(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
16 May 2002 (16.05.2002)

PCT

(10) International Publication Number
WO 02/37981 A2

(51) International Patent Classification[7]: A23K

(21) International Application Number: PCT/US01/51086

(22) International Filing Date: 26 October 2001 (26.10.2001)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
60/243,882 27 October 2000 (27.10.2000) US

(71) Applicant *(for all designated States except US)*: **MICHIGAN BIOTECHNOLOGY INSTITUTE** [US/US]; 3900 Collins Road, Lansing, MI 48910 (US).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)*: **SEVERIN, Blaine, F.** [US/US]; 4117 Spinaker Lane, Okemos, MI 48864 (US). **PONNAMPALAM, Elankovan** [US/US]; 1218 Starboard Drive, Okemos, MI 48864 (US). **MCEOWEN, Jack** [US/US]; 1240 Woodcrest Lane, East Lansing, MI 48823 (US).

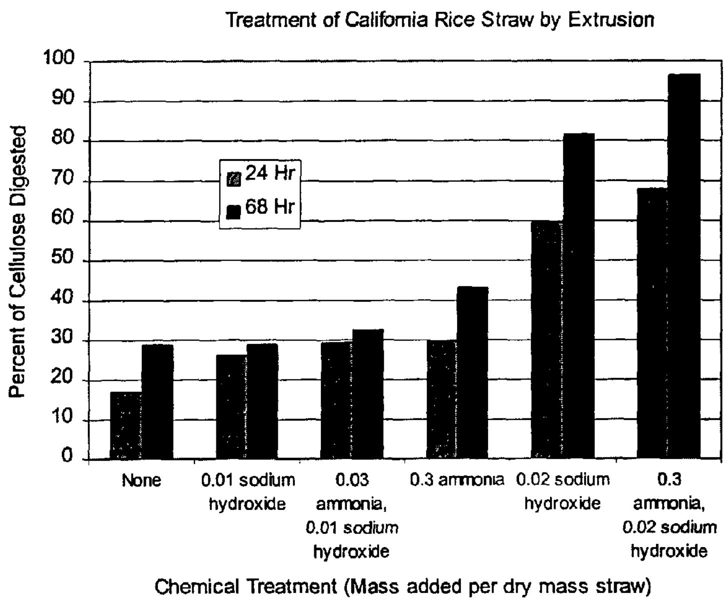
(74) Agent: **ROCHE, Richard, T.**; Quarles & Brady LLP, 411 E. Wisconsin Avenue, Milwaukee, WI 53202-4497 (US).

(81) Designated States *(national)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.

(84) Designated States *(regional)*: ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

[Continued on next page]

(54) Title: PHYSICAL-CHEMICAL TREATMENT OF LIGNIN CONTAINING BIOMASS



(57) **Abstract:** A method for increasing the digestibility of cellulose in biomass and for producing fermentation feedstocks and animal feeds from biomass is disclosed. The methood comprises adding a basic material to biomass, and feeding the basic material and the biomass through an extruder. The biomass may be selected from agricultural byproducts such as bagasse, corn stover, straw, and hulls. The basic material may be selected from calcium carbonate, sodium bicarbonate, sodium carbonate, urea, ammonium hydroxide, calcium hydroxide, magnesium hydroxide, hydrated lime, soidum hydroxide, and potassium hydroxide. Preferably, the basic material is added to the biomass in a dry form, and most preferably includes urea. Also disclosed is an animal feed formed by adding a basic material and molasses to biomass, and an animal feed produced from biomass by mixing a portion of acid treated biomass with a portion of base treated biomass.

WO 02/37981 A2

Published:
— *without international search report and to be republished upon receipt of that report*

Physical-Chemical Treatment of Lignin Containing Biomass

CROSS-REFERENCES TO RELATED APPLICATIONS

[0001] This application claims the benefit of United States Provisional Patent Application No. 60/243,882 filed October 27, 2000.

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH

[0002] Not Applicable.

BACKGROUND OF THE INVENTION

1. Field of the Invention

[0003] This invention relates to the physical-chemical treatment of cellulose-containing materials to render them more digestible or more chemically reactive. More particularly, this invention relates to the physical-chemical treatment of cellulose-containing waste agricultural materials to create highly digestible animal feeds.

2. Description of the Related Art

[0004] Agricultural biomass, such as rice straw, bagasse, corn stover, wheat straw, cotton gin trash, distiller's dried grains, and grasses, paper and municipal solid wastes, and forestry products, such as bark and wood pulp, are examples of readily available materials containing cellulose. However, many of these materials are considered waste by-products and present disposal problems. For example, rice straw is typically burned in the field, and bagasse (spent sugarcane) is stockpiled. In view of the longstanding needs for national energy independence, reduction in waste generation, and more efficient animal production, it is not surprising that alternatives to disposal, such as the use of these cellulose containing materials (in particular agricultural biomass) as animal feeds, have been suggested.

[0005] While residue agricultural fiber (substrate or materials) is not commonly used in commercial animal feedstuffs, the use of native biomass material such as bagasse in dairy cow rations has been reported. ("Native" material is defined herein as essentially raw material having no chemical or physical alteration designed to improve digestibility.) For example, Roman-Price, *et al.* in *Journal of Dairy Science* 58:1320-1327, 1975, Van Horn *et al.* in *Journal of Dairy Science* 63:1463-1474, 1980, and Marshall *et al.* in *Journal of Dairy Science* 58:896-900, 1975 describe the use of pelletized plant fiber, such as sugar cane bagasse and cottonseed hull, as fiber feedstocks in mixed ration animal diets. When supplemented with protein, protein equivalent as urea, or soy meal, satisfactory feeds have been made with up to 73% dry matter intake as bagasse, or 55% as cottonseed hull. In some of the tests, 10% molasses from rum was added. Geographic regions such as Florida, Louisiana and Hawaii of the United States that support dairy industries, but operate forage deficient agricultural bases, demonstrate the need to fully utilize residue agricultural fiber as suggested in these references. However, the lack of commercial use of materials such as bagasse points out that the problems associated with creating a superior and commercially viable feedstuff from agricultural residue have not been solved.

[0006] Utilization of residue agricultural biomass as animal feeds (or as a feedstock for industrial fermentations) has been hampered by the low efficiency with which organisms and enzymes are able to convert the cellulose in biomass into sugars. The low conversion efficiency for these cellulosic materials is the result of the fibrous nature of cellulose and the presence of lignin coating the cellulose fibers. Therefore, these materials in their native state make poor candidates for animal feeds or as feedstocks for industrial fermentations.

[0007] As detailed above, it would be particularly beneficial in certain regions if much greater quantities of agricultural biomass, such as rice straw, wheat straw, cotton gin trash, bagasse, corn stover, distiller's dried grains, grasses and the like, could be used for animal feeds. However, even ruminants (such as cattle and sheep) that are able to digest and grow on many kinds of cellulosic plant materials have limited ability to efficiently digest the lignocellulosic material in agricultural biomass because the lignin coating makes the cellulose largely unavailable for digestion by the digestive juices and the microbes that inhabit ruminant stomachs. For instance, it has been reported in U.S. Patent No. 5,292,410 that cellulosic wastes, such as cotton gin trash, straw, corn stalks and husks, cotton wastes, peanut shells, saw dust and the like, that include highly lignified cellulosic structures are digested poorly, if at all, by ruminants. It is stated that cotton gin trash is only digested about 36-44% and wheat straw is only digested about 35-40% by ruminants as compared to 55-60% for conventional forage such as alfalfa and 80-90% for grains.

[0008] It has been suggested that one key to increasing the digestibility of lignocellulose-containing biomass is to increase access to cellulose by the digestive juices and the microbes that inhabit ruminant stomachs. Thus, attempts have been made to break down the highly lignified cellulosic structures of biomass and thereby increase the reactive surface area of the cellulose. The greater the reactive surface area of cellulose in the biomass, the more access that the digestive juices or other agents have to the cellulose in the biomass. Accordingly, many different techniques have been used to treat lignocellulosic biomass specifically to increase the reactive surface area of the cellulose in the biomass. These techniques have resulted in varying degrees of effectiveness.

[0009] Acidic solutions have been used to chemically hydrolyze fibrous biomass. For example, U.S. Patent No. 4,515,816 demonstrates a method to process lignocellulose materials to a form which is suitable for feeding to ruminant animals. The materials are wetted with dilute acid, stored at ambient temperature and pressure in a low oxygen environment to effect mild hydrolysis of the materials. The digested product may be dried and partially neutralized with ammonia. U.S. Patent No. 4,427,453 teaches a method of two stage continuous hydrolysis of plant biomass to sugars. Chopped biomass is treated in a first stage in the presence of dilute acid, at temperatures and pressure conditions under which the hemicellulose and, partially, the cellulose are hydrolyzed to pentoses and partially, hexoses. The reaction mixture pressure is suddenly released and the hydrolysate is separated from the biomass. In a second stage, cellulose in the biomass is hydrolyzed in the presence of dilute mineral acid under more severe temperature and pressure conditions, to hexoses. The reaction mixture pressure is again suddenly released. The hydrolysate is separated from the remaining biomass.

[0010] While methods of using acid to treat biomass may be effective, they do have certain disadvantages. For instance, these methods require the use of solutions which add water to the overall process. Furthermore, many acidic materials are presently being scrutinized as toxic minerals. Furthermore, concentrated acid is corrosive and requires extreme care in handling, especially in the treatment of wastewater as many acids are considered pollutants.

[0011] Oxidants have also been used to treat fibrous biomass. For example, U.S. Patent No. 5,292,410 teaches that crop residues and feed grains for livestock may yield higher digestibility if treated with an aqueous solution of chlorite. The treated grains are satisfactory for ruminant animals, with an improved digestibility of 50%, and are non-toxic. In this process, solutions of mixed oxidant captured from the gas generated by an electrolytic cell are mixed with solutions of sodium hydroxide and the admixture is blended with the substrate in a slurry. However, the method of this patent requires the use of solutions which add water to the overall process. Furthermore, chlorites are presently being scrutinized as toxic minerals, and the reactions of chlorine in all forms is being scrutinized as precursors to production of carcinogenic products.

[0012] Methods of treating lignocellulosic materials, such as straw, with alkali solutions have been known since the beginning of the 20th century, and different systems have been tested with varying success. One example method is described in U.S. Patent No. 4,176,203 wherein straw is treated in an aqueous solution of sodium hydroxide. Some of these methods have disadvantages such as the formation of waste solutions which are difficult to handle and the great amounts of alkaline solutions that have to be handled in order to provide effective treatment. Also, chemical soaking of the fiber may yield tarry, caramelized, overly-wet material which is difficult to handle and requires extensive drying.

[0013] Ammonia has also been used to break down fibrous biomass. U.S. Patent Nos. 4,600,590 and 5,037,663 describe how to increase the reactivity of cellulose-containing materials such as animal feedstuffs by contacting the material in a pressure vessel with volatile liquid ammonia, which has a vapor pressure greater than atmospheric pressure at ambient temperatures. The contact is maintained for a time period sufficient for the ammonia to swell the cellulose of the material. The pressure is than rapidly reduced to atmospheric pressure thereby causing the ammonia to boil and explode the material. The ammonia is separated from the cellulose-containing material and recovered for recycling. This process has the main drawback that the high levels of ammonia recommended (1.5-2.0 w/w ratio to dry matter) and the subsequent recovery of the ammonia and the recycle in batch pressure vessels are prohibitive to efficient commercial production of the desired material. Also, the produced product has elevated ammonia content that can render the product unpalatable. Furthermore, elevated ammonia and urea in dairy feeds has been determined to be undesirable for maintenance of good cow health. In subsequent improvements to the processes described in U.S. Patent Nos. 4,600,590 and 5,037,663, the patentees demonstrate that the process of contacting liquid ammonia with biomass and causing the rapid and advantageous decompression of ammonia may be performed on a continuous basis in a screw-in-barrel process. See U.S. Patent Nos. 6,176,176 and 6,106,888. The barrel and screw are designed with internal tapering or flights to compress or pressurize the biomass and ammonia prior to explosive release to atmospheric pressure. While these patents teach that a method of continuous flow production may be implemented by use of an extruder, the other difficulties associated with ammonia addition remain.

[0014] Peroxides (such as hydrogen peroxide, a weak acid) have also been used to break down fibrous biomass. For example, Bas *et al.* in *Journal of Dairy Science,* Vol. 72, No. 5, pages 1217-1227, 1989 describe the beneficial use of alkaline hydrogen peroxide as a pre-digesting oxidizer of various types of residue cellulosic biomass. Also, in U.S. Patent No. 4,649,113, there is disclosed the alkaline peroxide treatment of nonwoody lignocellulosics. By treating agricultural crop residues and other nonwoody lignocellulosic plant substrates with H_2O_2 at a controlled pH within the range of about 11.2 to 11.8, the substrates are partially delignified and high levels of the cellulose and hemicellulose as insoluble fractions are made available for subsequent use. The products of this treatment are nontoxic and are characterized by low crystallinity and near quantitative cellulase digestibility. They are useful as carbohydrate sources in ruminant feeds and as microbial feedstocks for commercial process such as the production of alcohol and generation of single-cell protein. However, processes using peroxides may require extended treatment times, requiring that the resulting slurry be held in residence for up to 24 hours. While recovery of the peroxide is not necessarily required, special care must be used in handling this toxic chemical. Therefore, these methods are expensive due to high energy costs and toxic chemical handling costs, and can be inefficient due to the time required for treatment.

[0015] Grinding methods have been used to essentially chop the biomass into pieces small enough for effective sugar hydrolysis or other use. Huber *et al.* in

U.S. Patent No. 4,632,795 present a method and apparatus for extrusion processing of cellulose bearing materials. An improved, low cost, energy efficient extrusion device and method for processing of cellulose- or fiber-bearing materials (e.g., wood chips, crop residues, whole or ground soybeans) is described. This technique requires no chemicals, so chemical recovery is not a problem. However, the drawback to grinding is that it is very energy intensive, inefficient, and an expensive means of disintegrating fibrous biomass. To achieve very small particle sizes, the biomass must be ground repeatedly. Consequently, such grinding consumes a great deal of energy making grinding simply uneconomical as a means of treatment. The cost of grinding is prohibitive based on the energy consumption alone, not taking into account equipment costs, including the cost of repair and general wear of the machinery. Related mechanical techniques are also described in U.S. Patent Nos. 5,498,766 and 5,370,999 wherein a high-frequency, rotor-stator device is used to shred and disintegrate fibrous lignocellulosic biomass.

[0016] Combinations of two or more of the above-described chemical methods for breaking down fibrous biomass have also been proposed. In U.S. Patent No. 4,957,599, there is described an alkaline extraction and peroxide process for delignifying and bleaching nonwoody lignocellulosic material into products digestible by ruminants and ingestible by humans. The process comprises treating the substrate in a two step process in which the substrate is first treated in alkaline solution of about 1% w/w sodium hydroxide. The slurry is then treated with a second dose of 1-15% w/w sodium hydroxide solution and a peroxide solution at a pH of 8.5 to 11. The intent of the process is to provide extreme reaction conditions to produce a more purified and bleached product. Once again, the process is reliant on solution chemistry which may add unwanted water or toxic chemicals to the process.

[0017] Combinations of two or more of the above-described physical and chemical methods for breaking down fibrous biomass have also been proposed. Acids have been used with an extruder to both chemically and physically treat fibrous biomass. (See, for example, U.S. Patent No. 6,228,213.) Peroxides have also been used in conjunction with shear forces produced by an extruder device to both chemically and physically disintegrate fibrous biomass. The use of extrusion has been shown to lessen the chemical requirements for hydrogen peroxide in treating barley straw (Flachowsky *et al.*, "Effect of NaOH and H_2O_2 on the Degradability of Straw in Ruminants", *Archives of Animal Nutrition*, Berlin 38, 1988, 10, pages 953-964) and wheat straw (Gould *et al.*, "Treatment of Wheat Straw with Alkaline Hydrogen Peroxide in a Modified Extruder", *Biotechnology and Bioengineering,* Vol. 33, No. 2, pages 233-236, 1989). The use of extrusion with peroxides to treat biomass is also described by Helmling *et al.* in "Improving the Nutritive Value of Lignocellulosics: The Synergistic Effects Between Alkaline Hydrogen Peroxide and Extrusion Treatments", *Biotechnology and Bioengineering*, Vol. 33, No. 2, pages 237-241, 1989. Of course, the previously mentioned drawbacks with the use of peroxides are also present in these methods.

[0018] Alkali agents have also been used in conjunction with shear forces produced by an extruder device to both chemically and physically disintegrate fibrous biomass. In U.S. Patent No. 4,965,086, there is described a process for the chemical-mechanical treatment of lignocellulosic materials to improve their nutritive value. A plant substrate is treated with a sufficient amount of an alkaline material and hydrogen peroxide, or a compound capable of generating hydrogen peroxide, for a sufficient period of time and the reaction mass is extruded to produce a product having increased nutrient availability. It was found that the improvement in digestibility cannot be obtained by using extrusion alone, or by using alkaline hydrogen peroxide treatment alone. The preferred sodium hydroxide treatment is expressed as $\%NaOH = 3\% + (a)H_2O_2$ where $(a) > 0.5$ and is preferably 1.2. The value of (a) is determined by the upper limit of sodium allowed in the diet. One drawback to this method is that the treatment is limited by the nutritional restrictions of the animal feed.

[0019] Another example of the treatment of biomass using alkali agents in conjunction with shear forces produced by an extruder device is described in U.S. Patent No. 4,997,488. This patent discloses the combination of high-shear mechanical disruption and alkali and peroxide pretreatment in a high solids reaction mixture. The simultaneous application of these conditions greatly reduces the amounts of reagents otherwise required, and also eliminates the waste stream of liquid byproducts. Suitable sources of substrate treatable by this process include nonwoody plant parts, crop residues, and agricultural byproducts. The products of this treatment are nontoxic and characterized by high cellulose availability. These products are thereby useful as carbohydrate sources in ruminant feeds, as microbial feedstocks, and as sources of dietary fiber for humans and other monogastrics.

[0020] While each of the foregoing methods may serve to break down the highly lignified cellulosic structures of biomass and thereby increase the reactive surface area of the cellulose, each method has certain aforementioned disadvantages which limit the use of these methods in preparing a truly superior animal feed or feedstock for industrial saccharification or fermentation. For instance, it has been determined that a superior animal feed prepared from biomass must meet at least four criteria. First, the animal feed must provide improved digestibility above the native or raw biomass material, Second, the animal feed must have a controlled ion content to avoid dietary salt imbalance, and in particular, sodium ions must be controlled in the animal feed. Third, the animal feed must have a balanced pH for animal health, and in particular, an animal feed with a high pH must be avoided. Fourth, the treated biomass to be used for animal feed must have low moisture levels to avoid the high costs of drying materials for stable storage or reduced shipping weights. In addition, under certain circumstances, a superior animal feed may need to include non-protein nitrogen within a predetermined range.

[0021] Comparing these four criteria for a superior animal feed to the foregoing methods for breaking down the highly lignified cellulosic structures of biomass, it can be appreciated that none of the aforementioned prior methods can achieve these four criteria. For example, many of the chemical treatment methods introduce unwanted moisture into the biomass. Also, certain alkaline based chemical treatment methods produce treated biomass with an unacceptably high pH or a high level of sodium ions. Furthermore, these prior methods cannot provide for an animal feed with non-protein nitrogen at a predetermined level.

[0022] Therefore, there is a continuing need for an improved method for increasing the digestibility of cellulose in biomass wherein the method can provide an animal feed or feedstock for industrial saccharification or fermentation having controlled ion content, a balanced pH, low moisture levels, and non-protein nitrogen within a predetermined range.

BRIEF SUMMARY OF THE INVENTION

[0023] The foregoing needs are met by a method according to the invention for increasing the digestibility of cellulose in biomass and by feedstocks for industrial saccharification or fermentation and animal feeds produced by various versions of the method. The method comprises adding a basic material to biomass, and feeding the basic material and the biomass through an extruder. The biomass may be selected from bagasse, corn stover, wheat straw, rice straw, buckwheat straw, oat straw, rye straw, flax straw, barley hulls, rice hulls, oat hulls, alfalfa hay, cotton gin trash, distiller's dried grains, grasses, and mixtures thereof. The basic material may be selected from calcium carbonate, sodium bicarbonate, sodium carbonate, urea, ammonium hydroxide, calcium hydroxide, magnesium hydroxide, hydrated lime, sodium hydroxide, potassium hydroxide, and mixtures thereof. Preferably, the basic material is added to the biomass in a dry form, and most preferably includes sodium hydroxide. Typically, no acids are added to the biomass.

[0024] In one version of the method of the invention, urea is alone or with another basic material, and the nitrogen content of the urea remains stable throughout the method and is retained as non-protein nitrogen after the basic material and the biomass are fed through the extruder. Preferably, the basic material is selected in a composition and an amount such that at least one cation is retained in a predetermined range after the basic material and the biomass are fed through the extruder. It is also preferred that the basic material be selected in an amount such that the pH after the basic material and the biomass are fed through the extruder is in the range of 7 to 11, and most preferably 7 to 8.

[0025] It is known that soaking cellulosic materials in caustic solutions produces cellulose digestion. The soaking treatment method has several disadvantages compared to the present invention. Usually 24-48 hours are required to attain the same digestibility with a caustic soak as can be achieved in less than 30 seconds in an extruder. Also, the soak method involves excess moisture that must be dried from the product at a later time. The limitation of moisture creates the conditions for optimal extrusion, and limits the drying requirements. Furthermore, animal feeds or fermentation feed stocks needing stabilized, non-protein nitrogen, can be produced with the present invention by adding dry urea prior to extrusion. With minimized moisture, the urea produces stable nitrogen in the product. If the water content of the treatment is too high, however, urea degrades, as would occur with long soak times.

[0026] In a second aspect on the invention, there is provided a method for producing an animal feed in which a basic material and molasses are added to native biomass having lignocellulosic structures, and the basic material, molasses and native biomass are allowed to react for a period of time to produce a treated biomass that exhibits a higher percentage of dry matter that is digestible in rumen fluid compared to the native biomass. Optionally, the basic material, molasses and native biomass are also extruded.

[0027] In a third aspect of the invention, there is provided a method for producing an animal feed in which pH control, free sugar control and/or cation control may be exerted over an animal feed produced from biomass. In this method, a first portion of biomass is treated with a basic material and a second portion of biomass is treated with an acidic material. Optionally, the first portion of biomass and the basic material are extruded, and/or the second portion of biomass and the acidic material are extruded. A portion of the acid treated biomass is then mixed with a portion of the base treated biomass to create an animal feed. By controlling the mixing proportions of the acid treated biomass and the base treated biomass in the animal feed, pH control, free sugar control, and/or cation control can be exerted over the resulting animal feed. In this method, an animal feed is produced that solves the problems associated with undesirable pH or less than ideal cation levels in ruminant feed produced from chemically treated biomass.

[0028] It is therefore an advantage of the present invention to provide a method for increasing the digestibility of cellulose in biomass.

[0029] It is another advantage of the present invention to provide a method for increasing the digestibility of cellulose in biomass wherein the method produces treated biomass having a controlled ion content.

[0030] It is a further advantage of the present invention to provide a method for increasing the digestibility of cellulose in biomass wherein the method produces treated biomass having a pH within a predetermined range.

[0031] It is yet another advantage of the present invention to provide a method for increasing the digestibility of cellulose in biomass wherein the method produces treated biomass having low moisture levels so as to minimize drying of the treated biomass.

[0032] It is still another advantage of the present invention to provide a method for increasing the digestibility of cellulose in biomass wherein the method produces treated biomass having non-protein nitrogen within a predetermined range.

[0033] It is a still further advantage of the present invention to provide a method for increasing the digestibility of cellulose in biomass wherein the method produces treated biomass having free sugars within a predetermined range.

BRIEF DESCRIPTION OF THE DRAWINGS

[0034] These and other features, aspects, and advantages of the present invention will become better understood upon consideration of the following detailed description, appended claims, and drawings where:

[0035] Figure 1 is a graph showing the percent cellulose digested at 24 and 68 hour time periods for California rice straw treated according to one version of the present invention;

[0036] Figure 2 is a graph showing the conversion of cellulose to glucose at 24 and 68 hour time periods for corn stover treated according to another version of the present invention; and

[0037] Figure 3 is a graph showing the conversion of cellulose to ethanol at 24 and 68 hour time periods for corn stover treated according to another version of the present invention.

DETAILED DESCRIPTION

[0038] The present invention provides a method for increasing the digestibility of cellulose in biomass. Any biomass having lignocellulosic structures (i.e., structures having cellulose at least partially coated with lignin) can be beneficially treated using the method of the invention. Preferably, the method of the invention is used to treat waste stream components from the commercial processing of crop materials. Non-limiting examples of biomass materials suitable for use in the method include bagasse, corn stover, wheat straw, rice straw, buckwheat straw, oat straw, rye straw, flax straw, barley hulls, rice hulls, oat hulls, cotton gin trash, distiller's dried grains, grasses, and mixtures thereof. The biomass may be treated directly as obtained from the field or from the mill or processing plant, or the biomass may be chopped or ground to a convenient size to facilitate handling. One preferred biomass used in the method of the invention is sugar cane bagasse which may be treated directly as obtained from the mill or processing plant and may be chopped or ground to a convenient size to facilitate handling. In addition, it should be appreciated that this invention is also useful in improving the digestion of materials such as alfalfa hay, which are in their natural state utilized for animal feeds.

[0039] A basic material is added to the biomass and any suitable means for blending the biomass with the basic material may be employed if desired. The basic material and biomass are then conveyed to a conventional extruder, and treated in the extruder for a short period of time. The extruder can be also modified so as to accommodate the application of the basic material to the biomass in the extruder. The extruder achieves at least some structural disintegration of the lignocellulosic structure of the biomass and also allows for continuous processing. Enough moisture should be present in the combination of the basic material and the biomass throughout the extrusion operation to impart a sufficient degree of lubricity to the material such that it flows through the extruder without problems. However, an overly-wet combination of the basic material and the biomass material should be avoided as this combination may be difficult to handle and difficult to extrude. Preferably, the biomass used has a moisture content of from 15% to 150% of dry matter biomass, and most preferably, the biomass used has a moisture content of from 15% to 50% of dry matter biomass. Also, dry addition of the basic material to the biomass affords several benefits as will be explained below.

[0040] The basic material added to the biomass may be any basic material that serves to make the lignocellulosic structures of the biomass more digestible or more chemically reactive upon contact with the basic material. Non-limiting examples of the basic material include calcium carbonate, sodium bicarbonate, sodium carbonate, ammonium hydroxide, urea, calcium hydroxide, magnesium hydroxide, hydrated lime, sodium hydroxide, potassium hydroxide, and mixtures thereof. While the basic material may be added to the biomass in aqueous solution or in a dry form (such as a powder, flakes, granules, pellets or other like solid forms), it is preferable to add the basic material in a dry form to the biomass before extrusion. Dry addition of the basic material to moist biomass affords several benefits over addition of hydrated basic material. For example, (1) dry basic materials adhere to the surfaces of the moist biomass thereby yielding a higher concentration of basic material at the surface of the biomass than is attainable through the addition of pre-hydrated basic materials; (2) the heat of solution of the basic materials may be utilized to increase the temperature of the biomass, which increases the rate of destruction of the lignocellulosic structures of the biomass; (3) the captured heat of solution of the basic material increases the throughput of basic material and biomass through the extruder; and (4) the addition of dry basic material avoids the creation of tarry, caramelized, overly-wet biomass material which may be difficult to handle and difficult to extrude.

[0041] The choice of basic material depends on (among other things) the biomass selected for treatment. The following Examples demonstrate that when treated with a basic material, different types of biomass have a different degree of digestibility for a given dose of a selected basic material. Likewise, different basic materials provide for a different degree of digestibility for the same biomass. In general, the degree of treatment follows a trend based on the dry weight addition of the basic material. Generally, the same degree of digestibility can be obtained for the same biomass by adding a relatively small amount of a stronger basic material (as measured by reactivity) or a relatively large amount of a weaker basic material. Therefore, it is feasible to predetermine the degree of digestibility desired for the biomass, and match this with the required dose of one or more of the basic materials. For example, the exemplary basic materials listed above have a reactivity to biomass generally in the following order, from highest reactivity to lowest reactivity: potassium hydroxide, sodium hydroxide, magnesium hydroxide, calcium hydroxide, hydrated lime (typically 42% CaO, 27% MgO, 27.5 % water, 3.5% other), ammonium hydroxide, urea, sodium carbonate, calcium carbonate and sodium bicarbonate. Typically, the basic material is added to the biomass at a weight ratio of dry weight basic material to dry weight biomass of between 0.1% to 50%. Preferably, the basic material is added to the biomass at a weight ratio of dry weight basic material to dry weight biomass of between 0.1% to 10%. Most preferably, the basic material is added to the biomass at a weight ratio of dry weight basic material to dry weight biomass of between 0.1% to 6%.

[0042] After a type of biomass having a certain moisture content and a type and an amount of basic material are selected, the basic material is added to the biomass and the combination of the basic material and the biomass is extruded as described above. Typically, the basic material is applied to the biomass, and the basic material and biomass are blended until a substantially uniform blend is created. Then the basic material and the biomass are fed through a conventional extruder. In the alternative, the biomass and the basic material are simultaneously fed into the extruder. Since there are different heating zones and pressure ranges on a typical extruder, different heating regimes may be used. Both the barrel and the die of the extruder can be heated or one can be heated or neither can be heated. The extruder barrel and die temperatures for the method preferably range from about 170°F to about 325°F, and most preferably range from about 220°F to about 270°F. Residence time in the extruder varies with extruder design, and is typically on the order of seconds or a few minutes. Extruder pressure depends on a number of variables and is typically in the range of 50-250 psi. Conventional extrusion involves high pressure. However, the present invention provides a method wherein with the proper chemical addition, relatively low extrusion pressure may be practiced. This has the desired effect of providing highest material throughput, excellent temperature control, and fast reaction times, with minimized machine wear.

[0043] Biomass treated according to the method of the invention, in which biomass is covered a basic material and the basic material-covered biomass is fed through an extruder, has increased digestibility as measured by conventional cellulase digestion tests and conventional in vitro dry matter digestibility (IVTDMD) tests in rumen fluid. Therefore, the method according to the invention provides a method for converting biomass into a more digestible and more chemically reactive form that is useful as an animal feed or a feedstock for industrial saccharification or fermentation. It should be understood that in this invention the degree of cellulose digestibility required is dependent upon the intended use of the treated biomass material. For example, the degree of digestibility of biomass for ruminant animal feed is less than that required for swine or poultry feed, which in-turn, is less than that required for ethanol fermentation.

[0044] Various other versions of the method of the invention provide for even more advantageous animal feeds and feedstocks for industrial saccharification or fermentation. In one version of the method of the invention, the method produces treated biomass having a controlled ion content. By choosing a basic material of a certain composition, a specified cation balance can be achieved in the treated biomass product. For example, certain animal feeds should not contain high levels of sodium. Therefore, by balancing the composition of the basic material used to treat the biomass, it is possible arrive at a treated biomass having lower levels of sodium. For example, the basic material may be selected from a mixture of two or more of calcium carbonate, sodium bicarbonate, sodium carbonate, ammonium hydroxide, urea, calcium hydroxide, magnesium hydroxide, hydrated lime, sodium hydroxide and potassium hydroxide. Thus, the ratio of potassium, sodium, calcium and magnesium ions in the treated biomass product may be controlled. These mineral nutrients are supplied to the final treated biomass product while also serving as the cationic carriers of the bases used to carry out the biomass treatment. In this manner, a user of this method of the invention may select to enhance one or more of the cationic minerals.

[0045] In one specific application of this version of the invention, an animal feed can be created to meet the special dietary needs of "dry" dairy cattle. When dairy cattle are not producing milk, they are preparing themselves for their next lactation. During this time, the dairy cows are susceptible to milk fever. Milk fever occurs when levels of calcium become too high while the cow is not producing milk. During this phase of the cow's life, a feed with high levels of magnesium is considered a premium diet. Therefore, this version of the invention provides a method for feeding dairy animals that are susceptible to milk fever wherein magnesium hydroxide is added to biomass, the magnesium hydroxide and the biomass are fed through an extruder to form an extruded material, and the extruded material is fed to the dairy animals. Preferably, the biomass is selected from bagasse, corn stover, wheat straw, rice straw, buckwheat straw, oat straw, rye straw, flax straw, barley hulls, rice hulls, oat hulls, alfalfa hay, cotton gin trash, distiller's dried grains, grasses, and mixtures thereof, and most preferably, the biomass is sugar cane bagasse treated with magnesium hydroxide at a weight ratio of dry weight magnesium hydroxide to dry weight biomass of between 0.1% to 10%. As an example, a dairy ration was generated using Florida sugar cane bagasse and magnesium hydroxide as the basic material.

[0046] In another specific application of this version of the invention, an animal feed can be created for feeding dairy animals that are susceptible to ketosis. As dairy cows enter the calving phase, their energy needs greatly increase. If this dietary energy is met with soluble sugars, the dairy cows are subject to a metabolic illness, ketosis. With this disease, the dairy cow's digestive system produces ketones from excess soluble sugar. This dangerous condition may be avoided by product lacking in this form of digestible fiber. By selecting the basic material from calcium carbonate, sodium bicarbonate, sodium carbonate, ammonium hydroxide, urea, calcium hydroxide, magnesium hydroxide, hydrated lime, sodium hydroxide, potassium hydroxide, or a mixture thereof, the ratio of soluble sugars and digestible fiber in the treated biomass product may be controlled. Therefore, this version of the invention provides a method for feeding dairy animals that are susceptible to ketosis in which a basic material is added to biomass, the basic material and the biomass are fed through an extruder to form an extruded material, and the extruded material is fed to the dairy animals, wherein the basic material is added to the biomass in an amount such that the ratio of free sugars to digestible fiber in the extruded material is in a predetermined range.

[0047] In another version of the method of the invention, non-protein nitrogen may be incorporated into the treated biomass by using urea ($CO(NH_2)_2$) as at least a portion of the basic material added to the biomass before extrusion. Previously, it was thought that urea would be unstable in an extrusion process as urea tends to decompose into ammonia. However, it has been discovered that animal feeds or fermentation feed stocks needing stabilized, non-protein nitrogen can be produced by adding urea (preferably in dry form) to the biomass prior to extrusion. As long as the moisture level does not get excessively high in the biomass, the urea produces stable nitrogen in the treated biomass product. If the water content of the treatment is too high or the time between urea addition and extrusion is too long, however, the urea may degrade. Surprisingly, total kjeldahl nitrogen experimental data shows that the nitrogen content of the treated biomass product is nearly that of the basic material-covered biomass added to the extruder. Without intending to be limited, it has been shown that up to 18% nitrogen may be added to the treated biomass product by the use of the stable urea. Therefore, urea acts both as a basic material treatment chemical and as a stable source of non-protein nitrogen in the treated biomass product. This is unlike ammonium hydroxide, where free ammonia is readily generated throughout the treatment process such that only a maximum of about 3% dry weight as nitrogen may be retained in the treated biomass product. Typically, if the moisture content of the biomass is controlled to less than about 50%, then urea may be incorporated into the extruded material without the degradation of urea to ammonia. In this manner, a user of this method of the invention may select to add or remove non-protein nitrogen from the treated biomass product.

[0048] In a second aspect, the present invention provides an alternative method for producing an animal feed. In this method for producing an animal feed, a basic material and molasses are added to native biomass having lignocellulosic structures, and the basic material, molasses and native biomass are allowed to react for a period of time to produce a treated biomass that exhibits a higher percentage of dry matter that is digestible in rumen fluid compared to the native biomass. Preferably, the basic material, molasses and native biomass are extruded to produce the treated biomass.

[0049] The native biomass used in the animal feed of this version of the invention may be selected from bagasse, corn stover, wheat straw, rice straw, buckwheat straw, oat straw, rye straw, flax straw, barley hulls, rice hulls, oat hulls, alfalfa hay, cotton gin trash, distiller's dried grains, grasses, and mixtures thereof. Preferably, the native biomass material is sugar cane bagasse. The basic material used in this version of the invention may be selected from calcium carbonate, sodium bicarbonate, sodium carbonate, ammonium hydroxide, urea, calcium hydroxide, magnesium hydroxide, hydrated lime, sodium hydroxide, potassium hydroxide, and mixtures thereof, and preferably the basic material is added to the native biomass at a weight ratio of dry weight basic material to dry weight native biomass of between 0.1% to 10%.

[0050] The molasses used in the animal feed of this version of the invention is the thick liquid left after sucrose has been removed from the mother liquor in sugar manufacture. It is commercially available as an aqueous solution having a solids content rated at about 60° to 90° Brix and a consistency varying from a thin to a thick syrup. (Cane molasses is usually 80°-90° Brix. Beet molasses is usually 75°-85° Brix. Other molasses, e.g. wood and citrus, may be lower, about 60°-70° Brix.) While molasses from different sources may differ in both the identity and amount of non-sugar and colloidal materials contained therein, the molasses utilized in the method of the this invention may be any sugar-containing molasses, such as cane or blackstrap molasses (a mixture of approximately 20% sucrose, 20% reducing sugars, 10% ash, 20% organic nonsugars and 20% water), beet molasses, corn molasses, wood sugar molasses, citrus molasses, and the like. The most preferred molasses is cane or beet, since these are the most abundant molasses available in commerce. Preferably, the molasses is added to the native biomass at a weight ratio of wet weight molasses to dry weight native biomass of between 0.1% to 10%.

[0051] Optionally, a preservative may be used in the animal feed of this version of the invention. Example suitable preservatives may be selected from sorbic acid, propionic acid, acetic acid, benzoic acid, salts of sorbic acid, salts of propionic acid, salts of acetic acid, salts of benzoic acid, and mixtures thereof, and preferably, the preservative is added to the native biomass at a weight ratio of dry weight preservative to dry weight native biomass of between 0.1% to 4%.

[0052] Optionally, an acid treated biomass may also be used in the animal feed of this version of the invention. The acid treated biomass is produced by adding an acidic material is selected from hydrochloric acid, nitric acid, phosphoric acid, sulfuric acid, and mixtures thereof to biomass selected from bagasse, corn stover, wheat straw, rice straw, buckwheat straw, oat straw, rye straw, flax straw, barley hulls, rice hulls, oat hulls, alfalfa hay, cotton gin trash, distiller's dried grains, grasses, and mixtures thereof. Preferably, the native biomass material is sugar cane bagasse, and the acidic material is sulfuric acid added to the bagasse at a weight ratio of wet weight acidic material to dry weight native biomass of between 0.1% to 10%.

[0053] In a third aspect, the present invention provides another alternative method for producing an animal feed. In this method for producing an animal feed, base treated biomass is combined with acid treated biomass to produce an animal feed that is particularly useful as ruminant feed. In this method, a basic material is added to a first portion of native biomass material having lignocellulosic structures, and the basic material and the first portion of native biomass are allowed to react for a period of time to produce a treated first portion of biomass that exhibits a higher percentage of dry matter that is digestible in rumen fluid compared to the native biomass. Optionally, the basic material and the first portion of native biomass may be extruded using the extrusion techniques described above. Also, an acidic material is added to a second portion of native biomass material having lignocellulosic structures, and the acidic material and the second portion of native biomass are allowed to react for a period of time to produce a treated second portion of biomass that exhibits a higher percentage of dry matter that is digestible in rumen fluid compared to the native biomass. Optionally, the acidic material and the second portion of native biomass may be extruded using the extrusion techniques described above. The base treated first portion of biomass and the acid treated second portion of biomass are then mixed together to form an animal feed. In one embodiment, the treated first portion of biomass and the treated second portion of biomass are mixed together such that the treated first portion of biomass is present in the animal feed in the range of 25% to 75% by weight of the total weight of the animal feed and the treated second portion of biomass is present in the animal feed in the range of 25% to 75% by weight of the total weight of the animal feed.

[0054] In this method for producing an animal feed, the native biomass may be selected from bagasse, corn stover, wheat straw, rice straw, buckwheat straw, oat straw, rye straw, flax straw, barley hulls, rice hulls, oat hulls, alfalfa hay, cotton gin trash, distiller's dried grains, grasses, and mixtures thereof; the basic material may be selected from calcium carbonate, sodium bicarbonate, sodium carbonate, ammonium hydroxide, urea, calcium hydroxide, magnesium hydroxide, hydrated lime, sodium hydroxide, potassium hydroxide, and mixtures thereof; and the acidic material may be selected from hydrochloric acid, nitric acid, phosphoric acid, sulfuric acid, and mixtures thereof. In an example embodiment, the native biomass is sugar cane bagasse, the basic material is sodium hydroxide, and the acidic material is sulfuric acid.

[0055] This method for producing an animal feed is quite advantageous in that the base treated biomass and the acid treated biomass can be mixed in varying ratios in order to control selected physical and/or chemical properties of the resulting animal feed. For example, the base treated first portion of biomass, which has a basic pH, and the acid treated second portion of biomass, which has an acidic pH, can be mixed together such that the animal feed has a pH within a predetermined range. In an example embodiment, the animal feed produced by this method has a pH in the range of 1.5-10.5, preferably in the range of 6-8, and most preferably in the range of 6.5-7.5. Therefore, an animal feed produced by this version of the invention can solve the problems associated with undesirable pH in animal feeds produced from chemically treated biomass.

[0056] Also, the base treated first portion of biomass and the acid treated second portion of biomass may be mixed together such that the animal feed has a ratio of free sugars and digestible fiber within a predetermined range. For example, it has been discovered that immediately after chemical treatment under certain reaction conditions, acid treated biomass may contain about 30-40% free sugars in relation to total sugars liberated after cellulytic digestion of the acid treated biomass, whereas base treated biomass may contain about 5-15% free sugars in relation to total sugars liberated after cellulytic digestion of the base treated biomass. As a result, the base treated first portion of biomass (which has a relatively lower level of free sugars) and the acid treated second portion of biomass (which has a relatively higher level of free sugars) may be mixed together in various proportions such that the animal feed has a ratio of free sugars and digestible fiber within a predetermined range. Thus, an animal feed produced by this version of the invention can solve the problems associated with undesirable free sugar levels in certain animal feeds produced from chemically treated biomass, and therefore satisfies the need for an animal feed that minimizes ketosis.

[0057] In addition, the base treated first portion of biomass, which includes one or more ions such as magnesium or sodium, can be mixed with the acid treated second portion of biomass such that the animal feed has a level of each ion within a predetermined range. For instance, under certain reaction conditions in one example embodiment, sulfuric acid treated biomass may contain on the order of 0.1% sodium by dry weight, whereas sodium hydroxide treated biomass may contain on the order of 2% sodium by dry weight. The acid treated first portion of biomass (which has a relatively lower level of sodium ions) and the base treated second portion of biomass (which has a relatively higher level of sodium ions) may be mixed together in various proportions such that the animal feed has a sodium ion level within a predetermined range. Therefore, an animal feed produced by this version of the invention can solve the problems associated with undesirable cation levels in animal feeds produced from chemically treated biomass.

EXAMPLES

[0058] The following examples are intended only to further illustrate the invention and are not intended to limit the scope of the invention which is defined by the claims.

Example 1: Physical Chemical Treatment of Rice Straw

[0059] Rice straw was obtained from central California and initially had a moisture ratio of 10% water weight: 90% dry straw. The straw was shredded to a fiber length of approximately 1-3 inches with a hammer mill. Solutions of sodium hydroxide and ammonium hydroxide were mixed (wet addition) to portions of the milled straw to the provide the desired level of treatment chemical and to maintain a water mass balance of approximately 50% water to 50% dry straw. The first set of samples (Table 1) was created by adding the chemical solutions to the straw and letting the straw soak in the chemical for 120 hours. Soaked samples were subjected to cellulose digestion enzymes in buffered suspension for 24 and 68 hours. Digested cellulose was measured by the presence of glucose in the digest liquor.

[0060] The second set of samples (Table 2) was chemically treated and was left to react for approximately 1 hour before being subjected to extrusion. Samples of chemically treated straw were hand fed to the head of the extruder. The extruder was an "InstaPro Model 2000" available from Triple F Feeds, Des

Moines, Iowa, USA with a single-flighted screw tapered to double-flighted and operated by a 100 HP DC motor. The orifice diameter was ¾ inch and the barrel diameter was 6 inches. Three pressure ranges were tested by loosening the end *cone on the extruder from about ½ turn (high pressure) to 1 ¼ turn (medium* pressure) to 2 full turns open (low pressure). The extrusion temperature in all extruded samples ranged from approximately 215°-225°F. Treated samples were subjected to cellulose digestion enzymes in buffered suspension for 24 and 68 hours. Digested cellulose was measured by the presence of glucose in the digest liquor.

[0061] A comparison of untreated straw (sample 5, Table 2) to soaked straw (samples 1-4, Table 1) shows that only about a 6-10% improvement in cellulose digestion occurred with any treatment listed in Table 1. However, a high degree of digestion was obtained when similar chemical treatments were followed by extrusion. The relative strength of sodium hydroxide as compared to ammonium hydroxide is evident from the data in Table 2 and presented in Figure 1. Critical evaluation of these data show that ammonium hydroxide is 15-25 times less effective than sodium hydroxide.

TABLE 1

Physical Chemical Treatment of California Rice Straw (Soak Method)

Sample No.	Chemical Addition: Percent Dry Weight of Chemical to Straw	Treatment	Cellulose Digestion 24 HR (% wt.)	Cellulose Digestion 68 HR (% wt.)
1	3% NH_3 1% NaOH	no extrusion 120 hr. soak	32.4	36.3
2	1% NaOH	no extrusion 120 hr. soak	23.2	24.3
3	6% NH_3 1% NaOH	no extrusion 120 hr. soak	35.3	38.8
4	30% NH_3 2% NaOH	no extrusion 5 hr. soak	24.7	38.5

Note: Ammonium Hydroxide is the source of Ammonia.

TABLE 2

Physical Chemical Treatment of California Rice Straw With Extrusion				
Sample No.	Chemical Addition: Percent Dry Weight of Chemical to Straw	Extruded	Cellulose Digestion 24 Hr. (% wt.)	Cellulose Digestion 68 Hr. (% wt.)
5	No treatment	No	16.8	28.8
6	30% NH_3	low pressure	29.8	43.2
7	1% NaOH	low pressure	26.1	28.9
8	30% NH_3 1% NaOH	low pressure	29.2	32.6
9	2% NaOH	low pressure	59.5	81.5
10	30% NH_3 2% NaOH	low pressure	67.9	96.3
Note: Ammonium Hydroxide is the source of Ammonia.				

[0062] Another series of extrusions (Table 3) were performed with California Rice Straw in which sodium hydroxide was added as a solution to the straw then followed with extrusion at a temperature from 190° to 270°F. Sodium hydroxide was added as a percent of dry straw. The soak time was limited to less than thirty minutes before extrusion was performed. Cellulose digestion was measured at 24 and 48 hours. There was a uniform series of increased digestion as sodium hydroxide addition increased. The moisture content of the straw before extrusion was calculated from a material balance. Moisture after extrusion was measured by gravimetric analysis. Clearly, one result of extrusion at the prescribed temperature range results in a drying of the extruded material. In this case, the decrease in moisture content is about 17 to 25%.

TABLE 3

Physical Chemical Treatment of Rice Straw with Sodium Hydroxide added as a solution in water followed by extrusion at 190°-270°F.						
Sample Number	Added Chemical (wt. per dry wt. of straw)	Moisture Percent pre-extrusion	Median Extrusion Temp. (°F)	Moisture Percent post-extrusion	Percent cellulose digestion 24 hr.	Percent cellulose digestion 48 hr.
10a	no chemical	52.0	230	35.0	26.7	29.6
10b	1% NaOH	52.0	190	33.4	32.8	34.0
10c	2% NaOH	54.0	240	34.4	33.0	36.0
10d	3% NaOH	56.6	270	36.7	36.1	40.0
10e	4% NaOH	57.9	270	38.3	41.2	46.8
10f	5% NaOH	59.5	250	34.7	39.3	42.4
10g	6% NaOH	50.5	250	34.6	47.4	54.6
10h	7% NaOH	53.9	250	35.8	47.0	55.5

Example 2: Physical Chemical Treatment of Florida Bagasse

[0063] Two samples of bagasse were obtained from a Florida sugar cane processing company. Bagasse is highly processed sugar cane, and was collected as shredded fiber with length of approximately 1-2 inches. One sample contained low moisture (16% water weight: 84% dry bagasse) while the second contained high moisture content (79% water weight: 21% dry bagasse). The material was shredded with a 5-HP home-garden chipper-shredder to remove clumps and produce a more uniform fiber of about 1 inch long. Portions of each sample were mixed together to achieve a range of samples having different moisture content. Dry sodium hydroxide, urea, and hydrated lime were dry mixed in a ribbon mixer to samples of bagasse to provide the desired level of chemical treatment.

[0064] Table 4 shows the chemical additions to the test samples. Chemically treated bagasse was allowed to react for approximately 1 hour before being subjected to extrusion. Samples of chemically treated bagasse were machine fed (crammer feeder). The extruder was a Triple-F InstaPro 2000 with a single flight screw and operated by a 100 HP DC motor. Treated samples were subjected to cellulose digestion enzymes in buffered suspension for 24 and 68 hours. Digested cellulose was measured by the presence of glucose in the digest liquor.

TABLE 4

Physical Chemical Treatment of Florida Bagasse						
Sample Number	Initial % moisture	Chemical Addition: % dry wt. of Chemical per dry wt. Straw	Extrusion Temp. (°F)	Water Content after extrusion % Moisture	Final Keldahl Nitrogen	Cellulose Digestion 24 Hr.
11 (control)	79%	None	None	NA	0.61%	8.2%
12 (control)	3.92%	None	none	NA	0.33%	3.9%
13	46.8%	1% caustic 3% urea-N	219-250	33%	3.4%	17%
14	43.2%	1% caustic 5% urea-N	240-250	30%	4.2%	13.5%
15	49.3%	3% lime	250-270	39%	1.8%	15.7%
16	44.4%	7% lime	276-290	33%	0.8%	25.4%
17	NA	6% caustic	216-258	57%	1.3%	19.1%
18	81%	7% urea-N	246	67%	3.5%	12.6%
Note: Hydrated Lime = 42% CaO, 27% MgO, 27.5 % Water, 3.5% Other (Calculated herein as dry matter, active agents only) Urea = 46.7% Nitrogen Caustic = sodium hydroxide						

[0065] Critical observations from these data follow. Urea is apparently stable through the process and is recovered as fixed nitrogen after extrusion. A treatment with between 3%-7% agricultural lime is as effective as a 1-6% treatment with caustic. Urea is less effective than lime in producing the desired digestibility.

<u>Example 3: Physical Chemical Treatment of Corn Stover</u>

[0066] Corn Stover was obtained from the United States Department of Energy. Corn stover was delivered as shredded fiber with a length of approximately 1-2 inches and a moisture content of 6% water, 94% dry biomass. Water was hand mixed into the stover to obtain an initial moisture content of 35%. Dry sodium hydroxide was then hand mixed into different samples of corn stover to create a range of caustic addition from 0–8% of the dry biomass weight. Chemically treated corn stover was left to react for approximately 1 hour before being subjected to extrusion. Table 5 shows the chemical additions to the test samples. Samples of chemically treated corn stover were hand fed to the extruder. The extruder was a Triple-F InstaPro 2000 with a single flight screw and operated by a 100 HP DC motor. Treated samples were subjected to cellulose digestion enzymes in buffered suspension for 24 and 68 hours. Digested cellulose was measured by the presence of glucose in the digest liquor. Treated samples were also subjected to co-fermentation to ethanol by yeast in the presence of cellulose digestion enzyme in buffered suspension. Ethanol was measured by gas chromatography of the digest liquor.

[0067] A second set of corn stover digestion studies was conducted. This time caustic was added as pre-dissolved solution in amounts to deliver from 1 to 7 percent caustic per initial dry mass of biomass. The biomass was initially 7% water and 93% dry biomass. Due to the order of mixing the samples, subsequent additions of base (in solution) resulted in additional water mass added to the biomass. The water content of each test is presented in Table 6. In this test series, cellulose digestion was measured at 24 and 48 hours.

TABLE 5

Physical Chemical Treatment of Corn Stover							
Sample Number	Chemical Addition: % dry wt. of chemical to Stover	Extrusion Temp. (°F)	Percent Moisture after extrusion	Cellulose Digestion 24 Hr. (wt.%)	Cellulose Digestion 68 Hr. (wt %)	Ethanol 24 Hr. (wt.%)	Ethanol 68 Hr. (wt. %)
19 untreated	None	NA	83	23	25	ND	ND
20	None	200	90	25	29	6.7	9.3
21	2% NaOH	190	64	39	44	35.5	29.8
22	4% NaOH	190	62	47	51	42.4	38.2
23	6% NaOH	190	84	40	42	41.6	40.7
24	8% NaOH	190	74	87	116	64.1	65
Note: Cellulose digestion can be 110% of theoretical based on glucose production. Ethanol is presented as % of theoretical based on 100% glucose utilization.							

TABLE 6

Physical Chemical Treatment of Corn Stover					
Sample Number	Chemical Addition: % dry wt. of Chemical to Stover	Extrusion Temp. (°F)	Percent Moisture after extrusion	Cellulose Digestion 24 Hr. (wt. %)	Cellulose Digestion 48 Hr. (wt %)
25	1% NaOH	220	40	30	33
26	3% NaOH	250	34	32.4	35.6
27	5% NaOH	240	27	45	52.4
28	7% NaOH	240	23	57.6	69
Note: Cellulose digestion can be 110% of theoretical based on glucose production.					

[0068] The experimental trend relating the caustic dose and digestion of ethanol (Table 5, dry addition of caustic) are shown in Figures 2 and 3. A dose of 8% caustic per unit dry weight corn stover renders the cellulose 100% digestible. The active yeast culture is able to convert 65% of the cellulose to ethanol. Cellulose digestion data in Table 6 (wet addition of caustic) are consistent with the treatment data in Table 5, indicating that dry or wet addition of caustic results in the same treatment capacity.

Example 4: Physical Chemical Treatment of Distillers' Dried Grains and Solubles

[0069] Distillers' dried grains and solubles (DDGS) were obtained from Heartland Grain Fuels, LP, Aberdeen, South Dakota. Distillers' dried grains and solubles are the residual protein, yeast, oil, and undigested fiber that remains after ethanol fermentation. The material was dry sodium hydroxide granules mixed into the DDGS in a ribbon mixer to provide the desired level of chemical treatment. Table 7 shows the chemical additions to the test samples. Chemically treated DDGS was left to react for approximately 1 hour before being subjected to extrusion. Samples of chemically treated DDGS were machine fed (crammer feeder) to the extruder. The extruder was a Triple-F InstaPro 2000 with a single flight screw and operated by a 100 HP DC motor. The extruder was operated at two temperature ranges. The different temperature regimes are indicative of operation at two different pressure regimes. Treated samples were subjected to cellulose digestion enzymes in buffered suspension for 24 and 48 hours. Digested cellulose was measured by the presence of glucose in the digest liquor. Results of the cellulose digestion are presented in Table 7.

TABLE 7

Physical Chemical Treatment of Distillers' Dried Grains and Solubles					
Test Number	Chemical Addition: Mass of Chemical to Dry Weight DDGS	Extrusion Temperature (°F)	Water Content after extrusion Percent Moisture	Percent Cellulose Digestion 24 Hr.	Percent Cellulose Digestion 48 Hr.
7-0	None	Untreated Control	42.2%	21.6%	25.4%
7-1	1% NaOH	195-205	42.4%	25.6%	30.9%
7-2	2% NaOH	195-205	38.7%	25.7%	31.8%
7-3	3% NaOH	195-205	36.2%	27.4%	29.8%
7-4	4% NaOH	195-205	34.5%	31%	37%
7-5	1% NaOH	245-255	41.1%	21.8%	27.1%
7-6	2% NaOH	245-255	39.4%	21.8%	25.9%
7-7	3% NaOH	245-255	37.4%	26%	31.2%
7-8	4% NaOH	245-255	34.7%	29.4%	34.4%

[0070] DDGS are much less fibrous than the other materials tested, containing only about 6% crude fiber. For this product, digestion increased from 25% of the control to 34% of the control in the highest treatment. Increased caustic improved digestion, however, increased temperature (increased extruder pressure) did not improve treatment.

Example 5: Mixed Caustic and Acid Treatment of Bagasse

[0071] This example demonstrates that biomass with improved digestibility above the native state biomass may be made by mixing acid treated biomass and base treated biomass. The resultant mixture can be made to have a controlled pH, controlled alkali metal ions content, and with similar digestibility improvements as compared to material made from biomass treated with base alone. In particular, this example demonstrates that a feed may be produced with improved digestibility, controlled pH, and controlled cation content using a mixture of acid treated biomass and base treated biomass.

[0072] A sample of sugar cane bagasse with a dry matter content of 92.8% solids was split into two fractions. One fraction (500 grams dry matter) was treated with 50 milliliters of 10 N NaOH and the second fraction (500 grams dry matter) was treated with 50 milliliters of 5N H_2SO_4. The samples were then hydrolyzed for 60 minutes at approximately 122°C in an autoclave. Different amounts of the treated first fraction and the treated second fraction were then mixed together to form ten mixtures as shown in Table 8.

[0073] The pH of each mixture was then measured by wetting 50 grams of each material with 50 milliliters of deionized water, and taking the pH of the slurry. The pH of the native control bagasse (sample number 8-0) was 5.4, whereas, acid treated material (sample number 8-1) had a pH of 1.6 and base treated bagasse (sample number 8-10) had a pH of 10.6. Mixtures (sample numbers 8-1 to 8-9) of the acid treated bagasse and the base treated bagasse had an intermediate pH depending on the mixture ratio.

[0074] Equally important to the present invention is that the in vitro dry matter digestibility (IVTDMD) of the native material (sample number 8-0) was only 17.4%, whereas, acid treated material (sample number 8-1) had a digestibility of 29.3% and the base treated material (sample number 8-10) had a digestibility of 38%. The 50/50 mixture (sample number 8-5) of acid treated material and base treated material had a midrange digestibility of 32.7%.

[0075] Total digested, soluble sugars were measured with a Dionex Corporation (Westmont, Illinois, USA) Model 500 liquid chromatograph outfitted with an ED40 electrochemical detector. Samples were collected immediately after chemical treatment and again after cellulase digestion for 48 hours. Total sugars included arabinose, galactose, glucose, xylose, and mannose. The total liberated sugar was similar in the acid and base treated samples. However, immediately after chemical treatment, the acid treatment liberated about 33% free sugars in relation to total sugars after cellulytic digestion, whereas the base treatment liberated only about 8.2% free sugars in relation to total sugars after cellulytic digestion. The base treated sample, upon cellulase digestion, liberated more sugar than made available by cellulase digestion of the acid treated bagasse. This indicates that the mode of action of the two chemical treatments is different. The acid treatment frees more sugar immediately, whereas, the base treatment causes the fiber to be more digestible over a longer period of time. Since the balance of free sugars and digestible fiber is an important consideration in the dairy industry, this demonstrates that the present invention can provide an animal feed with a better balance of free sugars and digestible fiber in the resultant feedstuff.

[0076] Sodium is as an example of a cation that must be controlled in most animal diets. The sodium content of the acid treated bagasse (sample number 8-1) was 0.09% and the sodium content of the base treated bagasse (sample number 8-10) was 2.04%. Mixtures (sample numbers 8-2 to 8-9) of the acid and base treated bagasse samples had intermediate sodium content. Since cation levels (and in particular, sodium levels) are an important consideration in the dairy industry, this demonstrates that the present invention can provide an animal feed with controlled cation levels in the resultant feedstuff.

TABLE 8

Example of Controlling pH and Cation Content by using Mixtures of Acid and Base Treated Bagasse						
Sample Number	Percent of Mixture from Bagasse Treated with 4% NaOH	Percent of Mixture from Bagasse Treated with 1.6% H_2SO_4	pH of Slurry	IVTDMD 48 Hr. % wt	Total Sugars % wt	Sodium % dry wt.
8-0	Native control	Native control	5.4	17.4	4.9	0.04
8-1	0.0%	100.0%	1.6	29.3	11.3	0.09
8-2	12.5%	87.5%	2.5	NS	NS	NS
8-3	25.0%	75.0%	3.5	NS	12.4	0.43
8-4	37.5%	62.5%	4.9	NS	NS	NS
8-5	50.0%	50.0%	6.3	32.7	10.0	1.31
8-6	56.3%	43.8%	7.4	NS	NS	NS
8-7	62.5%	37.5%	8.2	NS	NS	NS
8-8	75.0%	25.0%	10.0	NS	11.7	1.51
8-9	87.5%	12.5%	9.9	NS	NS	NS
8-10	100.0%	0.0%	10.6	38.1	10.9	2.04
Note: NS = parameter not sampled						

Example 6: Preparation of an Animal Feed

[0077] The following example is one embodiment of a series of processes that may be used to treat biomass materials. The embodiment consists of a transporter means, a mixing means, a second transporter means, and an extruder means. The following equipment may be used to produce more than one ton of treated material in one hour using bagasse as the starting biomass material. A conveyor means, such as a front-end loader, is used to place between 1000 and 4000 pounds of bagasse into the mixer means. An example of a suitable mixer is the HARSH Model 720 agricultural material mixer outfitted with four horizontal auger screws. The auger screws are operated by a motor means, one example being the power take-off from a JOHN DEERE Model 6410 tractor. The charged bagasse, having a moisture content of between 40% and 70% moisture, with 50% being preferred, is amended with a strong alkali. An example is sodium hydroxide flakes or granules applied at a mass ratio of between 0.5% to 8% sodium hydroxide to bagasse on a dry weight basis. The preferred dose is about 4% sodium hydroxide. After about 20 minutes of mixing, molasses is added to the base treated bagasse at a rate of between 0% and 10% wet weight molasses to dry weight bagasse, with about 5% being the preferred addition of molasses.

Calcium propionate is then added at a dose rate of between 0 and 2% of the dry weight of bagasse, with about 0.5% being the preferred rate. This material is mixed for an additional 10 minutes.

[0078] This material is a suitable feed for cattle or dairy cows, however, the material may also be further treated. An example of a suitable conveyor to take the mixed material from the mixing unit to an extruder unit is an NJS USA (available from Lakeland Florida, USA) belt conveyor using high temperature, pressure, and shear as provided by an intense mixing as provided by an extruder. An acceptable example of an extruder is the INSTA-Pro Model 9600 screw feeder with a hopper unit above a 5 HP vertical screw feeder. The vertical screw forces material into a horizontal pressure screw in barrel unit having a tapered screw and a tapered barrel to cause compression of the material. One example of a suitable screw is a 4 foot long unit in a 7½ inch diameter barrel. The screw is operated by a 350 HP electric drive motor. Extruded material reaches a temperature of between 80°-180°C with 110°-135°C being a preferred range.

[0079] Table 9 is a summary of the chemical and biochemical properties of the bagasse utilized as the feedstock. The stock bagasse had an average moisture content of 55%, a protein content of 3.1%, and an ash content of 2%. Acid detergent fiber (ADF) and neutral detergent fiber (NDF) were 66% and 80%, respectively. The lignin content was 14.7%. Bagasse is naturally low in potassium and sodium due to the removal of these cations during the processing of sugar from the plant fiber. The pH was about 4.3. In vitro dry matter digestibility (IVTDMD) was measured as the dry matter digested using rumen fluid as the catalyst after 48 hours digestion. The IVTDMD was about 44.5% of the plant dry matter. Cellulose digestion is measured as the percent of the cellulose that is digestible in a commercial cellulase at 48 hours based on a standardized cellulose value present in the bagasse. Raw bagasse is about 38% cellulose by dry weight. Therefore, a cellulose digestion of 20% represents a digestion of 7.6% of the dry weight available to cellulase.

[0080] Table 10 is a summary of the chemical and biochemical properties of bagasse treated with sodium hydroxide, calcium propionate, and molasses. Molasses was added to the samples at a rate of 5-10% wet weight to dry bagasse. The molasses utilized had about 60% dry matter of which about 75% is digestible in the IVTDMD test method. Therefore, an addition of 5% molasses only increases the total digestibility ion by about 2.2%. Chemical additions of 4% sodium hydroxide, calcium propionate, and molasses had a net effect of increasing the ash content of the feed from the native material (2% ash) to a level of 6.5%. However, the IVTDMD increased from the native material (44.5%) to the chemically treated material at (55.3%). The sodium content of the chemically treated material was increased over the native bagasse by about 1.4% due mostly to the sodium hydroxide addition, but also because of sodium present in the molasses. The potassium content increased by about 0.4% due to the presence of potassium in the molasses. It is important to understand that the cellulose digestion test is performed on fiber that is rinsed with citrate buffer prior to enzyme treatment. The process of washing removes virtually all of the soluble sugars, so that the enzyme test truly reflects the amount of cellulose fiber that is digested. The chemical treatment increased the digestion of cellulose by about 5% above the native bagasse.

[0081] Table 11 is a summary of the chemical and biochemical properties of the chemically treated bagasse after extrusion. Most of the chemical parameters were similar to the chemically treated material with the exception that the extrusion process removes some moisture by virtue of the added mechanical and heat energy, and the reaction produces a higher range of cellulose digestion, 32.5 % versus 25.6%. The pH of the extruded material was also slightly higher than the non-extruded material.

[0082] A feed made of 89% sugar cane bagasse, 5% cane molasses, 4% sodium hydroxide and 2% calcium propionate (dry weight basis) was fed to a group of 1 mixed beef cattle pairs, as represented by the chemical and physical data in Table 12. Final feed was at 55% moisture and was fed at a rate of 15 pounds per head per day while the cattle were on grass pasture in Okeechobee, Florida, USA. The 11 cows gained an average of 34.3 lbs. per day and the calves gained an average of 90.18 lbs. per day in the period. The calves weighed 414.6 lbs. at the beginning of the trial and an average of 504.7 lbs. at the end of the trial. Detailed results on the cow/calf pairings are presented in Table 12. These data demonstrate that a palatable and beneficial feed may be created using the example formula of chemically treated and extruded bagasse.

TABLE 9

Raw (native) bagasse used for basis of the Okeechobee, Florida, USA Feedstock															
Sample	Molasses Added	Moisture	Protein %	Ash %	ADF %	NDF %	IVTDMD %	Lignin %	Ca %	Phos %	Mg %	K %	Na	pH	cellulose digested %
9-1	none	51.4%	3.2	2.1	53.6	84.6	45.1	8.9	0.2	0.0	0.1	0.2	0.0	3.8	16.3
9-2	none	45.4%	3.0	2.9	64.4	85.2	42.6	15.7	0.2	0.0	0.1	0.2	0.6	4.6	21.8
9-3	none	57.3%	2.8	1.4	69.8	83.2	43.4	13.7	0.2	0.4	0.7	0.2	0.0	3.8	21.8
9-4	none	50.9%	2.6	2.0	69.5	90.2	37.0	15.4	0.2	0.0	0.1	0.2	0.0	5.8	15.2
9-5	none	56.2%	3.1	1.9	73.0	85.7	44.4	13.7	0.2	0.0	0.1	0.2	0.0	3.6	26.8
9-6	none	55.9%	2.9	2.0	67.8	83.2	44.3	10.7	0.2	0.0	0.1	0.2	0.1	4.5	23.0
9-7	none	55.7%	2.9	2.0	62.9	84.4	46.0	19.3	0.1	0.0	0.1	0.3	0.1	6.0	15.6
9-8	none	50.3%	3.1	2.5	60.8	86.6	44.3	21.1	0.2	0.0	0.1	0.2	0.0	4.1	15.6
9-9	none	62.5%	3.6	2.3	80.7	35.9	48.3	15.2	0.2	0.0	0.1	0.2	0.0	4.3	19.9
9-10	none	63.6%	2.9	2.0	63.4	78.1	47.0	14.4	0.2	0.0	0.1	0.2	0.1	3.2	24.4
9-11	none	62.6%	2.9	2.3	63.8	75.2	48.8	15.6	0.1	0.0	0.1	0.2	0.1	4.9	22.7
9-12	none	46.6%	3.3	2.0	66.7	91.8	41.3	15.1	0.3	0.1	0.1	0.2	0.0	5.1	15.4
9-13	none	62.8%	4.0	1.2	68.1	80.4	46.0	11.9	0.2	0.0	0.1	0.1	0.0	3.8	23.9
Average (median*)	none	55.5%	3.1%	2.0%	66.5%	80.3%	44.5%	14.7%	0.2%	0.1%	0.1%	0.2%	0.1%	(4.3)*	20.2%

TABLE 10

Chemically Treated Bagasse used to charge the Extruder, basis of the Okeechobee, Florida, USA Feedstock															
Sample	Molasses Added	Moisture	Protein	Ash	ADF	NDF	IVTDMD	Lignin	Ca	Phos	Mg	K	Na	pH	cellulose digested
10-1	10.00%	42.5%	3.2%	3.4%	61.0%	79.1%	56.0%	20.9%	0.2%	0.0%	0.1%	0.6%	1.0%	5.9	16.3%
10-2	10.00%	59.1%	4.2%	6.0%	56.9%	72.0%	55.3%	10.7%	0.3%	0.0%	0.1%	0.8%	1.4%	5.6	30.3%
10-3	10.00%	53.6%	3.3%	6.0%	59.8%	74.4%	52.4%	14.4%	0.3%	0.0%	0.1%	0.7%	1.0%	5.2	21.8%
10-4	8.00%	49.1%	3.0%	6.3%	63.4%	82.1%	40.9%	15.5%	0.2%	0.0%	0.1%	0.6%	1.0%	5.4	21.8%
10-5	7.00%	59.8%	3.3%	7.2%	63.2%	71.8%	58.3%	16.5%	0.2%	0.0%	1.1%	0.8%	1.4%	7.0	39.8%
10-6	6.00%	56.0%	3.1%	6.8%	57.4%	76.6%	54.0%	16.8%	0.2%	0.0%	0.1%	0.8%	1.2%	7.0	28.2%
10-7	6.00%	50.8%	3.2%	6.0%	60.9%	83.0%	50.0%	13.9%	0.3%	0.0%	0.1%	0.6%	1.6%	8.3	23.0%
10-8	6.00%	53.9%	3.3%	7.5%	54.7%	76.3%	56.1%	13.0%	0.2%	0.1%	0.1%	0.6%	1.5%	7.3	17.2%
10-9	5.00%	62.4%	3.2%	7.8%	55.7%	74.7%	57.4%	16.7%	0.2%	0.0%	0.1%	0.6%	1.7%	8.2	30.8%
10-10	5.00%	58.0%	3.0%	6.8%	55.5%	69.5%	59.1%	13.5%	0.3%	0.0%	0.1%	0.6%	1.3%	7.2	26.8%
10-11	5.00%	50.2%	2.9%	4.7%	58.3%	76.9%	54.6%	13.9%	0.2%	0.0%	0.1%	0.0%	1.8%	7.7	22.0%
10-12	5.00%	59.1%	3.3%	8.4%	53.6%	70.7%	60.3%	8.7%	0.4%	0.0%	0.1%	0.7%	1.7%	5.9	32.2%
10-13	5.00%	60.3%	3.1%	7.0%	56.6%	72.7%	61.8%	12.0%	0.3%	0.0%	0.1%	0.5%	1.4%	6.4	33.2%
10-14	5.00%	61.4%	3.2%	6.8%	60.8%	76.5%	54.3%	16.5%	0.4%	0.0%	0.1%	0.4%	1.8%	6.6	14.3%
10-15	5.00%	59.0%	3.6%	7.2%	55.6%	70.9%	58.6%	16.6%	0.4%	0.0%	0.1%	0.6%	1.8%	6.6	15.5%
10-16	5.00%	56.9%	3.4%	6.7%	59.5%	69.7%	55.1%	12.9%	0.2%	0.0%	0.1%	0.6%	1.9%	5.9	36.0%
Average (median*)	5.00%	55.8%	3.3%	6.5%	58.3%	74.8%	55.3%	14.5%	0.3%	0.0%	0.2%	0.6%	1.5%	(6.6)*	25.6%

TABLE 11

Chemically Treated and Extruded Bagasse used for Feeding the Okeechobee, Florida, USA Feedstock															
Sample	Molasses Added	Moisture	Protein	Ash	ADF	NDF	IVTDMD	Lignin	Ca	Phos	Mg	K	Na	pH	cellulose digested
11-1	10.00%	39.5%	4.1%	5.6%	53.6%	71.1%	60.8%	11.8%	0.3%	0.1%	0.1%	0.9%	1.0%	7.8	17.5%
11-2	10.00%	55.8%	3.9%	6.4%	58.6%	71.1%	53.3%	14.8%	0.3%	0.0%	0.1%	1.0%	1.5%	5.9	36.9%
11-3	10.00%	49.5%	3.6%	5.7%	54.5%	68.8%	58.2%	15.7%	0.3%	0.1%	0.1%	0.8%	1.1%	6.5	29.6%
11-4	8.00%	41.9%	3.0%	6.0%	60.8%	82.8%	51.2%	13.2%	0.2%	0.0%	0.1%	0.6%	1.1%	7.0	27.7%
11-5	7.00%	52.5%	3.3%	6.7%	59.7%	73.3%	54.8%	14.3%	0.2%	0.0%	0.1%	0.8%	1.3%	7.0	44.5%
11-6	6.00%	53.7%	2.9%	6.7%	54.5%	72.6%	56.6%	15.9%	0.2%	0.0%	0.1%	0.7%	1.1%	9.1	31.0%
11-7	6.00%	45.0%	3.4%	6.5%	58.3%	78.0%	55.8%	15.8%	0.3%	0.4%	0.1%	0.6%	1.7%	8.8	25.1%
11-8	6.00%	46.5%	3.2%	7.9%	51.8%	70.3%	60.5%	11.4%	0.3%	0.0%	0.1%	0.8%	1.5%	8.3	29.8%
11-9	5.00%	55.6%	3.1%	7.8%	52.7%	73.1%	57.4%	12.8%	0.2%	0.0%	0.1%	0.6%	1.6%	6.0	35.8%
11-10	5.00%	54.3%	3.1%	6.9%	50.5%	69.7%	58.7%	13.2%	0.3%	0.0%	0.1%	0.7%	1.4%	7.5	28.2%
11-11	5.00%	44.9%	3.1%	5.5%	58.0%	77.5%	55.8%	11.1%	0.3%	0.0%	0.1%	0.5%	1.2%	8.0	28.4%
11-12	5.00%	54.7%	3.0%	7.0%	63.7%	84.2%	53.0%	12.3%	0.3%	0.0%	0.1%	0.4%	1.2%	9.2	24.2%
11-13	5.00%	58.8%	2.9%	5.3%	55.0%	73.9%	59.7%	13.0%	0.3%	0.0%	0.1%	0.5%	1.3%	6.6	39.8%
11-14	5.00%	59.1%	3.4%	7.2%	59.4%	73.5%	53.9%	14.9%	0.4%	0.0%	0.1%	0.5%	1.9%	6.8	40.3%
11-15	5.00%	54.0%	3.6%	7.1%	54.0%	72.9%	58.5%	13.5%	0.3%	0.0%	0.1%	0.6%	1.9%	7.5	39.6%
11-16	5.00%	54.6%	3.5%	6.8%	55.5%	68.8%	58.7%	14.8%	0.2%	0.0%	0.1%	0.7%	1.9%	7.4	42.2%
Average (median)*	5.00%	51.3%	3.3%	6.6%	56.3%	73.9%	56.7%	13.6%	0.3%	0.1%	0.1%	0.7%	1.4%	(7.4)*	32.5%

TABLE 12

Okeechobee, Florida, USA Free Range Beef Cattle Feeding Trial with Treated Bagasse							
Cow/Calf Pair ID	Cow Wt. Day 1 (lbs.)	Cow Wt. Day 47 (lbs.)	Cow Wt. Gain (lbs.)	Calf Wt. Day 1 (lbs.)	Calf Wt. Day 47 (lbs.)	Calf Wt. Gain (lbs.)	Calf Age At Day 1 (days)
20	1020	1080	60	350	455	105	151
M Brand	1070	1067	-3	385	475	90	174
141	955	1000	45	445	560	115	197
55	1070	1145	75	445	550	105	174
404	1075	1100	25	445	535	90	167
298	1025	1080	55	475	555	80	197
193	920	895	-25	400	460	60	201
414	920	965	45	395	490	95	172
59	945	965	10	360	460	100	174
352	1070	1140	70	465	525	60	209
218	875	895	20	395	487	92	175
Average	995	1029	34	415	505	90	

[0083] Although the present invention has been described in considerable detail with reference to certain embodiments, one skilled in the art will appreciate that the present invention can be practiced by other than the described embodiments, which have been presented for purposes of illustration and not of limitation. Therefore, the scope of the appended claims should not be limited to the description of the embodiments contained herein.

INDUSTRIAL APPLICABILITY

[0084] The invention provides methods for the physical-chemical treatment of cellulose-containing materials to render them more digestible or more chemically reactive. More particularly, the invention provides a method for the physical-chemical treatment of cellulose-containing waste agricultural materials to create highly digestible animal feeds.

CLAIMS

We claim:

1. A method for increasing the digestibility of cellulose in biomass, the method comprising:

adding a basic material to biomass; and

feeding the basic material and the biomass through an extruder.

2. The method of claim 1 wherein:

the basic material is added to the biomass in a dry form.

3. The method of claim 2 wherein:

the basic material is sodium hydroxide.

4. The method of claim 2 wherein:

the basic material is selected in an amount based on the heat of solution and the heat of reaction between the basic material and the biomass such that the reaction and rate of processing in the extruder can be controlled.

5. The method of claim 1 wherein:

the basic material comprises urea.

6. The method of claim 1 wherein:

the basic material comprises urea and a material selected from calcium carbonate, sodium bicarbonate, sodium carbonate, ammonium hydroxide, calcium hydroxide, magnesium hydroxide, hydrated lime, sodium hydroxide, potassium hydroxide, and mixtures thereof.

7. The method of claim 5 or 6 wherein:

the nitrogen content of the urea remains stable throughout the method and is retained as non-protein nitrogen after the basic material and the biomass are fed through the extruder.

8. The method of claim 1 wherein:

the basic material is a composition selected from calcium carbonate, sodium bicarbonate, sodium carbonate, ammonium hydroxide, calcium hydroxide, magnesium hydroxide, hydrated lime, sodium hydroxide, potassium hydroxide, and mixtures thereof; and

the basic material is selected in a composition and an amount such that at least one cation is retained in a predetermined range after the basic material and the biomass are fed through the extruder.

9. The method of claim 1 wherein:

the basic material is added to the biomass at a weight ratio of dry weight basic material to dry weight biomass of between 0.1% to 50%.

10. The method of claim 1 further comprising:

treating the biomass before the basic material is added to the biomass so that the moisture content of the biomass is at a weight ratio of 15% to 150% based on the dry weight of the biomass,

wherein the biomass is selected from bagasse, corn stover, wheat straw, rice straw, buckwheat straw, oat straw, rye straw, flax straw, barley hulls, rice hulls, oat hulls, alfalfa hay, cotton gin trash, distiller's dried grains, grasses, and mixtures thereof.

11. The method of claim 1 wherein:

the basic material is selected in an amount such that the pH after the basic material and the biomass are fed through the extruder is in the range of 7 to 11.

12. The method of claim 1 wherein:

no acids are added to the biomass.

13. A feedstock for industrial saccharification or fermentation, the feedstock being produced by the method of any of claims 1 to 12.

14. An animal feed produced by the method of any of claims 1 to 12.

15. A method for feeding dairy animals that are susceptible to milk fever, the method comprising:

adding magnesium hydroxide to biomass;

feeding the magnesium hydroxide and the biomass through an extruder to form an extruded material; and

feeding the extruded material to the dairy animals.

16. The method of claim 15 wherein:

the biomass is selected from bagasse, corn stover, wheat straw, rice straw, buckwheat straw, oat straw, rye straw, flax straw, barley hulls, rice hulls, oat hulls, alfalfa hay, cotton gin trash, distiller's dried grains, grasses, and mixtures thereof.

17. The method of claim 15 wherein:

the biomass is sugar cane bagasse.

18. A method for feeding dairy animals that are susceptible to ketosis, the method comprising:

adding a basic material to biomass;

feeding the basic material and the biomass through an extruder to form an extruded material; and

feeding the extruded material to the dairy animals,

wherein the basic material is added to the biomass in an amount such that the ratio of free sugars in the extruded material to total sugars liberated after cellulytic digestion of the extruded material is in a predetermined range.

19 The method of claim 18 wherein:

the biomass is selected from bagasse, corn stover, wheat straw, rice straw, buckwheat straw, oat straw, rye straw, flax straw, barley hulls, rice hulls, oat hulls, alfalfa hay, cotton gin trash, distiller's dried grains, grasses, and mixtures thereof.

20. The method of claim 18 wherein:

the biomass is sugar cane bagasse.

21. An animal feed comprising:

base treated biomass, the base treated biomass produced by adding a basic material and molasses to native biomass material having lignocellulosic structures such that the base treated biomass exhibits a higher percentage of dry matter that is digestible in rumen fluid compared to the native biomass material.

22. The animal feed of claim 21 wherein:

the base treated biomass is produced by adding the basic material and the molasses to the native biomass material and extruding the basic material, the molasses and the native biomass material.

23. The animal feed of claim 21 wherein:

the native biomass material is selected from bagasse, corn stover, wheat straw, rice straw, buckwheat straw, oat straw, rye straw, flax straw, barley hulls, rice hulls, oat hulls, alfalfa hay, cotton gin trash, distiller's dried grains, grasses, and mixtures thereof.

24. The animal feed of claim 21 wherein:

the native biomass material is sugar cane bagasse.

25. The animal feed of claim 21 wherein:

the basic material is selected from calcium carbonate, sodium bicarbonate, sodium carbonate, ammonium hydroxide, urea, calcium hydroxide, magnesium hydroxide, hydrated lime, sodium hydroxide, potassium hydroxide, and mixtures thereof, and

the basic material is added to the native biomass at a weight ratio of dry weight basic material to dry weight native biomass of between 0.1% to 10%.

26. The animal feed of claim 21 wherein:

the molasses is added to the native biomass at a weight ratio of wet weight molasses to dry weight native biomass of between 0.1% to 10%.

27. The animal feed of claim 21 wherein:

a preservative selected from sorbic acid, propionic acid, acetic acid, benzoic acid, salts of sorbic acid, salts of propionic acid, salts of acetic acid, salts of benzoic acid, and mixtures thereof is added to the native biomass, and

the preservative is added to the native biomass at a weight ratio of dry weight preservative to dry weight native biomass of between 0.1% to 4%.

28. The animal feed of claim 21 further comprising:

acid treated biomass, the acid treated biomass produced by adding an acidic material to a second portion of native biomass material having lignocellulosic structures such that the acid treated biomass exhibits a higher percentage of dry matter that is digestible in rumen fluid compared to the second portion of native biomass material.

29. The animal feed of claim 21 wherein:

the acidic material is selected from hydrochloric acid, nitric acid, phosphoric acid, sulfuric acid, and mixtures thereof, and

the acidic material is added to the native biomass at a weight ratio of wet weight acidic material to dry weight native biomass of between 0.1% to 10%.

30. A method for making animal feed, the method comprising:

adding a basic material and molasses to native biomass having lignocellulosic structures; and

allowing the basic material, molasses and native biomass to react for a period of time to produce a treated biomass that exhibits a higher percentage of dry matter that is digestible in rumen fluid compared to the native biomass.

31. The method of claim 30 further comprising:

extruding the basic material, the molasses and the native biomass material.

32. The method of claim 30 wherein:

the native biomass material is selected from bagasse, corn stover, wheat straw, rice straw, buckwheat straw, oat straw, rye straw, flax straw, barley hulls, rice hulls, oat hulls, alfalfa hay, cotton gin trash, distiller's dried grains, grasses, and mixtures thereof.

33. The method of claim 30 wherein:

the native biomass material is sugar cane bagasse.

34. The method of claim 30 wherein:

the basic material is selected from calcium carbonate, sodium bicarbonate, sodium carbonate, ammonium hydroxide, urea, calcium hydroxide, magnesium hydroxide, hydrated lime, sodium hydroxide, potassium hydroxide, and mixtures thereof, and

the basic material is added to the native biomass at a weight ratio of dry weight basic material to dry weight native biomass of between 0.1% to 10%.

35. The method of claim 30 wherein:

the molasses is added to the native biomass at a weight ratio of wet weight molasses to dry weight native biomass of between 0.1% to 10%.

36. The method of claim 30 wherein:

a preservative selected from sorbic acid, propionic acid, acetic acid, benzoic acid, salts of sorbic acid, salts of propionic acid, salts of acetic acid, salts of benzoic acid, and mixtures thereof is added to the native biomass, and

the preservative is added to the native biomass at a weight ratio of dry weight preservative to dry weight native biomass of between 0.1% to 4%.

37. An animal feed comprising:

base treated biomass, the base treated biomass produced by adding a basic material to a first portion of native biomass material having lignocellulosic structures such that the base treated biomass exhibits a higher percentage of dry matter that is digestible in rumen fluid compared to the first portion of native biomass material; and acid treated biomass, the acid treated biomass produced by adding an acidic material to a second portion of native biomass material having lignocellulosic structures such that the acid treated biomass exhibits a higher percentage of dry matter that is digestible in rumen fluid compared to the second portion of native biomass material.

38. The animal feed of claim 37 wherein:

the base treated biomass is produced by adding the basic material to the first portion of native biomass material and extruding the basic material and the first portion of native biomass material.

39. The animal feed of claim 37 wherein:

the acid treated biomass is produced by adding the acidic material to the second portion of native biomass material and extruding the acidic material and the second portion of native biomass material.

40. The animal feed of claim 37 wherein:

the native biomass material is selected from bagasse, corn stover, wheat straw, rice straw, buckwheat straw, oat straw, rye straw, flax straw, barley hulls, rice hulls, oat hulls, alfalfa hay, cotton gin trash, distiller's dried grains, grasses, and mixtures thereof.

41. The animal feed of claim 37 wherein:

the base treated biomass is present in the animal feed in the range of 25% to 75% by weight of the total weight of the animal feed, and

the acid treated biomass is present in the animal feed in the range of 25% to 75% by weight of the total weight of the animal feed.

42. The animal feed of claim 37 wherein:

the native biomass material is sugar cane bagasse.

43. The animal feed of claim 37 wherein:

the basic material is selected from calcium carbonate, sodium bicarbonate, sodium carbonate, ammonium hydroxide, urea, calcium hydroxide, magnesium hydroxide, hydrated lime, sodium hydroxide, potassium hydroxide, and mixtures thereof.

44. The animal feed of claim 37 wherein:

the acidic material is selected from hydrochloric acid, nitric acid, phosphoric acid, sulfuric acid, and mixtures thereof.

45. The animal feed of claim 37 wherein:

the base treated biomass has a basic pH and the acid treated biomass has an acidic pH, and

the base treated biomass is present in the animal feed in a first amount and the acid treated biomass is present in the animal feed in a second amount such that the animal feed has a pH within the range of 1.5 to 10.5.

46. The animal feed of claim 45 wherein:

the animal feed has a pH in the range of 6 to 8.

47. The animal feed of claim 37 wherein:

the base treated biomass has a first ratio of free sugars in the base treated biomass to total sugars liberated after cellulytic digestion of the base treated biomass,

the acid treated biomass has a second ratio of free sugars in the acid treated biomass to total sugars liberated after cellulytic digestion of the acid treated biomass, and

the base treated biomass is present in the animal feed in a first amount and the acid treated biomass is present in the animal feed in a second amount such that the animal feed has a third ratio of free sugars in the animal feed to total sugars liberated after cellulytic digestion of the animal feed.

48. The animal feed of claim 37 wherein:

the base treated biomass includes at least one ion, and the base treated biomass is present in the animal feed in a first amount and the acid treated biomass is present in the animal feed in a second amount such that the animal feed has a level of each ion within a predetermined range.

49. The animal feed of claim 37 wherein:

the base treated biomass includes sodium ions, and

the base treated biomass is present in the animal feed in a first amount and the acid treated biomass is present in the animal feed in a second amount such that the animal feed has a level of sodium ions within a predetermined range.

50. A method for making animal feed, the method comprising:

adding a basic material to a first portion of native biomass material having lignocellulosic structures;

allowing the basic material and the first portion of native biomass to react for a period of time to produce a treated first portion of biomass that exhibits a higher percentage of dry matter that is digestible in rumen fluid compared to the native biomass;

adding an acidic material to a second portion of native biomass material having lignocellulosic structures;

allowing the acidic material and the second portion of native biomass to react for a period of time to produce a treated second portion of biomass that exhibits a higher percentage of dry matter that is digestible in rumen fluid compared to the native biomass; and

mixing the treated first portion of biomass and the treated second portion of biomass together.

51. The method of claim 50 further comprising:

extruding the basic material and the first portion of native biomass material.

52. The method of claim 50 further comprising:

extruding the acidic material and the second portion of native biomass material.

53. The method of claim 50 wherein:

the native biomass material is selected from bagasse, corn stover, wheat straw, rice straw, buckwheat straw, oat straw, rye straw, flax straw, barley hulls, rice hulls, oat hulls, alfalfa hay, cotton gin trash, distiller's dried grains, grasses, and mixtures thereof.

54. The method of claim 50 wherein:

the treated first portion of biomass and the treated second portion of biomass are mixed together such that the treated first portion of biomass is present in the animal feed in the range of 25% to 75% by weight of the total weight of the animal feed and the treated second portion of biomass is present in the animal feed in the range of 25% to 75% by weight of the total weight of the animal feed.

55. The method of claim 50 wherein:

the native biomass material is sugar cane bagasse.

56. The method of claim 50 wherein:

the basic material is selected from calcium carbonate, sodium bicarbonate, sodium carbonate, ammonium hydroxide, urea, calcium hydroxide, magnesium hydroxide, hydrated lime, sodium hydroxide, potassium hydroxide, and mixtures thereof.

57. The method of claim 50 wherein:

the acidic material is selected from hydrochloric acid, nitric acid, phosphoric acid, sulfuric acid, and mixtures thereof.

58. The method of claim 50 wherein:

the treated first portion of biomass has a basic pH and the treated second portion of biomass has an acidic pH, and

the treated first portion of biomass and the treated second portion of biomass are mixed together such that the animal feed has a pH within the range of 1.5 to 10.5.

59. The method of claim 58 wherein:

the animal feed has a pH in the range of 6 to 8.

60. The method of claim 50 wherein:

the treated first portion of biomass has a first ratio of free sugars in the treated first portion of biomass to total sugars liberated after cellulytic digestion of the treated first portion of biomass,

the treated second portion of biomass has a second ratio of free sugars in the treated second portion of biomass to total sugars liberated after cellulytic digestion of the treated second portion of biomass

the treated first portion of biomass and the treated second portion of biomass are mixed together such that the animal feed has a third ratio of free sugars in the animal feed to total sugars liberated after cellulytic digestion of the animal feed.

61. The method of claim 50 wherein:

the treated first portion of biomass includes at least one ion, and

the treated first portion of biomass and the treated second portion of biomass are mixed together such that the animal feed has a level of each ion within a predetermined range.

62. The method of claim 50 wherein:

the treated first portion of biomass includes sodium ions, and

the treated first portion of biomass and the treated second portion of biomass are mixed together such that the animal feed has a level of sodium ions within a predetermined range.

Figure 1: Treatment of California Rice Straw by Extrusion

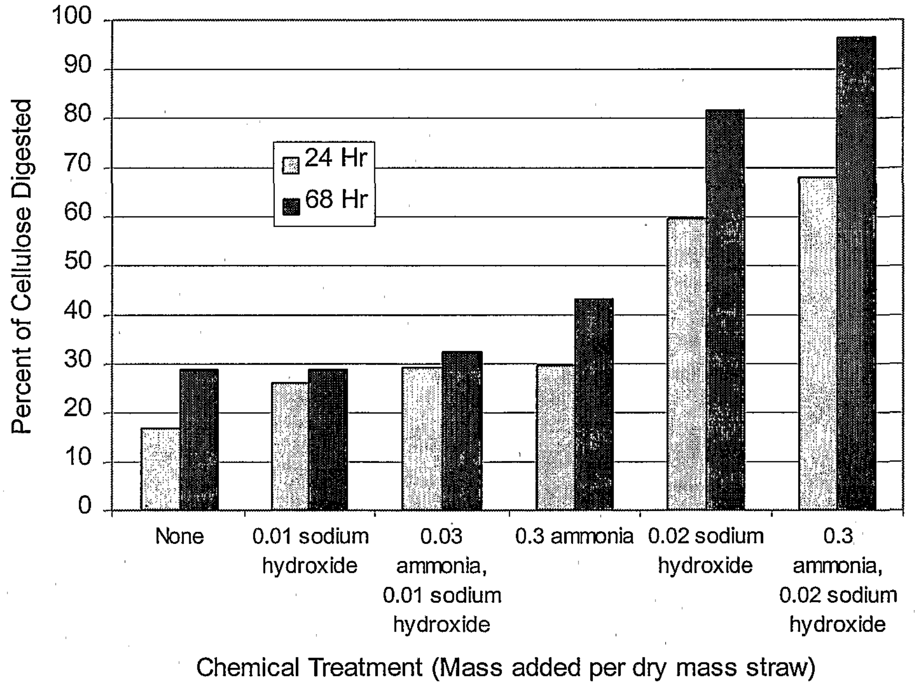


Figure 2: Conversion of Corn Stover Cellulose to Glucose with Sodium Hydroxide and Extrusion

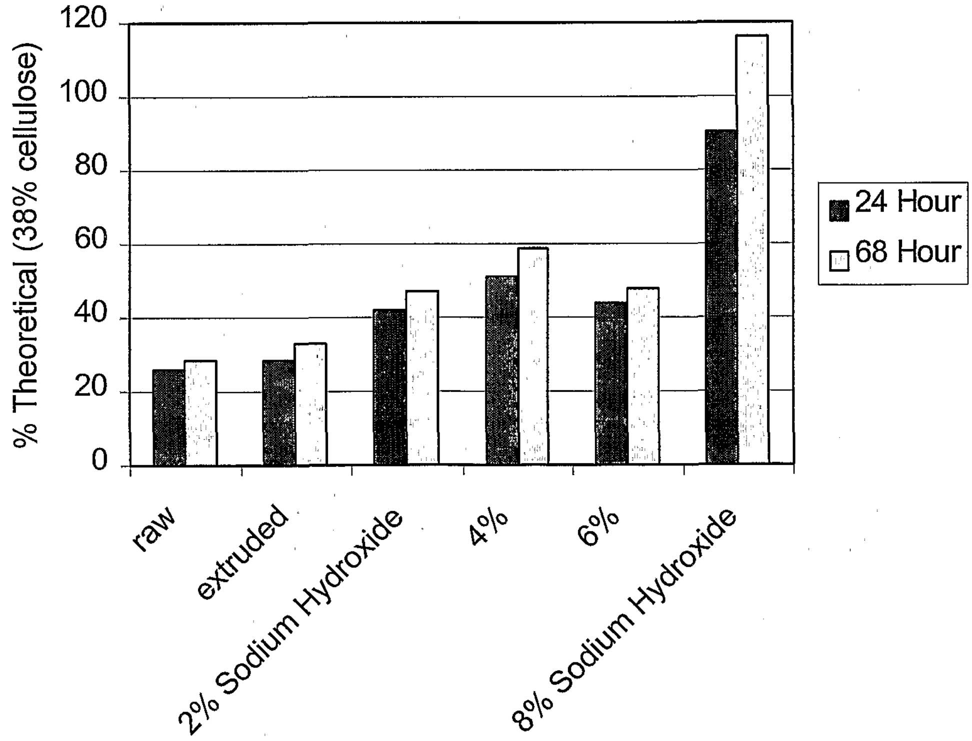


Figure 3: Conversion of Corn Stover to Ethanol