



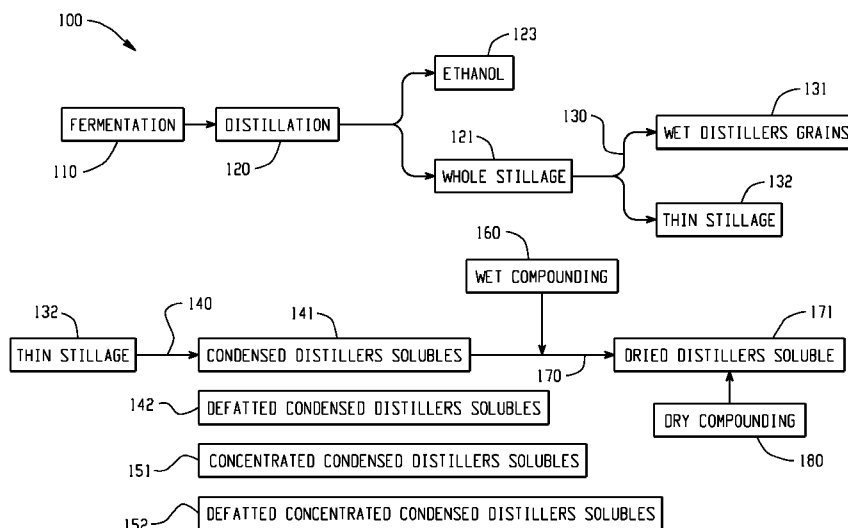
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(54) Title: BIOADHESIVES AND PROCESSES FOR MAKING SAME



(57) Abstract: A dried distiller soluble based bioadhesive composition and method for producing the dried distiller soluble based bioadhesives are disclosed, as well as derivatives thereof. The produced dried distillers solubles derives from co-products of corn fermentation facilities, and is advantageously comprised in part of water-soluble proteins. The method for producing the dried distillers solubles generally involves separation and/or introduction of targeted constituents and/or physiochemical treatment to facilitate use as an adhesive. Use of the method and bioadhesive compositions disclosed herein will improve the economics of fermentation by increasing co-product value, reducing plant-wide energy utilization, decreasing waste and emissions, and increasing overall product yield from each bushel of corn consumed.

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BIOADHESIVES AND PROCESSES FOR MAKING SAME

CROSS REFERENCE TO RELATED APPLICATION

This application claims priority to and the benefit of the U.S. Provisional Patent Application Nos. 61/599,215 filed on February 15, 2012 and 61/614,862 filed March 23, 2012, which are fully incorporated herein by reference.

BACKGROUND

[0001] The present disclosure generally relates to the renewable fuel, renewable chemical, polymer, plastic, elastomer, resin and adhesive production industries; and more specifically, to improving the production, product mix and economics of fermentation processes, such as corn to ethanol manufacturing processes and the like. More particularly, the present disclosure relates to bioadhesives formed from dried distillers solubles produced in the corn fermentation process.

[0002] Bioadhesives are natural polymeric materials that act as adhesives. Exemplary bioadhesives are those derived from soy flour. Soy flour suitable for use as bioadhesives was, and still is, generally obtained by removing some or most of the oil from the soybean, yielding a residual soy meal that was subsequently ground into extremely fine soy flour. The resulting soy flour was then, generally, denatured (i.e., the secondary, tertiary and/or quaternary structures of the proteins were altered to expose additional polar functional groups capable of bonding) with an alkaline agent and, to some extent, hydrolyzed (i.e., the covalent bonds were broken) to yield adhesives for wood bonding under dry conditions.

[0003] The use of soybeans as a bioadhesive has various limitations. First and foremost is that making a bioadhesive from soybeans requires removal of the soybean oil. Excessive soybean oil creates weaker bonds and creates issues during heat pressing of the adhesive, wherein a Maillard reaction can take place resulting in browning or blackening of the material, creating a distinct odor and weakening the overall adhesive value. Moreover, the removal of oil from soybeans typically uses a flammable hexane extraction process.

[0004] Soybeans naturally have a relatively high concentration of carbohydrates. The high concentration of carbohydrates can create moisture instability issues. In addition, the high carbohydrate levels in soy flour require more complex crosslinking techniques and chemistries to improve the water resistance problem of soybean bioadhesives. The use of soy protein isolates (SPI) have been used, wherein a chemical process is applied to the soy flour to remove starch and/or carbohydrates from the soybean meal. This process creates additional costs and mostly uses hazardous chemistry and methods.

[0005] Soybean protein flour also requires a separate hydrolyzation process to make the proteins have an adhesive nature. In most prior art, water is added to the soybean flour along with a caustic or chemical that can raise the pH sufficient to hydrolyze the proteins. Caustic chemicals such as sodium hydroxide, potassium hydroxides and other harmful chemicals are often used. Not only does the hydrolyzation process require additional and potentially harmful chemical processing steps, it further adds to the cost of such materials.

[0006] Because of the many limitations with the use of soybeans for preparing bioadhesives, other materials are now being investigated.

[0007] The U.S. ethanol industry is generally based on the fermentation of corn. It has grown significantly over the past 30 years, from an industry-wide output of 175 million gallons per year in 1980 to about 13.5 billion gallons in 2011. Demand for ethanol in the United States is expected to continue to increase due to a number of factors, including policies designed to reduce reliance on fossil fuels, volatile petroleum prices, heightened environmental concerns, and energy independence and national security concerns. Corn ethanol can thus be expected to comprise an increasingly larger portion of the U.S. liquid fuel supply during the next several years.

[0008] The production and use of renewable chemicals has also grown significantly in recent years for many of the same reasons, with an attendant increase in demand for renewable raw materials. As a result, there is substantial interest and ongoing research involving development of commercial processes for the conversion

of corn and its derivatives into various renewable fuels and chemicals, including substitutes for fossil fuel-derived chemicals and industrial polymers, such as plastics, elastomers, resins, and adhesives.

[0009] With its established corn fermentation infrastructure, the U.S. corn ethanol industry can be expected to be the most practical pathway to increase the production and use of such renewable fuels and chemicals on globally-meaningful scales. To participate in that growth, corn fermentation facilities will need to evolve to achieve improved production efficiencies.

[0010] Because of its relatively low investment and operational requirements, dry milling has become the primary method for corn to ethanol production. In the dry milling process, corn is first screened and ground to a flour. The resulting flour is combined with water and the starch within the corn is conventionally hydrolyzed into sugar by liquefaction and saccharification. The mixture is then fermented with yeast to convert the sugar into ethanol and carbon dioxide. About 30% of the mass of each kernel of corn accepted by corn ethanol producers is converted into ethanol in this manner. The output of fermentation, a mixture of ethanol, water, protein, carbohydrates, fat, minerals, solids and other unfermented components, is then distilled to boil off ethanol for recovery, purification and sale, leaving the remainder of the mixture in the bottom of the distillation stage.

[0011] The remainder in the bottom of the distillation stage is referred to as whole stillage and is typically subjected to a press or centrifugation process to separate the coarse solids from the liquid. The liquid fraction is commonly referred to as distillers solubles or thin stillage. Thin stillage is frequently concentrated in an evaporator to become condensed distillers solubles, which is also commonly referred to as thin stillage syrup or thin stillage concentrate. The coarse solids, or wet cake, collected from the centrifuge or press are known as wet distillers grains. Drying the distillers grains produces dried distillers grains. The distillers grains can be combined with the condensed distillers solubles to form what is commonly referred to as wet distillers grains with solubles, which can then be dried to form dried distillers grains with solubles (also referred to as dried distillers solubles). The dried distillers grains

or dried distillers grains with solubles typically have a moisture content of less than 20 % by weight to greater than 3% by weight although greater or lesser amounts of moisture content may be employed as may be desired for different applications. .

[0012] In some instances, the condensed distillers solubles is subjected to a high temperature drying process to form dried distillers solubles, which reportedly has been used as a thermoplastic additive with metal oxide and fiber in the preparation of extruded articles.

[0013] In other instances, partially concentrated thin stillage or condensed distillers solubles, prior to being combined with the wet distillers grains, is subjected to a corn oil extraction process to remove at least a portion of the oil contained therein. The extracted crude corn oil can be used as a feedstock for the production of biodiesel and other products. The remaining condensed distillers solubles with at least a portion of the oil removed is then typically combined with the wet distillers grains to form the wet distillers grains with solubles and further dried as dried distillers grains with solubles for use as animal feed. Exemplary corn oil extraction processes are disclosed in US Pat. Nos. 7,601,858, 7,608,729, 8,008,516, and 8,008,517, all of which are incorporated by reference in their entireties.

[0014] The non-fermentable byproducts of the corn to ethanol fermentation process are currently being investigated for use as bioadhesives. For example, US Pat. No. 7,618,660 to Mohanty et al. discloses the use of urea or caustic treated dried distillers grains with solubles to form a bioadhesive for paperboard binding. In Monhanty, distiller dried grains with solubles are treated with urea and/or a strong base such as sodium hydroxide to hydrolyze water-insoluble proteins. The resulting solution is then filtered to at least partially remove inert fiber (cellulose and hemicellulose) and other insoluble materials prior to final dewatering, leaving a complex mixture of low molecular weight compounds with low viscosity. The high solids and residual inert fiber content of the resulting distiller dried grains with solubles-derived adhesive reduces the overall percentage of active protein and thus decreases functionality in most resin and adhesive applications.

[0015] The usage of currently processed dried distillers grains or dried distillers grains with solubles is problematic for bioadhesives. Constituent carbohydrates and insoluble components within the grains must be processed with hazardous chemicals that require additional process stages, energy, and expensive equipment comprised of alloys having high corrosion resistance. Secondary processing to grind the dried distillers grains or dried distillers grains with solubles into a fine powder would also be required. Building and operating such processes at the scale would be very expensive and would yield an adhesive with functionality diminished by the presence of high concentrations of carbohydrates and insoluble materials.

[0016] Accordingly, it would be desirable for a more robust renewable material for bioadhesives that does not possess these limitations.

BRIEF SUMMARY

[0017] Disclosed herein are dried distiller soluble based bioadhesive compositions and processes for making the same. In one embodiment, a bioadhesive composition includes dried distillers solubles, which is derived from thin stillage.

[0018] In another embodiment, a method of making a bioadhesive composition comprises evaporating at least a portion of water from thin stillage obtained from a corn-to-ethanol fermentation process to form condensed distillers solubles; drying the condensed distillers solubles to form dried distillers solubles; and forming a bioadhesive composition with the dried distillers solubles.

[0019] In another embodiment, a process for bonding one component to another component comprises applying a bioadhesive composition to a surface of at least one of the components, wherein the bioadhesive composition comprises dried distillers solubles; and contacting the one component with the other component, wherein the bioadhesive composition is therebetween.

[0020] The disclosure may be understood more readily by reference to the following detailed description of the various features of the disclosure and the examples included therein.

BRIEF DESCRIPTION OF THE SEVERAL VIEWS OF THE DRAWING

[0021] Referring now to the figures wherein the like elements are numbered alike:

[0022] The Figure illustrates a process flow diagram for forming the dried distillers solubles in accordance with the present disclosure.

DETAILED DESCRIPTION

[0023] The present disclosure is generally directed to bioadhesives derived from dried distillers solubles and methods for making the same. The dried distillers solubles derive exclusively from the wet processing stream of the corn-to-ethanol fermentation process and can be comprised of water-soluble functionalized proteins, among other constituents. As will be discussed in greater detail, the use of dried distillers solubles in the bioadhesive composition overcomes many of the problems noted in the prior art as it relates to bioadhesives in general and as it relates to the prior art's use of dried distillers grains. Moreover, because of the uniqueness of the dried distillers solubles, the properties can be readily manipulated by the use of additives and/or by compositional changes as a function of processing and isolating the dried distillers solubles. With regard to compositional changes, because the dried distillers solubles is ultimately obtained from whole stillage (i.e., the residue remaining after ethanol distillation), it should be apparent that modification, physical or chemical, of the final bioadhesive properties can be made to any one of the product streams upstream from the dried distillers solubles as well as on the dried distillers solubles itself.

[0024] For ease in understanding the present disclosure, it is important to distinguish between dried distillers solubles and dried distillers grains. As is well known in the art, the left over byproducts of the corn-to-ethanol fermentation process are referred to as whole stillage, which is generally the non-fermentable grains, byproducts, and water that falls to the bottom of the distillation column once the ethanol is distilled. The whole stillage is typically mechanically treated (e.g., decanted, centrifuged, pressed, or the like) to produce two fractions: a substantially solids fraction referred to as wet distillers grains and a substantially aqueous based fraction referred to as thin stillage. The dried distillers solubles is derived from the substantially aqueous based thin stillage fraction and will include a relative high amount of water soluble proteins, which provides many unique properties.

[0025] The thin stillage can be concentrated by use of evaporators to produce condensed distillers solubles (also referred to as thin stillage concentrate, or thin

stillage syrup), which may be further treated to remove oil entrained therein. The condensed distillers solubles, once obtained, is oftentimes mixed with the wet distillers grains and further dried in a dryer to form dried distillers grains, which may then be used as animal feed. In some processes, the wet distillers grains may be dried without the addition of the thin stillage concentrate to form a dried grain product that is also referred to by those in the art as dried distillers grains, which may still or may not have an appreciable moisture content depending on the extent of drying.

[0026] The composition of the condensed distillers solubles can vary depending on the processing facility, ethanol process, and corn variety, growing season and post processing methods. However, on a dry matter weight basis condensed distillers solubles typically have about equal parts amino acids/proteins to fatty acid materials. One facility reported a composition of condensed distillers solubles as containing dry matter of 33.4% of which the composition included crude protein of 20.8%, crude fat of 22.2%, crude fiber of 2.8%, ADF of 2.3%, NDF of 4.3%, and ash of 9.2%.

[0027] In the present disclosure, at least a portion of the condensed distillers solubles is further dried to produce dried distillers solubles and employed in a bioadhesive composition, as is, modified, or in combination with other components. The dried distillers solubles may or may not have an appreciable moisture content depending on the extent of drying. Applicants have discovered that bioadhesives derived from the dried distillers solubles provide excellent adhesive properties that can be readily tailored for a variety of applications without the problems noted with the use of dried distillers grains or the expense related to the use of soybeans.

[0028] The dried distillers solubles resultant material by itself is generally in a compactable powder or granular form and, in some embodiments, can be used directly as an adhesive, wherein the dried distillers solubles forms an adhesive layer between two components, and by the usage of heat and pressure can be configured to flow and cure to form an adhered product. Alternatively, aqueous solutions of the dried distillers solubles and/or any dried distillers solubles precursor or co-product can readily be made and applied at a desired viscosity. Still further, the dried distillers

solubles based bioadhesive composition may further be compounded with other materials, wet and/or dry, to provide desired properties for a given application. The particular adhesive application is not intended to be limited. By way of example only, the dried distillers solubles bioadhesive can be used for its adhesive properties in papers, wood veneers, in the production of wood and agrifiber composite panels such as particleboard, medium density fiber board (MDF), oriented strand board (OSB), laminated lumber products, and the like.

[0029] The resultant dried distillers solubles material can also be used as a resin extender, wherein the dried distillers solubles is blended with another adhesive such as a soy protein based bioadhesive, for example, to lower its cost and provide various functional advantages in the final blend. As such, the dried distillers solubles can be an adhesive or resin extender for various resins currently used in the wood composites and paper industry such as phenol formaldehyde, and other types of resins.

[0030] Referring now to the Figure, process 100 illustrates a method for forming dried distillers solubles from the corn-to-ethanol fermentation process 110. After aqueous fermentation of the starch within the corn to produce ethanol, the ethanol 123 is removed in a distillation step 120 leaving behind an aqueous mixture of post fermentation byproducts, i.e., whole stillage (WS) 121. The whole stillage 121 is then separated in a separation process 130 into two fractions: the wet distillers grains (WDG) 131 and the thin stillage fraction (TS) 132. The thin stillage feedstream 132 is then subjected to an evaporation process 140 to remove moisture content so as to form condensed distillers solubles (CDS) 141. Typically, the thin stillage 132 is first fed to an evaporator e.g., a multistage evaporator, to remove at least a portion of the water contained therein, i.e., 1st removal: evaporation. In ethanol production facilities, the evaporation temperatures within the evaporator generally are in a range of about 100 to about 230°F, and more typically, in a range of about 110 to about 200°F. The condensed distillers with solubles 141 can then be subjected to an oil removal process to remove at least a portion of the oil contained therein so as to form defatted condensed distillers solubles 142 (CDS-F). The amount of oil that is removed can be

used to modify the properties of the condensed distillers solubles once dried, i.e., dried distillers solubles.

[0031] Optionally, the condensed distillers solubles 141 and/or the defatted condensed distillers solubles 142 can be further evaporated in a second evaporation step to remove additional moisture therein to form a super concentrated condensed distillers solubles 151, which may also be subject to an oil removal step or in the case of defatted condensed distillers solubles subjected to an additional oil removal step to form defatted concentrated distillers solubles. Further concentration and oil removal may be continued as may be desired.

[0032] The amount of oil (fat) removed and the removal method are not intended to be limited to any particular amount/process so long as at least a portion is removed relative to thin stillage by itself, wherein the amount removed can be used to tailor the adhesive properties. In addition to the production of dried distillers solubles 171 and its subsequent use as a bioadhesive, the extracted corn oil itself can be used for various applications including, but not limited to, production of biodiesel, thereby transforming what was previously considered as a low value product into a significant revenue stream for ethanol plant operator.

[0033] The condensed distillers solubles 141, concentrated condensed distillers solubles 151, defatted condensed distillers solubles 142, or defatted concentrated condensed distillers solubles 152 or like feed streams can be subject to wet compounding 160, which includes wet mixing the feedstream with other components, at least one of which may be a solution or water. In this step, additional additives, described in more detail below, can be incorporated to form a modified distillers solubles.

[0034] The condensed distillers solubles 141, concentrated condensed distillers solubles 151, defatted condensed distillers solubles 142, and/or defatted concentrated condensed distillers solubles, as well as the corresponding wet compounded distillers solubles can then be subjected to thermal drying at step 170, individually or in various combinations, to further reduce the moisture content therein

to an amount suitable for forming the dried distillers solubles 171 for the particular end application. The dried distiller solubles 171 which may be used as is or may be dry compounded with dry ingredients. Again, doing so can be used to manipulate the final adhesive properties as may be desired for different adhesive applications. For example, the adhesive properties for a given application may desire tacky adhesion, e.g., a post-it note, or may require a more permanent bond, e.g., formation of particle board, or may require a permanent bond that is water insensitive or may be hot melted. Likewise, bond strength can be varied.

[0035] Table 1 provides a general comparison on a dry matter basis of a condensed distillers solubles composition without oil extraction and a condensed distillers solubles composition with at least a portion of the oil removed. Reference to defatted condensed distillers solubles is not intended to infer that oil is completely removed from the dried distillers with solubles. In some embodiments, it may be beneficial to subject the condensed distillers solubles to multiple oil [and/or water] extraction steps to further decrease and manipulate the amount of oil [and/or water] contained in the dried distillers with solubles product material. In most embodiments, the oil content in the dried distillers with solubles product material is from 3 to 15% by weight although higher or lower amounts of oil may be desired in certain applications

Table 1.

	Condensed Distillers Solubles	Partially Defatted Condensed Distillers Solubles
Protein (%)	18	21
Fat (%)	20	7
Carbohydrates (%)	48	56
Ash (%)	14	16
Total (%)	100	100

[0036] As demonstrated in Table 1, the amount of oil can easily be varied, which can directly affect the final bioadhesive properties once the condensed distillers solubles are dried to form the dried distillers solubles. .

[0037] In a similar manner, the other constituents defining the dried distillers solubles composition can be varied. For example, the thin stillage 132 or condensed distillers with solubles 141 can be treated to remove a portion of the carbohydrates and/or a portion of the proteins contained therein. For example, a portion of the low molecular weight proteins, may be removed. Likewise, non-fermented starch and carbohydrates can be removed or partially removed to tailor the bioadhesive properties by CO₂ extraction, additional fermentation, or the like. Still further, upstream treatment may include filtration, membrane filtration or centrifugation technologies to isolate and reduce additional components such as the suspended solids (dines) or selected dissolved solids as may be desired for different applications.

[0038] Alternatively, the dried distillers with solubles can be treated as is or upstream to modify one or more of the constituents within the composition. For example, the proteins and/or carbohydrates can be functionalized with different materials to provide further manipulation of the bioadhesive properties. By way of example, protein modifications can include, for example, treating proteins with an acid, base or other agent that alters the structure of one or more of the amino acid side chains, which, in turn, alters the character of the protein and/or amino acids. For example, the high glutamine and asparagine of prolamines, particularly zein from corn, provides a means for manipulating the charge characteristics of the protein by deamidation, thereby providing a wide range of hydrophobicity. In one embodiment, deamidation involves mild acid catalyzed deamidation at a pH of about 1 at temperatures from about 25°C to about 65°C for a period of time sufficient to accomplish the desired level of deamidation. In some embodiments, acids that form stable dispersions and are useful within these classes include, without limitation, lactic acid, citric acid, malonic acid, phosphoric acid, fumaric acid, maleic acid, maleic anhydride, maleated propylenes, glutaric acid, transaconitic acid, acetic acid, propionic acid, sorbic acid, cysteine and glycyl glycine. In one embodiment, lactic acid in the form of polylactic acid is used. In another embodiment, maleated propylenes, such as G-3003 and G-3015 manufactured by Eastman chemicals are used.

[0039] The thin stillage and condensed distillers solubles feedstreams have conventionally been viewed as low-value by-products, i.e., waste products. Problematically, the chemical and physical characteristics of condensed distillers with solubles adversely affect (and dilute the value of) wet distillers grains when combined therewith. The resulting product stream, the precursor to dried distillers grains with solubles, has reduced protein content and is stickier and less tolerant to spoilage than it would be without addition of condensed distillers with solubles following evaporation. Consequently, producers have to burn more fossil fuel-derived natural gas to dry dried distillers grains with solubles longer than would otherwise be required in order to vaporize more water and to avoid handling and spoilage issues. Low moisture content translates directly into extended storage life. Producers have generally had little choice but to follow the standard industry practice of combining condensed distillers with solubles with wet distillers grains prior to drying for the want of an economically and technically feasible alternative. An object of this disclosure is to provide such an alternative and empower producers to reduce these inefficiencies by diverting and separately processing condensed distillers with solubles. As a result, the wet distillers grains does not require the extended drying times since spoilage as a function of moisture content is less of a concern.

[0040] Thin stillage and its more concentrated form of concentrated distillers solubles form are generally comprised of water, protein, fat, carbohydrates, ash, and relatively minor amounts of other fermentation byproducts. At least some of the protein in the feedstream has been hydrolyzed as a function of the fermentation process conditions and is water-soluble. The fat is substantially comprised of glycerides and is present in a free, bound and/or emulsified state. The carbohydrate fraction is further comprised of various sugars, partially-hydrolyzed starch, and insoluble polysaccharides (cellulose, hemicellulose and lignin). Ash includes residual minerals. Fermentation byproducts include glycerol, lactic acid, acetic acid, yeast, and the like.

[0041] By the time concentrated distillers solubles exits the evaporators, its protein and other constituents have changed significantly due to continuous treatment

during the fermentation process with hot water, enzymes, caustic, acid, urea and/or other chemicals, at times under pressure and/or vacuum, for more than two days. Many of these process conditions are severe and are generally known to facilitate at least some degree of hydrolysis, denaturation and other presently favorable reactions and reactants.

[0042] By way of example, ethanol facilities using the method taught by Winsness in U.S. Pat. App. No. 11/908,891 incorporated herein by reference in its entirety, iteratively wash the whole stillage with at least a portion of the thin stillage after initial separation of whole stillage into wet distillers grains and thin stillage. This step increases the content of lower density, low molecular weight and soluble components in the thin stillage to enhance derivative co-product value, e.g., dried distiller solubles. Moreover, as disclosed by Winsness, fat removal efficiencies can be optionally increased by chemical addition and/or by increasing temperature and/or concentrated thin stillage or concentrated distillers solubles residence time at targeted temperatures. Using such methods, concentrated distillers solubles might be held at an elevated temperature for an extended period of time at a pH of, for example, 3.5 to 4.5, before removing at least some fat (oil) and directing the condensed distillers solubles for final evaporation.

[0043] The dried distillers solubles is produced by introducing the liquid feedstream into a drying gas stream and recovering the dried distillers solubles from the drying gas stream. An exemplary process is a high temperature pulse combustion process as described in US Pat. No. 7,937,850 to Tate et al., incorporated herein by reference in its entirety. In this process, the condensed distillers solubles are introduced into the drying gas stream at a temperature of about 600°F to about 1800°F.

[0044] In another embodiment, the dried distillers solubles is obtained using a low temperature process. In this manner, the proteins contained within the dried distillers solubles are subjected to a less thermally aggressive process relative to the preceding pulse combustion process and as a result, less denaturing of the proteins and oxidation of the various constituents contained within the feedstream may occur. In this method, some or all of the liquid feedstream is conducted to a vessel or vessels

for thermal treatment, with or without one or more additive(s) in one or more sequential stages under proscribed conditions and times. The vessel or vessels used in this method can be operated in batch or continuous fashion, and can incorporate one or more devices for accomplishing thermal treatment by convection, conduction and/or radiation, in sequence and/or concurrently.

[0045] The low temperature drying process applied can be applied to the liquid fraction, e.g., thin stillage, condensed distillers solubles, defatted condensed distillers solubles, and the like and generally includes a fluidized bed apparatus configured to heat the liquid fraction e.g., CDS (or thin stillage) to a temperature less than 300°F in most embodiments, less than 250°F in other embodiments, and less than 200°F in still other embodiments. In one embodiment, the drying process is configured to provide the DDS in a powder and/or granular form with a moisture content of about 3 to about 20% by weight, and in other embodiments, about 5 to about 12% by weight. The various additives can be added by wet mixing prior to the drying process or dry mixing.

[0046] In another embodiment, the dried distillers solubles is obtained using a low temperature process. In this manner, the proteins contained within the DDS are subjected to a less thermally aggressive process relative to the preceding pulse combustion process and as a result, less denaturing of the proteins and oxidation of the various constituents contained within the feedstream may occur. In this method, some or all of the liquid feedstream is conducted to a vessel or vessels for thermal treatment, with or without one or more additive(s) in one or more sequential stages under proscribed conditions and times. The vessel or vessels used in this method can be operated in batch or continuous fashion, and can incorporate one or more devices for accomplishing thermal treatment by convection, conduction and/or radiation, in sequence and/or concurrently.

[0047] In an exemplary mode of this method, the liquid feedstream is conducted through one or more nozzles into a manifold at the top of vessel or vessels comprising an initial stage of thermal treatment ("TT1"). A gas or gasses are simultaneously fed into TT1 through one or more inlets, at flow rates and

temperatures that are metered to precisely control intermediate temperature, residence time and other relevant process variables such that, for example, moisture is removed while avoiding undesirable particle deformation or reactions. In an alternative embodiment, TT1 may also incorporate use of a fluidized bed (“FB1”) at the base of the TT1 vessel or vessels, into which a gas or gases are fed at rates and temperatures sufficient to achieve incipient fluidization and, as desired, to facilitate heat and/or mass transfer, reactions and/or other relevant process objectives during TT1. The temperatures and process conditions used in this process can be configured to maintain the DDS product material during drying at a temperature less than 300°F in most embodiments, less than 250°F in other embodiments, and less than 200°F in still other embodiments.

[0048] Another aspect involves further conveyance of the intermediate feedstream from TT1 into a single or plurality of additional thermal treatment zones (TT2, TT3 and so on), each incorporating a means of convection, conduction and/or radiation to achieve desired process objectives. In one method, such stage or stages incorporate a fluidized bed (FB2, FB3 and so on), into which a gas or gases are fed at rates and temperatures as may be sufficient to, for example, gently heat and/or cool the intermediate at iteratively lower temperatures. Air adjusted weirs can be additionally incorporated into the method to manage residence times.

[0049] Alternatively, the drying apparatus may be configured to supplement the convective processes with conductive processes, such as by incorporating an induction heater or intercooler into the base of a fluid bed. Emissive methods can also be incorporated, such as by adding infrared energy emitters into the housing walls, or by adding a zone in which the feed material is treated by electromagnetic radiation at wavelengths, intensities and times sufficient to gently heat the interior of particles to enable more efficient, lower temperature convection while avoiding excessive surface dehydration and degradation, or other adverse reactions that could impair functionality.

[0050] By way of a further example, any of the foregoing thermal treatment methods could optionally involve introduction of one or more additives, which may

include liquid feedstream or any co-product from a prior or subsequent stage of this invention or the fermentation facility, during any stage of thermal treatment to regulate the characteristics as desired to, for example, prevent degradation or otherwise render the resulting DDS suitable for further processing and/or its anticipated end use.

[0051] The thermal treatment processes described above may also be utilized to facilitate targeted reactions, such as functionalization, polymerization, crosslinking and the like, as may be necessary to condition the DDS for its intended end use.

[0052] Other thermal treatment method can be used to supplement convective processes with conductive methods, such as by incorporating an induction heater or intercooler into the base of a fluid bed. Emissive methods can also be incorporated, such as by exposing the liquid fraction to infrared energy emitters, or by adding a zone in which the liquid feed material is treated by electromagnetic radiation at wavelengths, intensities and times sufficient to gently heat the interior of particles to enable more efficient, lower temperature convection while avoiding excessive surface dehydration and degradation, or other adverse reactions which could impair functionality.

[0053] By way of a further example, any of the foregoing thermal treatment methods could optionally involve introduction of one or more additives, which may include liquid feedstream or any co-product from a prior or subsequent stage of this invention, during any stage of thermal treatment to regulate the characteristics as desired to, for example, prevent degradation or otherwise render the resulting dried distillers solubles suitable for further processing and/or its anticipated end use. Any additive can be incorporated in a finishing step of dry compounding.

[0054] The drying thermal treatment processes described above may also be utilized to facilitate targeted reactions, such as functionalization, polymerization, crosslinking and the like, as may be necessary to condition the dried distillers solubles for its intended end use.

[0055] The dried distillers solubles and/or derivative or any of the upstream intermediate product feedstreams including, but not limited to, whole stillage, thin stillage, condensed distillers solubles, defatted condensed distillers soluble, and the like, can comprise at least another component, to manipulate the properties of the bioadhesive such as, but not limited to, improving and/or controlling the viscosity, adhesive properties, shelf-life, and stability. Non-limiting examples of additional components include tackifiers, plasticizers (plasticizing oils or extender oils), waxes, antioxidants, UV stabilizers, colorants or pigments, fillers, flow aids, biocides, lubricants, water, oil, coupling agents, crosslinking agents, surfactants, catalysts solvents, hydrolyzing agents, and combinations thereof. The foregoing additives can be incorporated before or after drying thermal treatment.

[0056] In some embodiments, the dried distillers solubles and/or derivative or any of the upstream product feedstreams disclosed herein can comprise a tackifier or tackifying resin or tackifier resin. The tackifier may modify the properties of the composition such as viscoelastic properties (e.g., tan delta), rheological properties (e.g., viscosity), tackiness (i.e., ability to stick), pressure sensitivity, and wetting property. In some embodiments, the tackifier is used to improve the tackiness of the composition. In other embodiments, the tackifier is used to reduce the viscosity of the composition. In further embodiments, the tackifier is used to render the composition a pressure-sensitive adhesive. In particular embodiments, the tackifier is used to wet out adherent surfaces and/or improve the adhesion to the adherent surfaces.

[0057] Any tackifier known to a person of ordinary skill in the art may be used and is generally added to the bioadhesive composition as opposed to upstream feedstreams. Tackifiers suitable for the compositions disclosed herein can be solids, semi-solids, or liquids at room temperature. Non-limiting examples of tackifiers include (1) natural and modified rosins (e.g., gum rosin, wood rosin, tall oil rosin, distilled rosin, hydrogenated rosin, dimerized rosin, and polymerized rosin); (2) glycerol and pentaerythritol esters of natural and modified rosins (e.g., the glycerol ester of pale, wood rosin, the glycerol ester of hydrogenated rosin, the glycerol ester of polymerized rosin, the pentaerythritol ester of hydrogenated rosin, and the phenolic-

modified pentaerythritol ester of rosin); (3) copolymers and terpolymers of natured terpenes (e.g., styrene/terpene and alpha methyl styrene/terpene); (4) polyterpene resins and hydrogenated polyterpene resins; (5) phenolic modified terpene resins and hydrogenated derivatives thereof (e.g., the resin product resulting from the condensation, in an acidic medium, of a bicyclic terpene and a phenol); (6) aliphatic or cycloaliphatic hydrocarbon resins and the hydrogenated derivatives thereof (e.g., resins resulting from the polymerization of monomers consisting primarily of olefins and diolefins); (7) aromatic hydrocarbon resins and the hydrogenated derivatives thereof; (8) aromatic modified aliphatic or cycloaliphatic hydrocarbon resins and the hydrogenated derivatives thereof; and combinations thereof.

[0058] In further embodiments, the dried distillers solubles and/or derivative or any of the upstream product feedstreams disclosed herein optionally can comprise or incorporate a plasticizer or plasticizing oil or an extender oil that may reduce viscosity and/or improve tack properties. Any plasticizer known to a person of ordinary skill in the art may be used in the adhesion composition disclosed herein. Non-limiting examples of plasticizers include olefin oligomers, low molecular weight polyolefins such as liquid polybutene, phthalates, mineral oils such as naphthenic, paraffinic, or hydrogenated (white) oils (e.g. Kaydol oil), vegetable and animal oil and their derivatives, petroleum derived oils, and combinations thereof. In some embodiments, the plasticizers include polypropylene, polybutene, hydrogenated polyisoprene, hydrogenated polybutadiene, polypiperylene and copolymers of piperylene and isoprene, and the like having average molecular weights between about 350 and about 10,000. In other embodiments, the plasticizers include glyceryl esters of the usual fatty acids and polymerization products thereof.

[0059] In some embodiments, a suitable insoluble plasticizer may be selected from the group which includes dipropylene glycol dibenzoate, pentaerythritol tetrabenzoate; polyethylene glycol 400-di-2-ethylhexoate; 2-ethylhexyl diphenyl phosphate; butyl benzyl phthalate, dibutyl phthalate, dioctyl phthalate, various substituted citrates, and glycerates.

[0060] In further embodiments, the dried distillers solubles and/or derivative or any of the upstream product feedstreams disclosed herein optionally can comprise a wax that may reduce the melt viscosity in addition to reducing costs. Any wax known to a person of ordinary skill in the art can be used in the adhesion composition disclosed herein. Non-limiting examples of suitable waxes include petroleum waxes, polyolefin waxes such as low molecular weight polyethylene or polypropylene, synthetic waxes, paraffin and microcrystalline waxes having melting points from about 55 to about 110° C, Fischer-Tropsch waxes and combinations thereof. In some embodiments, the wax is a low molecular weight polyethylene homopolymer or interpolymer having a number average molecular weight of about 400 to about 6,000 g/mole.

[0061] In further embodiments, the dried distillers solubles and/or derivative or any of the upstream product feedstreams disclosed herein optionally can comprise an antioxidant or a stabilizer. Any antioxidant known to a person of ordinary skill in the art may be used in the adhesion composition disclosed herein. Non-limiting examples of suitable antioxidants include amine-based antioxidants such as alkyl diphenylamines, phenyl- α -naphthylamine, alkyl or aralkyl substituted phenyl- α -naphthylamine, alkylated p-phenylene diamines, tetramethyl-diaminodiphenylamine and the like; and hindered phenol compounds such as 2,6-di-t-butyl-4-methylphenol; 1,3,5-trimethyl-2,4,6-tris(3',5'-di-t-butyl-4'-hydroxybenzyl)benzene; tetrakis(methylene(3,5-di-t-butyl-4-hydroxyhydrocinnamate)]methane (e.g., IRGANOX™ 1010, from Ciba Geigy, N.Y.); octadecyl-3,5-di-t-butyl-4-hydroxycinnamate (e.g., IRGANOX™ 1076, commercially available from Ciba Geigy) and combinations thereof.

[0062] In further embodiments, the dried distillers solubles and/or derivative or any of the upstream product feedstreams disclosed herein optionally can comprise an UV stabilizer that may prevent or reduce the degradation of the compositions by UV radiation. Any UV stabilizer known to a person of ordinary skill in the art may be used in the adhesion composition disclosed herein. Non-limiting examples of suitable UV stabilizers include benzophenones, benzotriazoles, aryl esters, oxanilides, acrylic esters, formamidine, carbon black, hindered amines, nickel quenchers, hindered

amines, phenolic antioxidants, metallic salts, zinc compounds and combinations thereof.

[0063] In further embodiments, the dried distillers solubles and/or derivative or any of the upstream product feedstreams disclosed herein optionally can comprise a colorant or pigment. Any colorant or pigment known to a person of ordinary skill in the art may be used in the adhesion composition disclosed herein. Non-limiting examples of suitable colorants or pigments include inorganic pigments such as titanium dioxide and carbon black, phthalocyanine pigments, and other organic pigments.

[0064] In further embodiments, the dried distillers solubles and/or derivative or any of the upstream product feedstreams disclosed herein optionally can comprise a filler. Any filler known to a person of ordinary skill in the art may be used in the adhesion composition disclosed herein. Non-limiting examples of suitable fillers include sand, talc, dolomite, calcium carbonate, clay, silica, mica, wollastonite, feldspar, aluminum silicate, alumina, hydrated alumina, glass bead, glass microsphere, ceramic microsphere, thermoplastic microsphere, barite, wood flour, magnesium carbonate, calcium hydroxide, calcium oxide, magnesium oxide, aluminum oxide, silicon oxide, iron oxide, boron nitride, titanium oxide, talc, pyrophyllite clay, silicate pigment, polishing powder, mica, sericite, bentonite, pearlite, zeolite, fluorite, dolomite, quick lime, slaked lime, kaolin, chlorite, diatomaceous earth, and combinations thereof.

[0065] In further embodiments, the dried distillers solubles and/or derivative or any of the upstream product feedstreams disclosed herein optionally can comprise a catalyst. Suitable catalysts include without limitation, metallic catalysts and non-metallic catalysts. Metal catalysts include, without limitation, metal oxides, including, for example, zinc oxide, titanium dioxide, copper oxides, (cuprous oxide and/or cupric oxide), aluminum oxide, calcium oxide, stannous oxide, lead oxide and other metal oxides; and metals, for example, zinc, titanium, copper, iron, nickel, zirconium, and aluminum. Other catalysts include, without limitation, fly ash and Portland cement.

[0066] Some oxides also assist with odor reduction and increase the shelf life. Without being bound by theory, oxides, such as titanium dioxide, may reduce auto-oxidation.

[0067] In further embodiments, the dried distillers solubles and/or derivative or any of the upstream product feedstreams disclosed herein optionally can comprise a crosslinker. Crosslinking agents also have the ability to increase the mechanical and physical performance of the present bioadhesive. As used herein, crosslinking generally refers to linking at least two polymer chains comprised, for example, of proteins, peptides, polysaccharides, and/or synthetic polymers or the corn protein material.

[0068] Suitable crosslinking agents include one or more of metallic salts (e.g., NaCl or rock salt) and salt hydrates (which may improve mechanical properties), urea, formaldehyde, urea-formaldehyde, polyesters, phenol and phenolic resins, melamine, methyl diisocyanide (MDI), polymeric methyl diphenyl diisocyanate (pMDI), polymeric hexamethylene diisocyanate (pHMDI), amine-epichlorohydrin adducts, epoxides, zinc sulfate, aldehydes and urea-aldehyde resins epoxides, aldehyde, aldehyde starch, dialdehyde starch, glyoxal, urea glyoxal, urea-aldehyde, polyamine epichlorohydrin resin, polyamidoamine-epichlorohydrin resin, polyalkylene polyamine-epichlorohydrin, amine polymer-epichlorohydrin resin epoxy, resin mixtures, combinations thereof, and the like. The same or similar agents may also serve as binders.

[0069] The amine-epichlorohydrin adducts are defined as those prepared through the reaction of epichlorohydrin with amine-functional compounds. Among these are polyamidoamine-epichlorohydrin resins (PAE resins), polyalkylenepolyamine-epichlorohydrin (PAPAE resins) and amine polymer-epichlorohydrin resins (APE resins). The PAE resins include secondary amine-based azetidinium-functional PAE resins, tertiary amine polyamide-based epoxide-functional resins and tertiary amine polyamidourylene-based epoxide-functional PAE resins. It is also possible to use low molecular weight amine-epichlorohydrin condensates.

[0070] Additional additives can include a fiber additive. Suitable fibers include any of a variety of natural and synthetic fibers. Cellulose fibers include, without limitation, those from wood, agricultural fibers, including flax, hemp, kenaf, wheat, soybean, switchgrass, and grass, fibers obtained from paper and other fiber recycling, including, without limitation, household and industrial paper recycling streams, fibrous waste from the paper or wood industries, including paper mill sludge. Synthetic fibers include fiberglass, Kevlar, carbon fiber, nylon; mixtures or combinations thereof, and the like. Mineral or silica additives may also be used. The fiber can modify the performance of the biopolymers. For example, longer fibers can be added to impart higher flexural and rupture modulus to the cured or dried bioadhesive.

[0071] Nanomaterials may also be used as fillers, including NanoCell (LDI Composites), which is a blend of cellulose, minerals and clay that has been processed into a submicron material. It is derived from paper mill sludge. NanoCell also contains small percentages of metals and titanium dioxide. Other forms of nanomaterials, such as nanofibers, nanotubes, nanocellulosics, nanoclays and other forms of nanomaterials may also be included in the dried distillers solubles biocomposite additive and/or the biopolymer.

[0072] Other materials that can include components found in latex paint, including, without limitation, latex compounds, including, without limitation, acrylic latexes such as styrenated acrylic latex; calcium carbonate, colorants, dispersants, such as, for example, naphthalene sulfonic acid condensation products; ammonium hydroxide; surfactants; glycol ethers, including (propylene glycol) methyl ether; 2,2,4-trimethylpentanediol-1,3-monoisobutyrate; sodium nitrite; ethylene glycols, such as triethylene glycol bis(2-ethylhexanoate); drying agents, such as metal oxides, including, without limitation, zirconium oxides, cobalt oxides and iron oxides, as well as ethylene oxides and ethylene oxide derivatives and condensates, including, without limitation, fatty alcohol ethoxylate, alkylphenol ethoxylate, fatty acid ethoxylate, ethoxylated fatty amines, and the like; preservatives, emulsifiers and thickeners.

[0073] Additional additives include citric acid including citric acid monohydrate contains many carboxyl groups that are expected to interact with both proteins and cellulosic based materials at elevated temperatures.

[0074] The dried distillers solubles can also be dry blended with a wide range of additional powder resin as a bioextender to either lower the cost of the petrochemical resin powder or provide functional advantages to the overall adhesive blend. Dried distillers solubles can also be added to various formaldehyde resins wherein the proteins can scavenge the residual formaldehyde and increase the biobased content of the adhesive. Such powder or liquid resins include but not limited to: phenol formaldehyde, urea formaldehyde and melamine formaldehyde adhesives.

[0075] The following examples are presented for illustrative purposes only, and are not intended to limit the scope of the invention.

Example 1.

[0076] In this example, condensed distillers solubles with at least a portion of the oil removed was further evaporated in an evaporator to a moisture content of about 50% by weight. The liquid was then placed into a fluidized bed spray drier in which the material was recirculated to provide a granular mixture. The granular mixture was dried to two different moisture contents.

[0077] One sample had a moisture percentage of about 12% and the other sample had a moisture content of 5% by weight. The granular material had a very light bright yellow color and emitted minimal odor. The granular material was sandwiched between a particle board and a wood veneer panel and heat pressed at 300°F and 10 pounds per square inch (psi). Once cooled to room temperature, the veneer was qualitatively tested for adhesion by physically attempting to separate the veneer from the particle board by hand. In this example, the veneer panel could not be separated from the particle board.

Example 2.

[0078] In this example, the dried distillers solubles with at least a portion of the oil removed in accordance with Example 1 was blended with glycerine obtained from biodiesel production at a 50% ratio and mixed. The material was used to laminate two kraft papers together using heat and pressure.

Example 3.

[0079] In this example, the dried distillers solubles with at least a portion of the oil removed in accordance with Example 1 was blended with water at a 1:1 ratio by weight and mixed. The material was used to laminate two particle boards together. The sample was clamped to maintain pressure for about 24 hours. The clamps were removed and physical separation of the particle boards by hand was not achieved, thereby indicating good adhesion.

Example 4.

[0080] In this example, the dried distillers solubles with at least a portion of the oil removed in accordance with Example 1 was blended with water at a 1:1 ratio by weight and mixed. 5% Lactic Acid was added and mixed. Then 5% magnesium oxide was added and mixed. The material was used to laminate two particle boards together. The sample was clamped to maintain pressure for about 24 hours. The clamps were removed and physical separation of the particle boards by hand was not achieved, thereby indicating good adhesion.

Example 5.

[0081] In this example, the dried distillers solubles with at least a portion of the oil removed in accordance with Example 1 was blended with water at a 1:1 ratio by weight and mixed. 5% Ammonium Polyphosphate was added and mixed. Then 5% magnesium oxide was added and mixed. The material was used to laminate two particle boards together. The sample was clamped to maintain pressure for about 24 hours. The clamps were removed and physical separation of the particle boards by hand was not achieved, thereby indicating good adhesion.

Example 6.

[0082] In this example, the dried distillers solubles with at least a portion of the oil removed in accordance with Example 1 was blended with water at a 1:1 ratio by weight and mixed. Separately, a magnesium chloride solution was made with 25 parts of hydrated magnesium chloride mixed with 15 parts water and mixed, then 60 parts of magnesium oxide was added to create the magnesium chloride solution. 10% of the magnesium chloride solution was then added with the aqueous solution containing the dried distillers solubles and mixed. This material was used to laminate 2 layers of kraft paper together.

[0083] This written description uses examples to disclose the invention, including the best mode, and also to enable any person skilled in the art to make and use the invention. The patentable scope of the invention is defined by the claims, and may include other examples that occur to those skilled in the art. Such other examples are intended to be within the scope of the claims if they have structural elements that do not differ from the literal language of the claims, or if they include equivalent structural elements with insubstantial differences from the literal languages of the claims.

WHAT IS CLAIMED IS:

1. A bioadhesive composition comprising dried distillers solubles.
2. The bioadhesive composition of claim 1, further comprising an additive, wherein the additive is a tackifier selected from the group consisting of natural rosins, modified rosins, copolymers of natural terpenes, polyterpene resins, aliphatic hydrocarbon resins, and combinations thereof.
3. The bioadhesive composition of claim 1, further comprising an additive, wherein the additive is a plasticizer selected from the group consisting of olefin oligomers, phthalates, mineral oils, vegetal oils, animal oils, and combinations thereof.
4. The bioadhesive composition of claim 1, further comprising an additive, wherein the additive is a crosslinker.
5. The bioadhesive composition of claim 1, further comprising an additive, wherein the additive is a wax selected from the group consisting of petroleum waxes, polyolefin waxes, synthetic waxes, paraffin, microcrystalline waxes, and combinations thereof.
6. The bioadhesive composition of claim 1, wherein the dried distillers solubles comprise modified water soluble proteins.
7. The bioadhesive composition of claim 1, further comprising a soy bean protein isolate.
8. The bioadhesive composition of claim 1, further comprising an additive, wherein the additive is a filler selected from the group consisting of sand, talc, clay, silica, mica, magnesium oxide, mica, silicon dioxide, kaolin, iron oxide, and combinations thereof..
9. The bioadhesive composition of claim 1, further comprising an additive, wherein the additive is a fiber selected from cellulose fibers and synthetic fibers.

10. A method of making a bioadhesive composition comprising:
 - evaporating at least a portion of water from thin stillage obtained from a corn-to-ethanol fermentation process to form condensed distillers solubles;
 - drying the condensed distillers solubles to form dried distillers solubles; and
 - forming a bioadhesive composition with the dried distillers solubles.
11. The method of claim 10, further comprising wet compounding the dried distillers solubles with an additive.
12. The method of claim 10, further comprising dry compounding the dried distillers solubles with an additive.
13. The method of claim 11, wherein the additive comprises a plasticizer, a crosslinker, a wax, a filler material, a soy protein isolate, an antioxidant, a UV stabilizer, a colorant, a flow aid, a biocide, a lubricant, an oil, a coupling agent, a fiber, a tackifier, a metal oxide, a surfactant, a catalyst, a solvent, or a hydrolyzing agent, or mixtures thereof.
14. The method of claim 11, wherein the plasticizer is selected from the group consisting of olefin oligomers, phthalates, mineral oils, vegetal oils, animal oils, and combinations thereof.
15. The method of claim 11, wherein the tackifier is selected from the group consisting of natural rosins, modified rosins, copolymers of natural terpenes, polyterpene resins, aliphatic hydrocarbon resins, and combinations thereof.
16. The method of claim 11, wherein the wax is selected from the group consisting of petroleum waxes, polyolefin waxes, synthetic waxes, paraffin, microcrystalline waxes, and combinations thereof.
17. The method of claim 11, wherein the filler is selected from the group consisting of sand, talc, clay, silica, mica, magnesium oxide, mica, silicon dioxide, kaolin, iron oxide, and combinations thereof.

18. The method of claim 12, wherein the additive comprises a plasticizer, a crosslinker, a wax, a filler material, a soy protein isolate, a fiber, a metal oxide or mixtures thereof.
19. The method of claim 12, wherein the plasticizer is selected from the group consisting of olefin oligomers, phthalates, mineral oils, vegetal oils, animal oils, and combinations thereof.
20. The method of claim 12, wherein the tackifier is selected from the group consisting of natural rosins, modified rosins, copolymers of natural terpenes, polyterpene resins, aliphatic hydrocarbon resins, and combinations thereof.
21. The method of claim 12, wherein the wax is selected from the group consisting of petroleum waxes, polyolefin waxes, synthetic waxes, paraffin, microcrystalline waxes, and combinations thereof.
22. The method of claim 12, wherein the filler is selected from the group consisting of sand, talc, clay, silica, mica, magnesium oxide, mica, silicon dioxide, kaolin, iron oxide, and combinations thereof.
23. The method of claim 10, further comprising chemically modifying at least one of a whole stillage, thin stillage, the condensed distillers solubles and dried distillers solubles.
24. The method of claim 10, further comprising removing a selected amount of oil from the condensed distillers solubles such that the dried distillers solubles contains a desired amount of oil therein.
25. The method of claim 10, further comprising treating the thin stillage or the condensed distillers solubles with an acid or base.
26. The method of claim 10, wherein drying comprises convection at an elevated temperature.

27. The method of claim 10, wherein drying is a drying gas stream at a temperature of about 600 °F to about 1800 °F.

28. The method of claim 10, wherein evaporating the condensed distillers solubles comprises reducing the moisture content to less than about 50% by weight.

29. A process for bonding one component to another component, the process comprising:

applying a bioadhesive composition to a surface of at least one of the components, wherein the bioadhesive composition comprises dried distillers solubles;
and

contacting the one component with the other component, wherein the bioadhesive composition is therebetween.

30. The process of claim 29, wherein the dried distillers solubles is a compactable powder.

31. The process of claim 29 wherein the composition further comprises a tackifier, a plasticizer, a wax, an antioxidant, a UV stabilizer, a colorant, a filler, a flow aid, a biocide, a lubricant, an oil, a coupling agent, a crosslinking agent, a surfactant, a catalyst, a solvent, or a hydrolyzing agent.

