of free fatty acids to monoglycerides and/or diglycerides, such that the converted feedstock has a lowered level of free fatty acids.

In some preferred aspects, the glycerolysis is conducted by a thermodynamic reaction at temperatures between about 150° C. and about 250° C., and in some aspects between about 175° C. and about 225° C., for a period of time between about 30 minutes and about 180 minutes, and in some aspects between about 60 minutes and about 120 minutes, wherein a glycerin to free fatty acid molar ratio is at least 1.1:1, in some aspects at least 1.25:1, in some aspects at least 1.5:1. In some other preferred aspects, the temperature of the thermodynamic reaction can be adjusted by using high pressures, such as pressures in the range of 100-200 bar, such that one of ordinary skill in the art will appreciate the relationship between the desired temperatures at higher pressures.

In some preferred aspects, the glycerolysis conducted by a thermodynamic reaction is

conducted in the absence of a catalyst. In some other preferred aspects, the glycerolysis conducted by the thermodynamic reaction is conducted in the presence of one or more catalysts.

Without wishing to be bound by theory, conducting glycerolysis of a feedstock having a high level of free fatty acids in the presence of a molar excess of glycerin under heat and/or high pressure results in three primary reactions shown in Equations 1-3 below:



In some preferred aspects, the glycerolysis is conducted by an enzymatic reaction, wherein the solvent to fat ratio is about 2:1 (v/w), the glycerin to fat ratio is at least 1.5:1, and the enzyme concentration is greater than about 10% (w/w). In some aspects, the enzyme can be a commercially available enzyme, which is an immobilized lipase.

In some preferred aspects, the glycerolysis reaction is not completed to eliminate the free fatty acid content of the renewable source feedstock, but instead reduces the levels of free fatty acids in the renewable source feedstock to an acceptable level, such that there is a residual level of free fatty acids remaining.

In some other aspects, glycerolysis reaction is conducted until completion to eliminate the free fatty acid content of the renewable source feedstock, such that there is essentially no residual level of free fatty acids remaining.

In some preferred aspects, the levels of free fatty acids in the renewable source feedstock prior to glycerolysis is greater than 1%, in some aspects greater than about 2%, in some aspects greater than about 3%, in some aspects greater than about 4%, in some aspects greater than about 5%, in some aspects greater than about 6%, in some aspects greater than about 7%, in some aspects greater than about 8%, in some aspects greater than about 9%, in some aspects greater than about 10%, in some aspects greater than about 11%, in some aspects greater than about 12%, in some aspects greater than about 13%, in some aspects greater than about 14%, and in some other aspects up to about 15%, by mass of total fat. In some preferred aspects, the free fatty acid content of the renewable source feedstock prior to glycerolysis is between about 1% and about 15% by mass of total fat, more preferably between about 5% and about 15% by mass of total fat.

In some preferred aspects, the levels of free fatty acids in the renewable source feedstock is reduced by glycerolysis in an amount of at least 1%, in some aspects in an amount of at least 2%, in some aspects in an amount of at least 3%, in some aspects in an

amount of at least 4%, in some aspects in an amount of at least 5%, in some aspects in an amount of at least 6%, in some aspects in an amount of at least 7%, in some aspects in an amount of at least 8%, in some aspects in an amount of at least 9%, in some aspects in an amount of at least 10%, in some aspects in an amount of at least 11%, in some aspects in an amount of at least 12%, in some aspects in an amount of at least 13%, and in some aspects in an amount of at least 14%, by mass of total fat.

In some preferred aspects, the free fatty acid content of the renewable source feedstock is reduced by glycerolysis by an amount between about 1% and about 14%, in some aspects between about 2% and about 13%, in some aspects between about 3% and about 12%, in some aspects between about 4% and about 11%, and in some aspects between about 5% and about 10%, by mass of total fat.

In some preferred aspects, the free fatty acid content of the renewable source feedstock prior to glycerolysis is greater than 5% and the resultant free fatty acid content of the renewable source feedstock after glycerolysis is less than 5%.

In some preferred aspects, the levels of free fatty acids in the feedstock after glycerolysis is less than about 4%, in some aspects less than about 3%, in some aspects less than about 2%, in some aspects less than about 1%, in some less than about 0.9%, in some aspects less than about 0.8%, in some aspects less than about 0.7%, in some aspects less than about 0.6%, and in some aspects less than about 0.5%, by mass of total fat. In some preferred aspects, the free fatty acid content of the feedstock after glycerolysis is between about 0.1% and less than 4%, in some aspects between about 0.25% and less than 3%, and in some other aspects between about 0.5% and less than 2% by mass of total fat.

In some preferred aspects, the glycerolysis process converts up to 80%, in some aspects up to 85%, in some aspects up to 90%, in some aspects up to 95%, in some aspects up to 98%, and in some other aspects up to 99% of free fatty acids of the feedstock to monoglycerides, diglycerides, or a combination thereof.

In some preferred aspects, the glycerolysis process converts at least 80%, in some aspects at least 85%, in some aspects at least 90%, in some aspects at least 95%, in some aspects at least 98%, and in some other aspects at least 99% of free fatty acids of the feedstock to monoglycerides, diglycerides, or a combination thereof.

In some preferred aspects, the glycerolysis process is conducted with a molar excess of glycerin to the free fatty acids in the renewable oil source. In some aspects, the molar excess of glycerin to the free fatty acids is at least 1.1:1, in some aspects at least 1.25:1, in some aspects at least 1.5:1.

In some preferred aspects, the glycerolysis process is conducted under a molar excess of glycerin to the fatty acids in the renewable oil source. In some aspects, the free fatty acid content of the renewable oil source prior to glycerolysis contains between about 75% and about 95% triacylglycerides, between about 5% and about 12% diacylglycerides and less than about 5%, in some aspects less than about 4%, in some aspects less than about 3%, and in some aspects less than about 2% monoacylglycerides, such that the total content of the diacylglycerides and monoacylglycerides in the renewable oil source is less than 15%. In some aspects, at least 80% and up to 99% of the free fatty acid content of the renewable oil source is converted by the glycerolysis process to at least 15% monoglycerides, diglycerides, or a combination thereof. In some aspects, at least 80% and up to 99% of the free fatty acid content of the renewable oil source is converted by the glycerolysis process to at least 15% monoglycerides, diglycerides, or a combination thereof.

In some aspects, glycerolysis is conducted on the free fatty acid content of the renewable oil source in the presence of a source of glycerin to provide a feedstock having a reduced triacylglycerides portion, wherein at least 80% of the free fatty acid content of the renewable oil source is converted by glycerolysis to at least 15% monoglycerides, diglycerides, or a combination thereof. In some aspects, at least 80% of the free fatty acid content of the renewable oil source is converted by glycerolysis to at least 16% monoglycerides, diglycerides, or a combination thereof. In some aspects, at least 80% of the free fatty acid content of the renewable oil source is converted by glycerolysis to at least 17% monoglycerides, diglycerides, or a combination thereof. In some aspects, at least 80% of the free fatty acid content of the renewable oil source is converted by glycerolysis to at least 18% monoglycerides, diglycerides, or a combination thereof. In some aspects, at least 80% of the free fatty acid content of the renewable oil source is converted by glycerolysis to at least 19% monoglycerides, diglycerides, or a combination thereof. In some aspects, at least 80% of the free fatty acid content of the renewable oil source is converted by glycerolysis to at least 20% monoglycerides, diglycerides, or a combination thereof.

Any excess glycerin not utilized during the glycerolysis reaction can be recycled. In some aspects, the excess glycerin is recycled back to the glycerin source.

Sources of glycerin may be plant-based or animal-based, preferably such that the glycerin source is renewable. In some aspects, the glycerin source is a byproduct of biodiesel production, such as the transesterification of a renewable oil source. In some aspects, the plant-based glycerin may be from processing corn oil, while in some other aspects from processing palm oil. The source of glycerin may also be animal-based from processing

animals. In some aspects, the glycerin source is provided from splitting or transesterification of fats or oils. In some other preferably aspects, the glycerin source can be crude glycerin, or alternatively refined glycerin.

A pre-treatment step may be conducted on the feedstock prior to conducting glycerolysis. A pre-treatment step may be conducted on the converted feedstock after glycerolysis prior to a renewable diesel process. Alternatively, a pre-treatment step may be conducted prior to and also after conducting glycerolysis. The pre-treatment step could be conducted to reduce metals, other ions, or other byproducts of the solvent extraction and/or glycerolysis processes. In some aspects, the pre-treatment step could comprise drying, filtration and/or treatment with one or more organic acids along with adsorption on bleaching earth or other structured media, such as silica gel. In some aspects, drying is carried out using temperature and vacuum.

The converted feedstock can then be used for biodiesel production and/or renewable fuel production. In some aspects, the converted feedstock can be mixed with the renewable oil source, such as to provide a mixed feedstock having a desirable free fatty acid content. In some aspects, the mixed feedstock comprises a blend of a first portion of the converted feedstock and a second portion of the renewable oil source, wherein the mixed feedstock has a free fatty acid level that is lower than that of the renewable oil source.

Referring again to FIG. 1, which illustrates an embodiment of a solvent extraction process that may be applied to DDGS, as a first step, DDGS meal is fed into an extractor. In some aspects, the DDGS meal may optionally be ground before being fed into an extractor to reduce the particle size of the DDGS meal. In some aspects, the DDGS meal is ground such that about 80%, in some aspects about 85%, in some aspects about 90%, in some aspects about 95%, in some aspects about 99%, and in some aspects about 100% of the DDGS meal has a particle size less than about 1 millimeter.

The crude oil extracted from DDGS in FIG. 1 may be used as a renewable feedstock to produce green renewable fuels. The converted feedstock and/or mixed feedstock produced as a result of the glycerolysis reaction may also be used as a renewable feedstock to produce green renewable fuels.

As illustrated in FIG. 4, the renewable feedstock, whether crude oil extracted from DDGS, the converted feedstock and/or the mixed feedstock, may be subjected to a hydro-treating process, which involves the hydrogenation of the double bonds of the side chains of the triglycerides in the renewable oil feedstock and the removal of oxygen on the metal sites of the catalysts. The hydro-treating of the renewable oil feedstock leads to the production of

C14-C20 hydrocarbons, in some aspects C15-C18 straight chain and branched paraffins, which is a liquid mixture with the boiling point range of diesel, such that the renewable diesel can be a fuel replacement for petro-diesel.

Factors affecting hydro-treating process are temperature, hydrogen/oil ratio, pressure, catalyst and space velocity. While the hydro-treatment of vegetable oils is a mature technology, it is not believed that the hydro-treating process has utilized the unique renewable oil feedstocks of the present invention.

In the hydro-treating process, the renewable oil feedstock may be mixed with recycle hydrogen and/or make-up hydrogen before being provided at process pressure in a reactor system comprising one or more catalytic hydrodeoxygenation reactors. In some aspects, the reactor is a multi-stage adiabatic, catalytic hydrodeoxygenation reactor. In the reactor, the renewable oil feedstock is saturated and completely deoxygenated to yield deoxygenated hydrocarbon products. The primary deoxygenation reaction by-products are propane, water and carbon dioxide, which along with other low molecular weight hydrocarbons may be separated from the deoxygenated product. In some aspects, the deoxygenated product is processed in a second reactor packed with a selective hydrocracking catalyst whereby both cracking of larger molecules and hydroisomerization takes place. In some aspects, the deoxygenated product is mixed with additional hydrogen gas for the hydroisomerization process. The excess hydrogen and the isomerized product may be separated in a conventional gas/liquid separator. The resulting product then undergoes separation in a fractional distillation column where the various products are produced, including green renewable propane and light ends, green renewable naphtha product, and green renewable diesel product. The green renewable diesel product may include a green renewable jet product and a green renewable diesel product.

In some aspects, the green renewable diesel product comprises renewable diesel meeting current low-carbon fuel standards. In some aspects, the green renewable diesel product comprises renewable diesel meeting ASTM D975 specification for petroleum diesel in the United States and EN 590 in Europe.

In some aspects, the green renewable jet product comprises renewable jet fuel, otherwise known as sustainable aviation fuel, meeting ASTM D7566 standards. In some aspects, the sustainable aviation fuel can be blended with convention jet fuel meeting ASTM D1655 standards.

Further Processing of the Crude, Extracted Oil

After extraction from the DDGS, the crude oil may be further processed as desired. For example, the crude oil may be filtered, degummed, neutralized, bleached and/or deodorized to provide a food grade oil for consumer use. For example, in one embodiment, the crude oil may be degummed, caustic refined, and subjected to a soap removal step according to commercially available processes, such as water washing. Following these steps the oil may then be subjected to one or more clay bleaching steps to achieve an oil of desired content and color. Where one or more clay bleaching steps are used, the clay may be an acid activated clay or a non-acid activated clay, a silica based product, other adsorptive filtration media and/or combinations thereof and may include, by way of example, an acid activated clay or a non-acid activated clay at 0.1%-1%, 1-5%, 2-4%, or 2-3%. In addition to or as an alternative to clay bleaching, after the crude oil has been degummed, caustic refined and subjected to a soap removal step, a food grade oil of a desired color, very low free fatty acid content, improved flavor and improved stability may be achieved using a deodorization step whereby thermal decomposition of color bodies and removal of volatile components takes place under high temperature and high vacuum. Suitable processes for degumming, caustic refining, and soap removal are also described herein in relation to the pretreatment steps for biodiesel and glycerine production from the crude oil. Degumming, neutralization, bleaching and/or deodorization are also accessible to those of skill in the art and can be utilized as described herein to achieve a food grade oil and industrial grade oils.

Alternatively, the crude oil extracted from DDGS may be used to produce biodiesel and glycerine. A flow-chart representation of a process for refining biodiesel and glycerine from the crude extracted oil is shown in FIG. 2. There are several processes that may be used to produce biodiesel from oils and fats, including base catalyzed transesterification, direct acid catalyzed transesterification and/or esterification, enzyme catalyzed transesterification and/or esterification, high pressure transesterification (i.e. Henkel process), and/or a combination of same for conversion of the oil to biodiesel. Biodiesel production technologies and equipment are commercially available from, for example, Crown Iron Works Company of Minneapolis, Minn., U.S.A., and from Lurgi AG of Frankfurt, Germany. To produce biodiesel and glycerine from the crude oil extracted from the DDGS, an acid catalyzed esterification or caustic neutralization, followed by a transesterification process may be used.

In one embodiment, of the refining process outlined in FIG. 2, the crude extracted oil is crude corn oil, and before the crude corn oil is subjected to a transesterification process, it may be pretreated. Pretreatment of the crude corn oil may be carried out, for example, to remove gums included in the oil or to remove or neutralize free fatty acids. As part of a

degumming process, an acid, such as phosphoric acid, may be added to the crude corn oil and the crude oil may be heated, for example, using steam. In such a process, the acid and steam work to hydrate the gums so that the gums can be separated from the crude corn oil, such as by centrifugation or another suitable separation technique.

5 Free fatty acids in the crude corn oil are generally undesirable because they form soaps within the oil as they react with the base catalyst used to drive the transesterification reaction. If the crude corn oil is also pretreated with a degumming step, the addition of the strong base intended to neutralize the free fatty acids may occur after addition of the acid in the degumming step. In this manner, the base added to neutralize the free fatty acids can also
10 work to neutralize the acid used in the degumming step. The soap stock that results from degumming and neutralization of the crude corn oil may be separated from the corn oil using standard equipment, such as a centrifugal separator. Alternatively, the free fatty acids can be removed and acid esterified to form biodiesel, or combined with glycerine to form triglycerides, which are then transesterified to form biodiesel.

15 Treatment of the crude corn oil may also include one or more bleaching steps, such as one or more heat bleaching or clay bleaching steps as described above, to remove residual color or other impurities from the corn oil.

Where pretreatment of the crude corn oil includes degumming and neutralization of free fatty acids, prior to a transesterification process, the degummed and neutralized oil is
20 typically washed prior to transesterification. Washing may include, for example, mixing the pretreated corn oil with warm wash water. After washing, the oil and wash water are separated, and the pretreated corn oil is dried, such as by a vacuum-dryer, to a desired water content.

In one embodiment, the pretreated corn oil can be subjected to a transesterification
25 reaction to provide biodiesel and glycerine. The transesterification reaction is based on the chemical reaction of triglycerides contained in the crude corn oil with an alcohol in the presence of an alkaline catalyst. The alkaline catalyst used in the transesterification reaction may be selected from several different alkaline materials. Suitable catalysts are strong bases and include, for example, NaOH (caustic soda), KOH (potash), and CH_3NaO (sodium
30 methyllate). The alcohol used in the transesterification reaction may be selected from, for example, methanol or ethanol.

As the transesterification reaction is carried out, the alcohol and catalyst may be delivered into the corn oil in parallel, as separate reaction components, or the alcohol and catalyst can be delivered to the crude corn oil as a mixture. When delivered as a mixture, the

catalyst may be dissolved in the alcohol by any suitable means prior to charging the mixture into the corn oil. Alternatively, the catalyst may be provided as a liquid and mixed with the alcohol, limiting the need for dissolution of the catalyst in the alcohol prior to mixing the alcohol and catalyst with the corn oil. Where the catalyst is mixed with the alcohol as a liquid, the catalyst may be added to the alcohol by, for example, one or more metering pumps. In addition, because an alkaline catalyst might be sensitive to water, the catalyst may be stored in a pump tank protected with a nitrogen layer.

In carrying out the transesterification reaction, the alcohol, catalyst and corn oil may be charged into a closed reaction vessel. The reaction system can be closed to the atmosphere to prevent loss of the alcohol used in the transesterification reaction. As the reaction components are mixed, the mixture may be kept just below the boiling point of the alcohol to speed the reaction time. In addition, an excess amount of alcohol is typically used to ensure total conversion of the corn oil triglycerides into the desired ester product. The transesterification reaction produces a two-phase reaction product that includes an ester-rich phase (crude biodiesel) and a glycerine-rich phase (crude glycerine). The crude glycerine is much more dense than the crude biodiesel and the two phases can be easily separated by gravity separation or, if needed or desired, centrifugation.

In one embodiment, transesterification of the corn oil takes place in one or more mixer-settler units. In such units, the transesterification reaction occurs in a mixer or reactor included in the mixer-settler units. The crude biodiesel and crude glycerine resulting from the transesterification reaction form two distinct phases that can be separated in the settlers. If two or more mixer-settler units are used as the reaction vessels, the feedstock and the intermediate product, respectively, may flow successively through the two or more mixer-settler units. Each mixer-settler unit can be supplied with the desired alcohol and catalyst in parallel. The reactors included in the mixer-settler units can be multi-stage in design, comprising various reaction chambers in order to achieve maximum conversion efficiency to the ester product. The settlers allow phase separation to approach the limit of solubility, which eases downstream purification of the biodiesel and glycerine products.

At the transesterification stage, vapors vented from the reaction vessel, such as the one or more mixer-settlers, may be routed to a condenser where they are partly or completely condensed and returned to the reaction process. The same may be done with the vessel used to store or deliver the alcohol used in the transesterification reaction. Even further, where the catalyst is provided in liquid form, it too may be stored and delivered from a storage vessel, and any vapors vented from the catalyst storage vessel may also be captured, partly or

completely condensed, and returned to the reaction process in liquid form.

Once the transesterification reaction is complete, two major products exist: glycerine and biodiesel. The glycerine is included in the crude glycerine phase and the biodiesel is incorporated in the crude biodiesel phase. Each of these crude phases may include a substantial excess of the alcohol used in the reaction. Moreover, the crude reaction products may include other impurities such as excess catalyst, soaps and high boiling impurities. If desired, some of these impurities may be treated or removed from the crude reaction products before the crude biodiesel and the crude glycerine phases are separated. For example, a suitable acid may be added to and mixed with the reaction products to neutralize excess catalyst and further help break any emulsions. Additionally, excess alcohol may be removed from the crude reaction products using standard distillation equipment and techniques.

After the crude biodiesel and crude glycerine are separated, they are typically subjected to further refining. For example, after separation, the crude biodiesel may contain residual alcohol, glycerine, small amounts of catalyst, and soaps. This may be the case even if the crude reaction products are refined to remove or neutralize impurities prior to separation. If they have not already been refined to neutralize excess catalyst or remove excess alcohol, or if residual catalyst and excess alcohol still remain in the separated reaction products, the crude biodiesel and crude glycerine may be treated with a suitable acid to neutralize the residual catalyst and subjected to, for example, a flash evaporation process or distillation to remove the excess alcohol.

Even where steps are taken to neutralize residual catalyst and remove excess alcohol, the refined biodiesel may still include water soluble impurities. In order to remove such water-soluble substances, the refined biodiesel may be washed and dried. To avoid the formation of emulsions during washing, the biodiesel may be pH adjusted, for example, by the addition of an acid to the biodiesel to be washed. Dilute HCl, such as a 3.7% strength HCl, is suitable for such an application and can be prepared and added as necessary. The biodiesel wash process may simply include gentle mixing of the biodiesel with warm water, which will work to remove residual, water soluble impurities as they are taken up in the aqueous phase.

If the biodiesel is processed through such a washing step, the refined and washed biodiesel may contain excess water. Such excess water may be removed, for example, by subjecting the biodiesel to a drying step. The drying step may include, for example, vacuum drying the biodiesel to a desired water content in a dryer circuit. The dried biodiesel, which is ready for use, distribution or sale, is collected and stored. Though the biodiesel is serviceable

at this point, if desired, it can be subjected to further distillation to remove any color bodies and other higher molecular weight impurities remaining to provide a colorless biodiesel.

The separated, crude glycerine phase may also be further refined after separation. In particular, the crude glycerine may be neutralized with a suitable acid, the excess alcohol may
5 be removed by distillation or flash evaporation, and the crude glycerine may be dried to remove residual water. Even if the crude reaction products of the transesterification process are neutralized and the excess alcohol present in the crude reaction products is removed prior to separation, the separated, crude glycerine may still contain residual catalyst or alcohol. Where that is the case, the separated, crude glycerine may be subjected to additional
10 neutralization, absorptive filtration, and/or distillation steps to neutralize any residual catalyst and remove any remaining alcohol. Once such neutralization, distillation and drying steps are complete, the crude product typically contains approximately 80-88% pure glycerine. This crude glycerine can be further refined to a purity of 99% or higher, as is known in the art, such that the glycerine product is suitable for use in cosmetic or pharmaceutical applications.

15 In order to minimize loss of the alcohol used in the transesterification reaction, all vessels which contain alcohol, whether in substantially pure form or as part of a crude reaction product, may be connected to a vent system to capture any alcohol vapors. Captured alcohol vapors may be fed into a condensing system that recovers the alcohol and recycles the alcohol back into the refining process.

20 Still alternatively, the crude oil extracted from DDGS may be used to produce other oleochemicals, particularly oleochemicals for the personal care products and home care products industries. A flow-chart representation of oleochemical processing of crude oil extracted from DDGS is shown in FIGS. 5A-5D. There are several processes that may be used to produce various oleochemicals after the crude oil undergoes a splitting (or hydrolysis)
25 process of the triglycerides into crude fatty acids and glycerol/glycerine, followed by additional processing including esterification, fractionation, distillation, hydrogenation, epoxidation, ethoxylation, conjugation, hardening, chlorination and/or sulfation. After the splitting process, additional processing may be utilized prior to such processes, including evaporation, purification and/or bleaching to produce glycerol/glycerine and crude fatty
30 acids. The crude fatty acids and/or glycerine can be subjected to further chemical and enzymatic reactions to produce desired oleochemicals for personal care products and home care products.

In some aspects, the glycerine is subjected to esterification and distillation processing to yield distilled fatty esters of glycerine.

In some aspects, the crude fatty acids are subjected to esterification processing to yield fatty acid esters, esterification and distillation processing to yield distilled fractionated fatty esters, and/or esterification and epoxidation processing to yield alkyl epoxy esters. In some aspects, the crude fatty acids are subjected to ethoxylation processing to yield fatty acid ethoxylates. In some aspects, the crude fatty acids are subjected to conjugation processing to yield conjugated fatty acids. In some aspects, the crude fatty acids are subjected to hardening processing to yield saturated fatty acids. In some aspects, the crude fatty acids are subjected to hardening processing and then hydrogenation processing to yield fatty alcohols. In some aspects, the crude fatty acids are subjected to esterification processing to yield fatty acids methyl esters and then hydrogenation to yield fatty alcohols. In some aspects, the fatty alcohols derived from fatty acids may then be subjected to Guerbet reaction to yield Guerbet alcohols, chlorination to yield alkyl chlorides, ethoxylation to yield fatty alcohol ethoxylates, sulfation to yield fatty alcohol sulfates and/or esterification to yield esters. The fatty alcohol ethoxylates may further under propoxylation to yield fatty alcohol alkoxyates, sulfation to yield fatty alcohol ether sulfates, phosphatization to yield fatty alcohol ether phosphates and/or sulfitation to yield fatty alcohol sulfosuccinates. In some aspects, the crude fatty acids are subjected to fractionation processing to yield C12, C14, C16 and/or C18 fractionated fatty acids, with the remaining fraction subjected to esterification and distillation to yield distilled fractionated fatty esters.

Examples of common personal care ingredients ultimately derived from these fatty acids according to aspects of the present invention may include octyl stearate, glyceryl stearate, PEG distearate and stearylalkonium chloride. Examples of materials used in producing home care products ultimately derived from these fatty acids according to aspects of the present invention may include sulfonated methyl esters and stearyl alcohol.

Still alternatively, the crude oil extracted from DDGS may be used to produce a green renewable diesel fuel. As illustrated in FIG. 4, the crude oil extracted from DDGS may be subjected to a hydro-treating process, which involves the hydrogenation of the double bonds of the side chains of the triglycerides in the crude oil extracted from DDGS and the removal of oxygen on the metal sites of the catalysts. The hydro-treating of the crude oil extracted from DDGS leads to the production of C14-C20 hydrocarbons, which is a liquid mixture with the boiling point range of diesel.

In the hydro-treating process, crude oil extracted from DDGS is the feedstock, which may be mixed with recycle hydrogen and/or make-up hydrogen before being provided at process pressure in a reactor system comprising one or more catalytic hydrodeoxygenation

reactors. In some aspects, the reactor is a multi-stage adiabatic, catalytic hydrodeoxygenation reactor. In the reactor, the crude oil extracted from DDGS is saturated and completely deoxygenated to yield deoxygenated hydrocarbon products. The primary deoxygenation reaction by-products are propane, water and carbon dioxide, which along with other low molecular weight hydrocarbons may be separated from the deoxygenated product. In some aspects, the deoxygenated product is processed in a second reactor packed with a selective hydrocracking catalyst where both cracking of larger molecules and hydroisomerization takes place. In some aspects, the deoxygenated product is mixed with additional hydrogen gas for the hydroisomerization process. The excess hydrogen and the isomerized product may be separated in a conventional gas/liquid separator. The resulting product then undergoes separation in a fractional distillation column where the various products are produced, including green propane and light ends, green naphtha product, and green diesel product. The green diesel product may include a green jet product and a green diesel product. The hydro-treating process for producing green diesel operates in mild conditions and integrates well within existing petroleum refineries. In some aspects, the hydro-treating process can be conducted onsite at an ethanol facility.

Distillers Meal & Distillers Meal as an Animal Feed or Animal Feed Supplement

The distillers meal produced by a solvent extraction method as described herein retain desired nutritional properties. The solvent extraction process applied to the DDGS may be chosen and tailored to provide a distillers meal that exhibits nutritional properties suitable for animal feed applications. For example, in one embodiment, the DDGS are subjected to a solvent extraction process that provides distillers meal that retains substantially all the crude protein and fiber content of the DDGS prior to solvent extraction. In another embodiment, the distillers meal is corn distillers meal that retains substantially all of the crude protein and fiber content of the DDGS prior to solvent extraction. In yet another embodiment, distillers meal is corn distillers meal that retains substantially all of the crude protein and fiber content of the DDGS prior to solvent extraction and is the product of a hexane extraction process conducted on corn DDGS produced by a dry-grind corn ethanol biorefinery.

DDGS are often used as a feed supplement for livestock and poultry fed high grain content finishing diets. Before solvent extraction, DDGS may have approximately 30% by weight crude protein ("CP") and 20% crude fiber ("CF"). Solvent extraction as described herein removes most of the oil from the DDGS so that such oil can be processed or refined to provide additional products of commercial value. However, because most of the oil present in

DDGS is removed in producing distillers meal, the energy potential of the distillers meal from the fat content is lower than that exhibited by the DDGS prior to solvent extraction. Despite the lower energy potential resulting from oil extraction, distillers meal as described herein provides a high-quality, low-cost protein feed that can be fed at higher inclusion rates for animals, such as domestic pets, livestock or poultry. In addition, as described herein, livestock feed distillers meal exhibit desirable carcass traits, and the nutritional properties of distillers meal may provide a superior feed or feed supplement.

In one embodiment, the distillers meal disclosed herein may be used to supplement animal diets at a desired percentage of the total diet, on a dry matter basis. In one embodiment, the distillers meal may be used as a CP supplements in livestock and poultry feed diets. In addition, the distillers meal described herein may also be used as an animal feed or feed supplement that provides desired amounts of carbohydrates, fiber or non-protein nitrogen (NPN) containing compounds. The distillers meal can be used at a percentage of the total feed that maximizes the nutritional components of the feed. The relative amount of distillers meal incorporated into an animal diet may depend on, for example, the species, sex, or agricultural use of the animal being fed. Additionally, the relative amount of distillers meal incorporated into a particular diet may depend on the nutritional goals of the diet.

In one embodiment, distillers meal may be used to provide approximately 50% to approximately 75% by weight, on a dry matter basis, of a total diet for use in an animal feed. In one such embodiment, the distillers meal is corn distillers meal as described herein and is used to provide approximately 50% to 55%, 50% to 60%, 50% to 65%, or 50% to 70% by weight, on a dry matter basis, of the total diet. In some aspects, the distillers meal is substituted in an animal feed diet for soybean meal, corn, DDGS and/or other protein supplements in rations for such animal. In another such embodiment, the distillers meal is corn distillers meal as described herein and is used to provide approximately 50% to 55%, 55% to 60%, 55% to 70%, 60% to 65%, 60% to 70%, or 70% to 75% by weight, on a dry matter basis, of the total diet. In some aspects, the corn distillers meal is substituted in an animal feed diet for soybean meal, corn, DDGS and/or other protein supplements in rations for such animal.

In some aspects, the distillers meal as described herein is used as a feed supplement or formula feed for beef cattle, including the beef cattle classes of calves, cattle on pasture and/or feedlot cattle, dairy cattle, particularly veal milk replacer and/or herd milk replacer, starter, growing heifers, bulls and dairy beef, lactating dairy cattle and/or non-lactating dairy cattle, equine, including foal, mare, breeding and/or maintenance equine, swine, including

pre-starter, starter, grower, finisher, gilts, sows and adult boars, lactating gilts and/or lactating sows, poultry including layer chickens (starting/growing, finisher, laying and/or breeder), broiler chickens (starting/growing, finisher and/or breeder), broiler breeder chickens (starting/growing, finishing and/or laying) and/or turkeys (starting/growing, finisher, laying and/or breeder), geese and/or ducks, goat, including starter, grower, finisher, breeder and/or lactating goats, sheep, including starter, grower, finisher, breeder and/or lactating sheep, fish, including trout, catfish, salmon, and other species other than trout, catfish or salmon, and rabbit, including grower and/or breeder.

Distillers meal as describe herein, which results from solvent extracted DDGS that is the result of at least a portion of high-oil content corn, may contain one or more signature protein traits that are not available in standard #2 yellow dent corn.

In some preferred aspects, the distillers meal is derived from a corn grain blend of low-oil content corn and high-oil content corn, wherein the corn grain blend having at least 5% high-oil content corn, wherein a portion of the distillers meal derived from the high-oil content corn can be determined by one or more signature protein traits expressed in the high-oil content corn that are not available in standard #2 yellow dent corn.

Various embodiments of systems, devices, and methods have been described herein. These embodiments are given only by way of example and are not intended to limit the scope of the claimed inventions. It should be appreciated, moreover, that the various features of the embodiments that have been described may be combined in various ways to produce numerous additional embodiments. Moreover, while various materials, dimensions, shapes, configurations and locations, etc. have been described for use with disclosed embodiments, others besides those disclosed may be utilized without exceeding the scope of the claimed inventions.

Persons of ordinary skill in the relevant arts will recognize that the subject matter hereof may comprise fewer features than illustrated in any individual embodiment described above. The embodiments described herein are not meant to be an exhaustive presentation of the ways in which the various features of the subject matter hereof may be combined. Accordingly, the embodiments are not mutually exclusive combinations of features; rather, the various embodiments can comprise a combination of different individual features selected from different individual embodiments, as understood by persons of ordinary skill in the art. Moreover, elements described with respect to one embodiment can be implemented in other embodiments even when not described in such embodiments unless otherwise noted. Still further, the methods, systems, and compositions disclosed and claimed herein can comprise,

consist of, or consist essentially of the essential elements and limitations of the methods, systems and compositions described herein.

Although a dependent claim may refer in the claims to a specific combination with one or more other claims, other embodiments can also include a combination of the dependent claim with the subject matter of each other dependent claim or a combination of one or more features with other dependent or independent claims. Such combinations are proposed herein unless it is stated that a specific combination is not intended.

Any incorporation by reference of documents above is limited such that no subject matter is incorporated that is contrary to the explicit disclosure herein. Any incorporation by reference of documents above is further limited such that no claims included in the documents are incorporated by reference herein. Any incorporation by reference of documents above is yet further limited such that any definitions provided in the documents are not incorporated by reference herein unless expressly included herein.

For purposes of interpreting the claims, it is expressly intended that the provisions of 35 U.S.C. § 112(f) are not to be invoked unless the specific terms “means for” or “step for” are recited in a claim.

CLAIMS

1. Distillers meal derived from the extraction of crude corn oil from distillers dried grains with solubles, wherein the distillers dried grains with solubles is a co-product produced in a dry-grind ethanol facility configured to process a corn grain feedstock, and wherein the
5 corn grain feedstock comprises a first portion of high-oil content corn grain and an optional second portion of low-oil content corn grain.

2. Crude corn oil extracted from distillers dried grains with solubles using an extraction process, wherein the distillers dried grains with solubles is a co-product produced in a dry-
10 grind ethanol facility configured to process a corn grain feedstock, and wherein the corn grain feedstock comprises a first portion of high-oil content corn grain and an optional second portion of low-oil content corn grain.

3. A method of producing one or more renewable fuels or one or more biofuels from a
15 renewable oil source, the method comprising:

providing a renewable oil source derived from the extraction of crude corn oil from distillers dried grains with solubles using an extraction process, wherein the distillers dried grains with solubles is a co-product produced in a dry-grind ethanol facility configured to process a corn grain feedstock, and wherein the corn grain feedstock comprises a first portion
20 of high-oil content corn grain and an optional second portion of low-oil content corn grain;

conducting glycerolysis on a free fatty acid content of the renewable oil source in the presence of a source of glycerin to provide a feedstock having a reduced free fatty acid content; and

subjecting the feedstock to a conversion process to produce one or more renewable
25 fuel or one or more biofuels.

4. A system for producing a feedstock from a renewable oil source, the feedstock capable of being used in a renewable fuel process for producing one or more renewable fuels or a biofuel process for producing one or more biofuels, the system comprising:

30 a renewable oil derived from the extraction of crude corn oil from distillers dried grains with solubles using an extraction process, wherein the distillers dried grains with solubles is a co-product produced in a dry-grind ethanol facility configured to process a corn

grain feedstock, and wherein the corn grain feedstock comprises a first portion of high-oil content corn grain and an optional second portion of low-oil content corn grain;

a source of glycerin; and

a reactor vessel for combining the renewable oil source and the glycerin source into a reaction mixture, the reactor vessel including a means for conducting a glycerolysis reaction on a free fatty acid content of the renewable oil source to provide a feedstock having a reduced free fatty acid content;

wherein the feedstock is capable of being subjected to a conversion process to produce one or more renewable fuels or one or more biofuels.

5. A renewable fuel or a biofuel produced from a renewable oil source derived from the extraction of crude corn oil from distillers dried grains with solubles using an extraction process, wherein the distillers dried grains with solubles is a co-product produced in a dry-grind ethanol facility configured to process a corn grain feedstock, and wherein the corn grain feedstock comprises a first portion of high-oil content corn grain and an optional second portion of low-oil content corn grain; wherein the renewable oil source has undergone a glycerolysis reaction in the presence of glycerin to provide a feedstock having a reduced free fatty acid content, and wherein the feedstock subjected to a conversion process to produce the renewable fuel or the biofuel.

6. A feedstock produced from a renewable oil source, wherein the renewable oil source is derived from the extraction of crude corn oil from distillers dried grains with solubles using an extraction process, wherein the distillers dried grains with solubles is a co-product produced in a dry-grind ethanol facility configured to process a corn grain feedstock, and wherein the corn grain feedstock comprises a first portion of high-oil content corn grain and an optional second portion of low-oil content corn grain, and wherein the renewable oil source has undergone a glycerolysis reaction in the presence of glycerin to provide the feedstock having a reduced free fatty acid content, and wherein the feedstock capable of being subjected to a conversion process to produce one or more renewable fuels or one or more biofuels.

7. Any of the foregoing claims 1-6, wherein the extraction process is a solvent extraction process.

8. Any of the foregoing claims 3-6, wherein the renewable oil source is provided from a solvent extraction of distillers dried grains with solubles (DDGS), distillers dried grains (DDG), or a combination thereof, the solvent extraction using at least one non-polar solvent comprising one or more C5-C7 alkanes, preferably one or more isomers, enantiomers or mixtures of C5-C7-alkanes, preferably the one or more isomers, enantiomers or mixtures of C5-C7-alkanes including one or more of n-pentane, n-hexane and n-heptane, as well as the structural isomers thereof (i.e., isopentane, neopentane, isohexane, 2-methylpentane, 2,3-dimethylbutane, neohexane, isohexane, 2-methylhexane, 2,2-dimethylpentane, 2,3-dimethylpentane, 2,4-dimethylpentane, 3-ethylpentane, and 2,2,3-trimethylbutane) and petroleum ether.

9. Any of the foregoing claims 3-6, wherein the renewable oil source is provided from a solvent extraction of distillers dried grains with solubles (DDGS), distillers dried grains (DDG), or a combination thereof, the solvent extraction using at least one at least one renewable solvent, the at least one renewable solvent preferably comprising 2-methyloxolane.

10. Any of the foregoing claims 3-6, wherein the renewable oil source is a renewable corn oil source provided from solvent extraction of distillers dried grains with solubles (DDGS), distillers dried grains (DDG), or a combination thereof, wherein the solvent extraction using at least one solvent having a boiling point in the range of about 36° C. to about 99° C.

11. Any of the foregoing claims 3-6, wherein the glycerolysis process is a thermodynamic reaction conducted at a reaction temperature between about 150° C. and about 250° C., and in some aspects between about 175° C. and about 225° C., for a period of time between about 30 minutes and about 180 minutes, and in some aspects between about 60 minutes and about 120 minutes, wherein the glycerolysis reaction has a glycerin to free fatty acid molar ratio of at least 1.1:1, in some aspects at least 1.25:1, in some aspects at least 1.5:1.

12. Any of the foregoing claims 3-6, wherein the one or more biofuels comprises biodiesel.

13. Any of the foregoing claims 3-6, wherein the one or more renewable fuels is chosen from the group consisting of renewable hydrogen, renewable propane, renewable naphtha, renewable jet fuel and renewable diesel.

14. Any of the foregoing claims 1-6, wherein the first portion of high-oil content corn grain has an oil content of more than 5%, in some aspects at least 6%, in some aspects up to 30%, in some aspects up to 20%, in some aspects up to 10%, in some aspects up to 9.5%, and
5 in some aspects up to 9.0%, on a dry weight basis of the corn grain.

15. Any of the foregoing claims 1-6, wherein the first portion of high-oil content corn grain has an oil content between 6% and 30%, in some aspects between 6% and 20%, in some aspects between 6% and 10%, in some aspects between 6.0% and 9.5%, in some
10 aspects between 6.1% and 9.5%, in some aspects between 6.2% and 9.5%, in some aspects between 6.3% and 9.5%, in some aspects between 6.4% and 9.5%, in some aspects between 6.5% and 9.5%, in some aspects between 6.5% and 9.4%, in some aspects between 6.5% and 9.3%, in some aspects between 6.5% and 9.2%, in some aspects between 6.5% and 9.1%, in some aspects between 6.5% and 9.0%, on a dry weight basis of the corn grain.

16. Any of the foregoing claims 1-6, wherein the first portion of high-oil content corn grain has an oil content greater than the average oil content of #2 yellow dent corn grain.

17. Any of the foregoing claims 1-6, wherein the first portion of high-oil content corn grain comprises at least 1%, in some aspects at least 2%, in some aspects at least 3%, in some
20 aspects at least 4%, in some aspects at least 5%, in some aspects at least 6%, in some aspects at least 7%, in some aspects at least 8%, in some aspects at least 9%, in some aspects at least 10%, of the corn grain feedstock.

18. Any of the foregoing claims 1-6, wherein a ratio of the first portion of high-oil content corn grain to the second portion of low-oil content corn is at least 1:20, in some aspects at least 3:50, in some aspects at least 7:100, in some aspects at least 4:25, in some aspects at least 9:100, and in some aspects at least 1:10.

19. Any of the foregoing claims 1-6, wherein a ratio of the first portion of high-oil content corn grain to the second portion of low-oil content corn is up to 1:1, in some aspects up to 2:5, in some aspects up to 3:10, in some aspects up to 1:4, and in some aspects up to 1:5.

20 Any of the foregoing claims 1-6, wherein a ratio of the first portion of high-oil content corn grain to the second portion of low-oil content corn is between 1:100 and 1:1, in some aspects between 1:50 and 2:5, in some aspects between 1:20 and 3:10, in some aspects between 1:20 and 1:4, in some aspects between 1:20 and 1:5, and in some preferred aspects
5 between 1:10 and 1:5.

21. Any of the foregoing claims 16, wherein the first portion of high-oil content corn grain comprises at least 5% and up to 25% by weight of the corn grain feedstock, preferably at least 5% up to 20% by weight of the corn grain feedstock, preferably at least 5% up to 15%
10 by weight of the corn grain feedstock, more preferably at least 10% up to 20% by weight of the corn grain feedstock.

22. Any of the foregoing claims 2-6, wherein an amount of crude corn oil derived from the first portion of high-oil content corn grain of the corn grain feedstock can be determined
15 by one or more signature protein traits.

23. Any of the foregoing claims 1-6, wherein the distillers dried grains with solubles is derived from a corn feedstock, such that the distillers dried grains with solubles prior to solvent extraction has an average oil content that is greater than a comparable distillers dried
20 grains with solubles derived from #2 yellow dent commodity corn.

24. Any of the foregoing claims 1-6, wherein the distillers dried grains with solubles is derived from a corn feedstock comprising a corn grain blend having a first portion of low-oil content corn grain having an oil content having an average oil content less than 5% on a dry
25 weight basis of the corn grain and a second portion of high-oil content corn grain having an oil content having an average oil content of at least 6% on a dry weight basis of the corn grain, such that the distillers dried grains with solubles prior to solvent extraction has an average oil content that is greater than a comparable distillers dried grains with solubles derived from the first portion of low-oil content corn grain alone.

25. Any of the foregoing claims 1-6, wherein the distillers dried grains with solubles is derived from a corn feedstock comprising a corn grain blend having a first portion of low-oil content corn grain having an oil content having an average oil content less than 5% on a dry
30 weight basis of the corn grain and a second portion of high-oil content corn grain having an

oil content having an average oil content of at least 6% on a dry weight basis of the corn grain, such that the distillers dried grains with solubles prior to solvent extraction has an average oil content greater than 10%, in some aspects greater than 11%, and in some aspects greater than 12%.

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26. Any of the foregoing claims 1-6, wherein the distillers dried grains with solubles is derived from a corn feedstock comprising a corn grain blend having a first portion of low-oil content corn grain having an oil content having an average oil content less than 5% on a dry weight basis of the corn grain and a second portion of high-oil content corn grain having an oil content having an average oil content of at least 6% on a dry weight basis of the corn grain, such that the distillers dried grains with solubles prior to solvent extraction has an average oil content between 11% and 22%, in some other aspects between 12% and 20%, in some other aspects between 13% and 19%, and in some aspects between 14% and 17%, on a dry weight basis of the corn grain.

10

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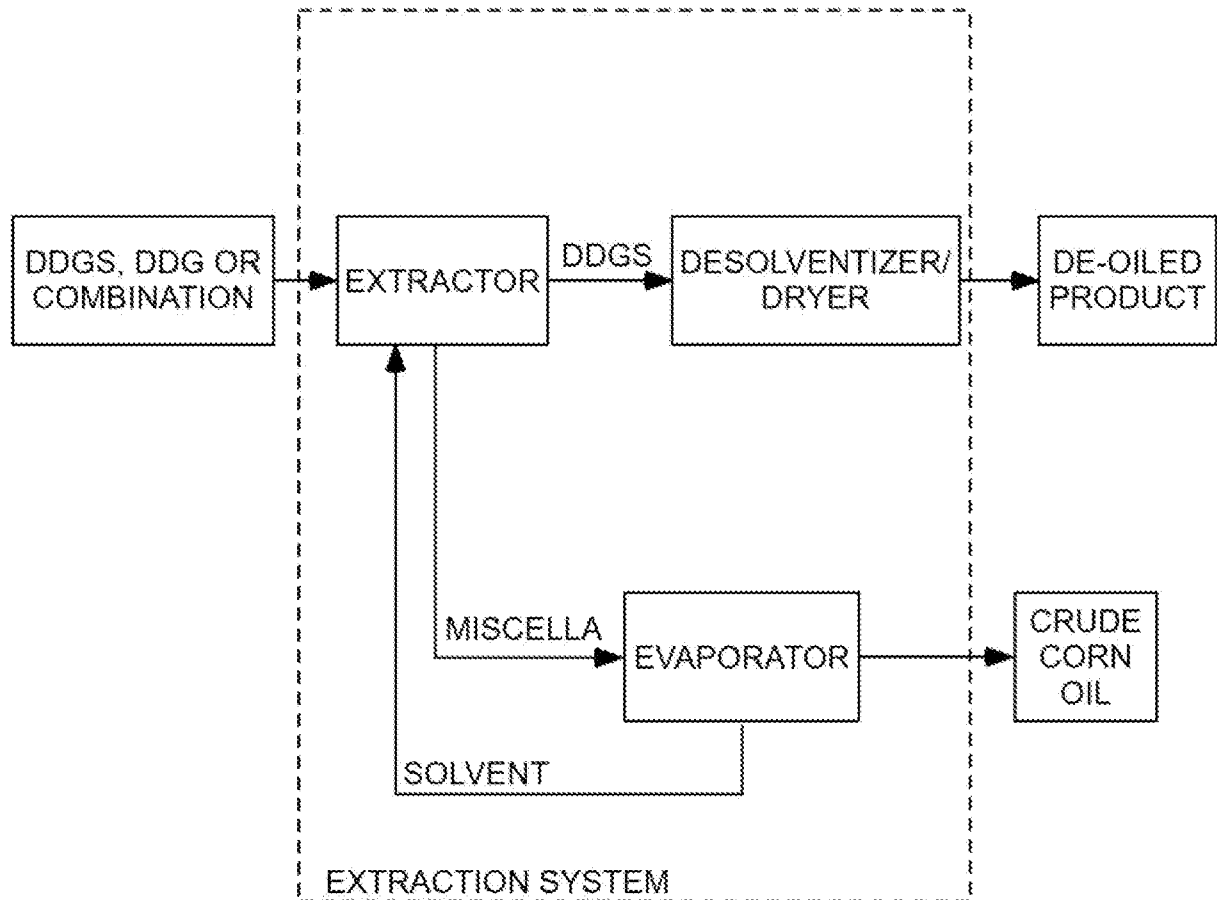


FIG. 1

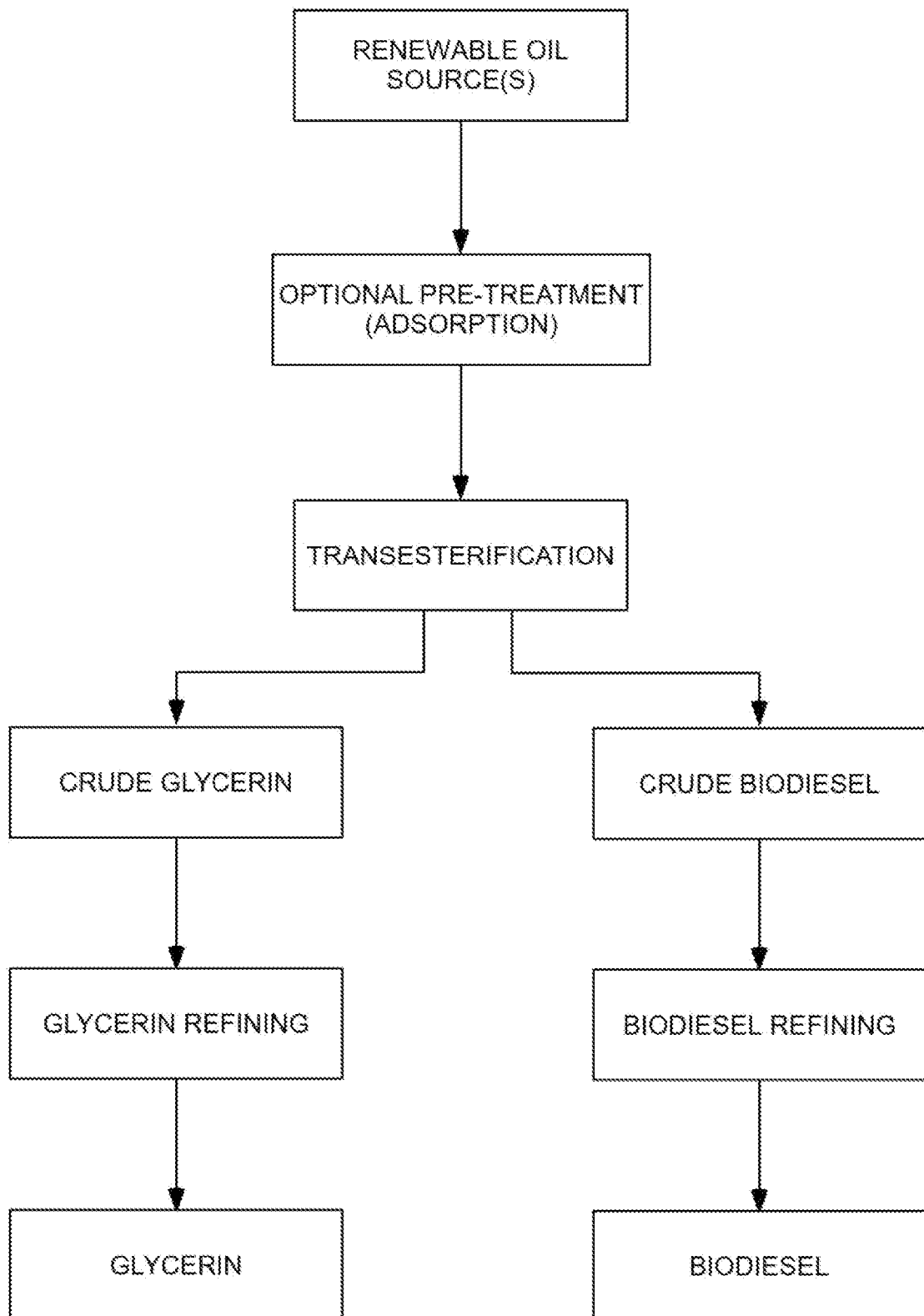


FIG. 2

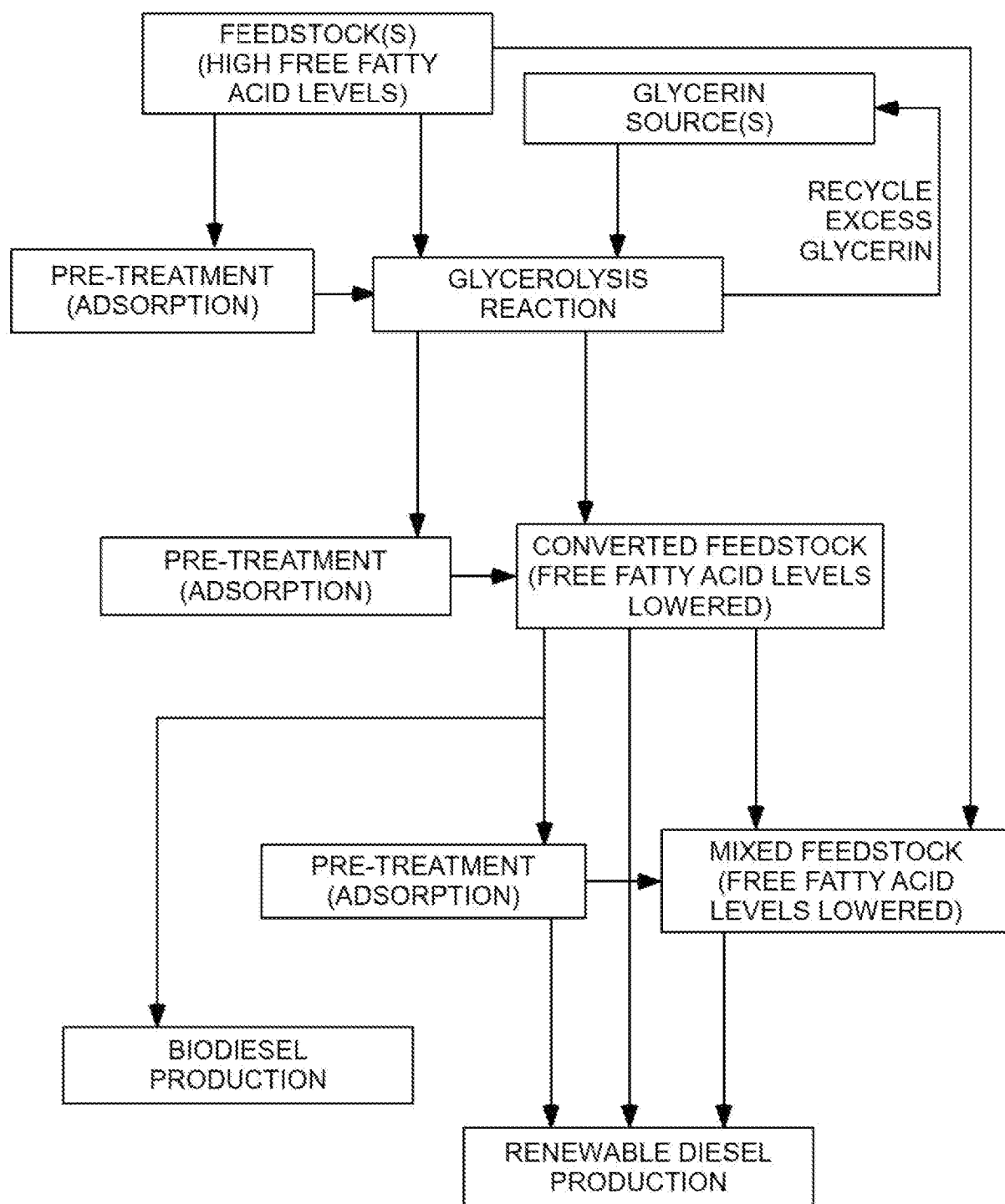


FIG. 3

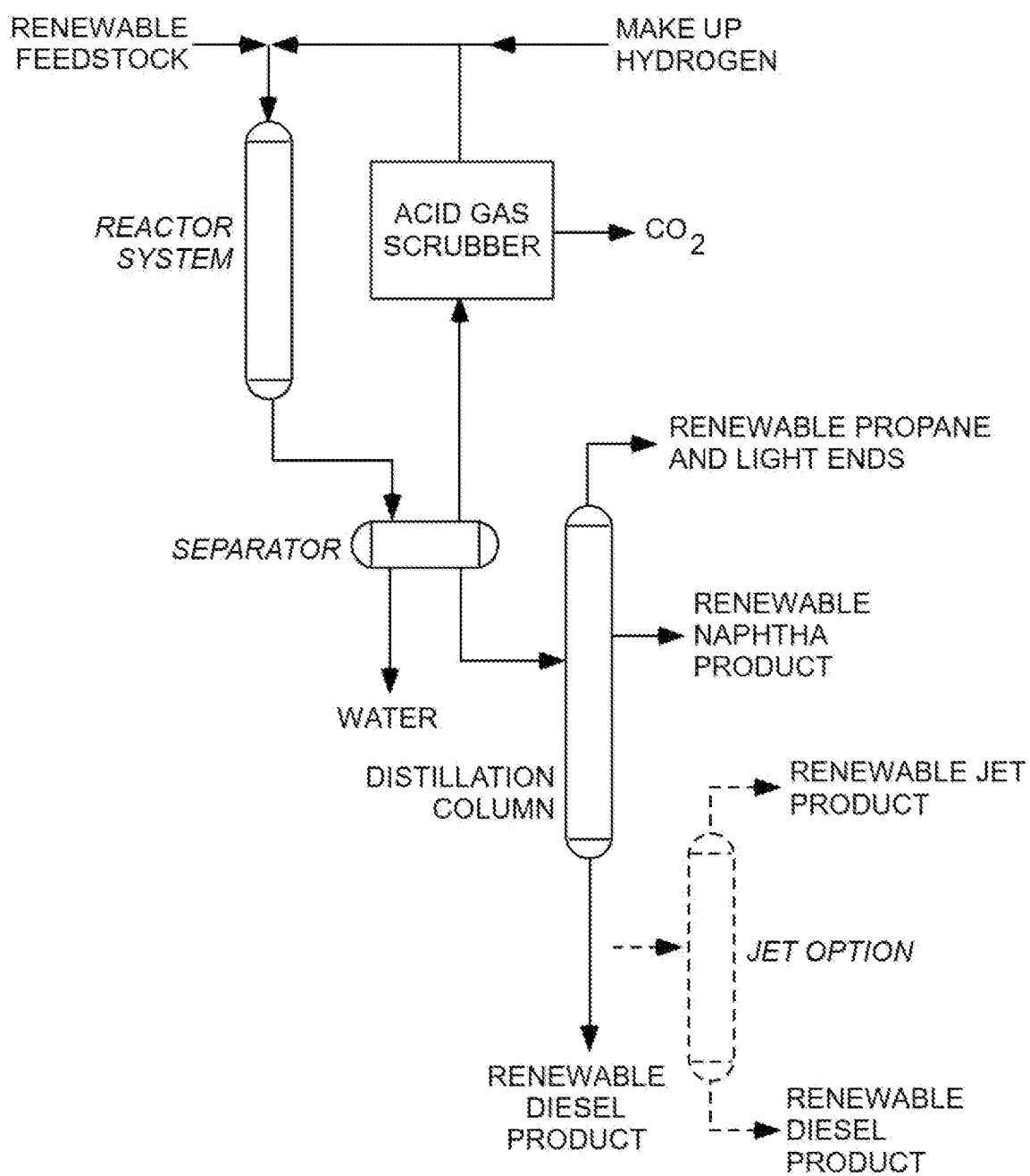


FIG. 4

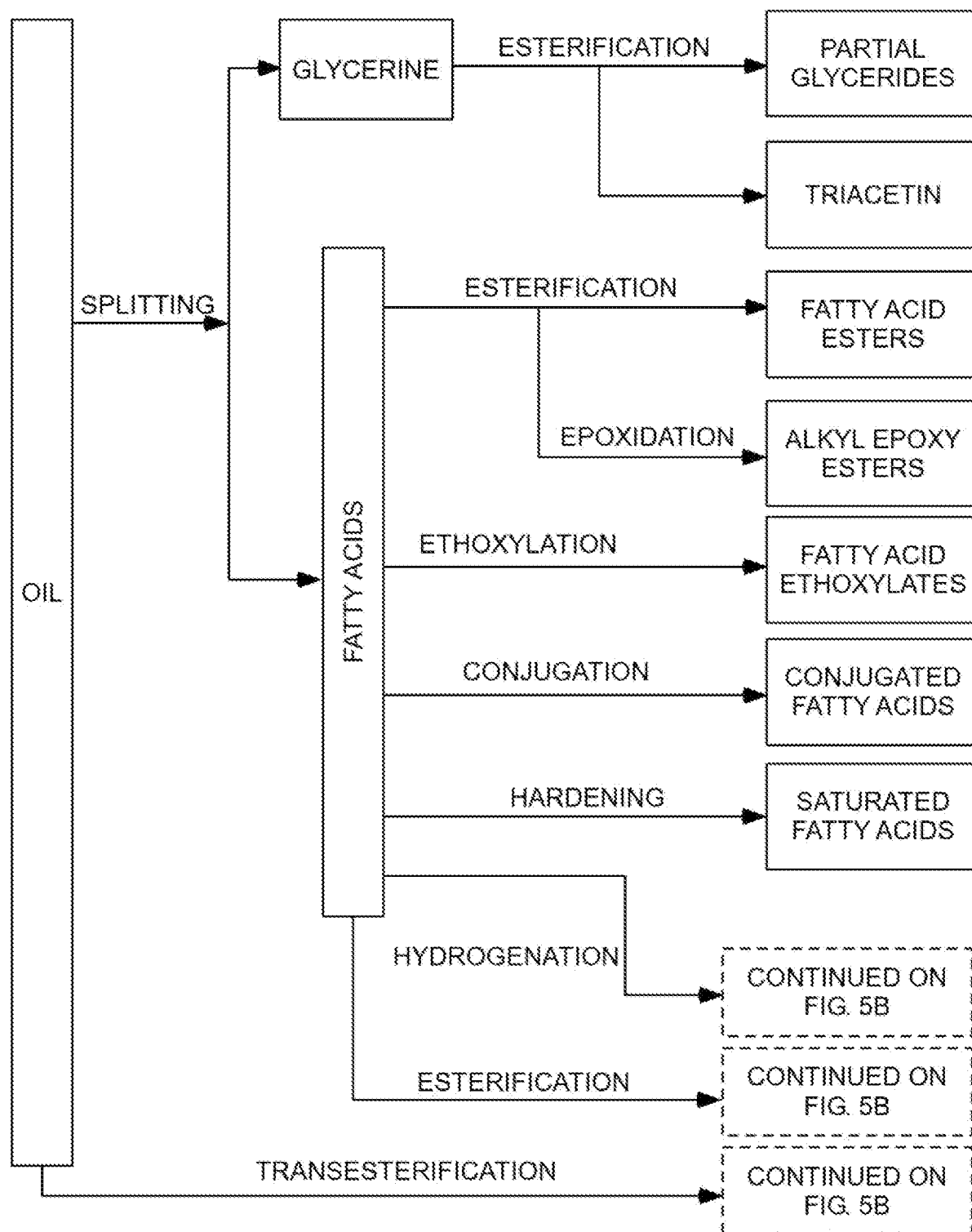


FIG. 5A

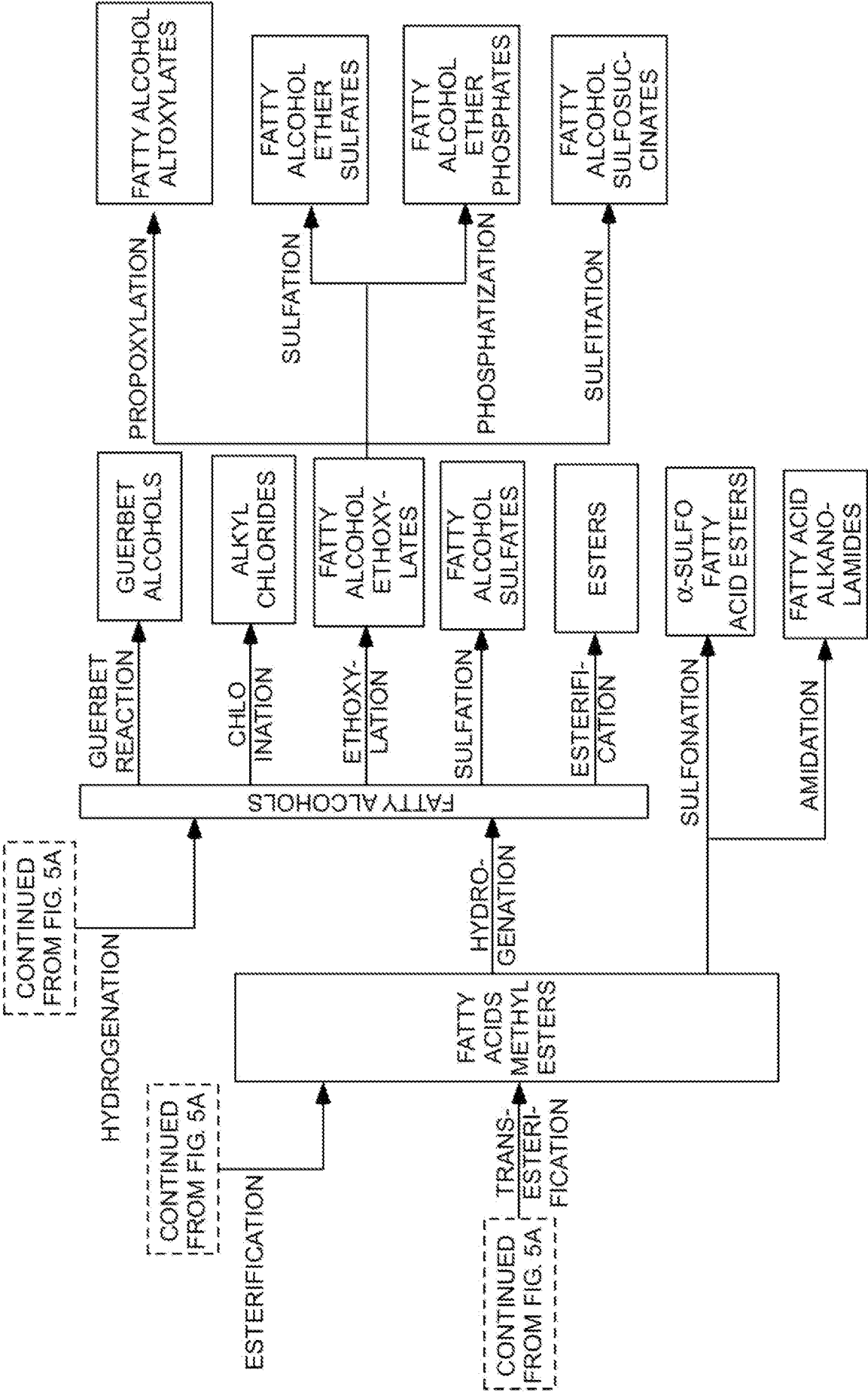


FIG. 5B

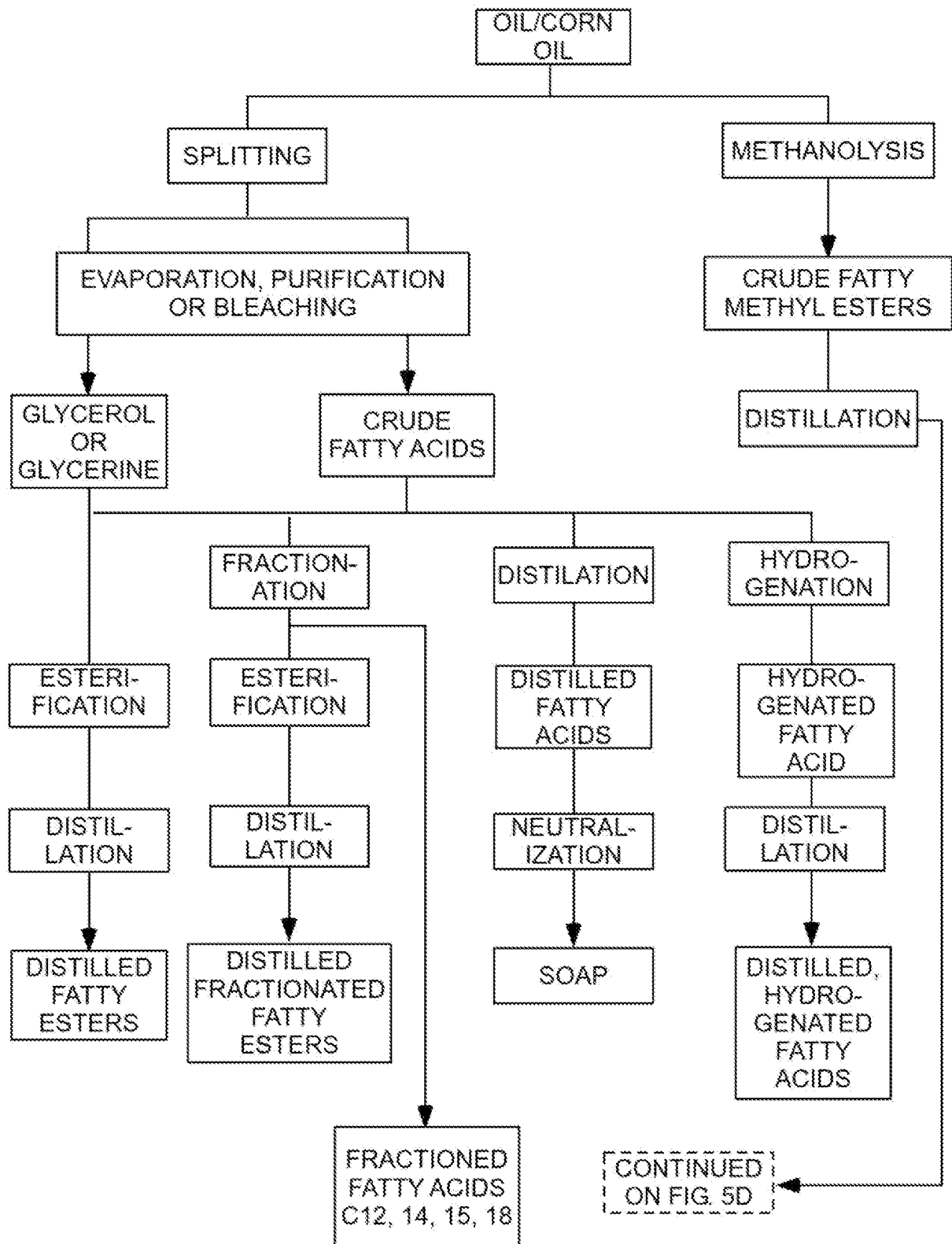


FIG. 5C

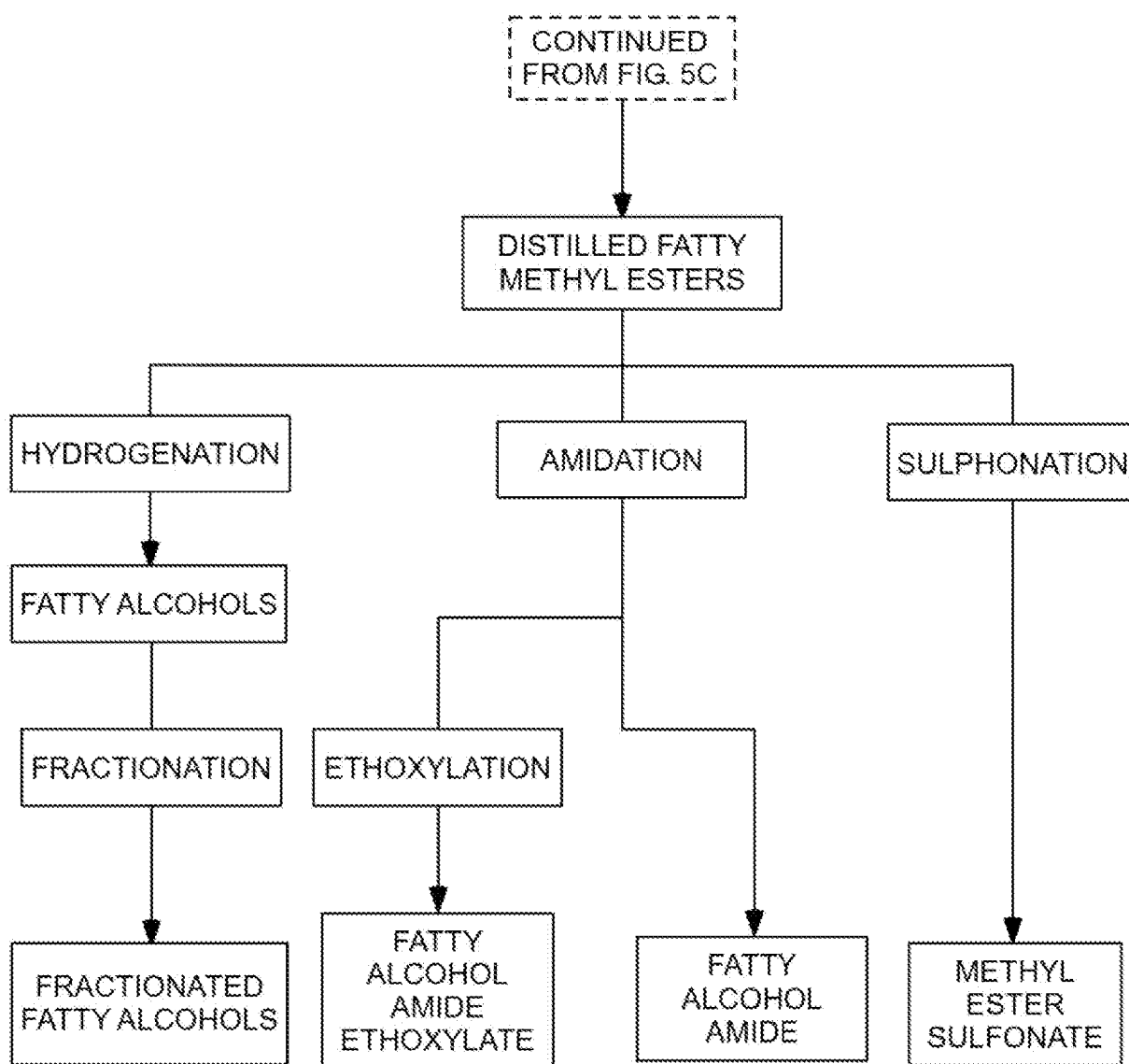


FIG. 5D