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(54) TREATMENT OF LIGNOCELLULOSIC SUBSTRATES WITH OZONE

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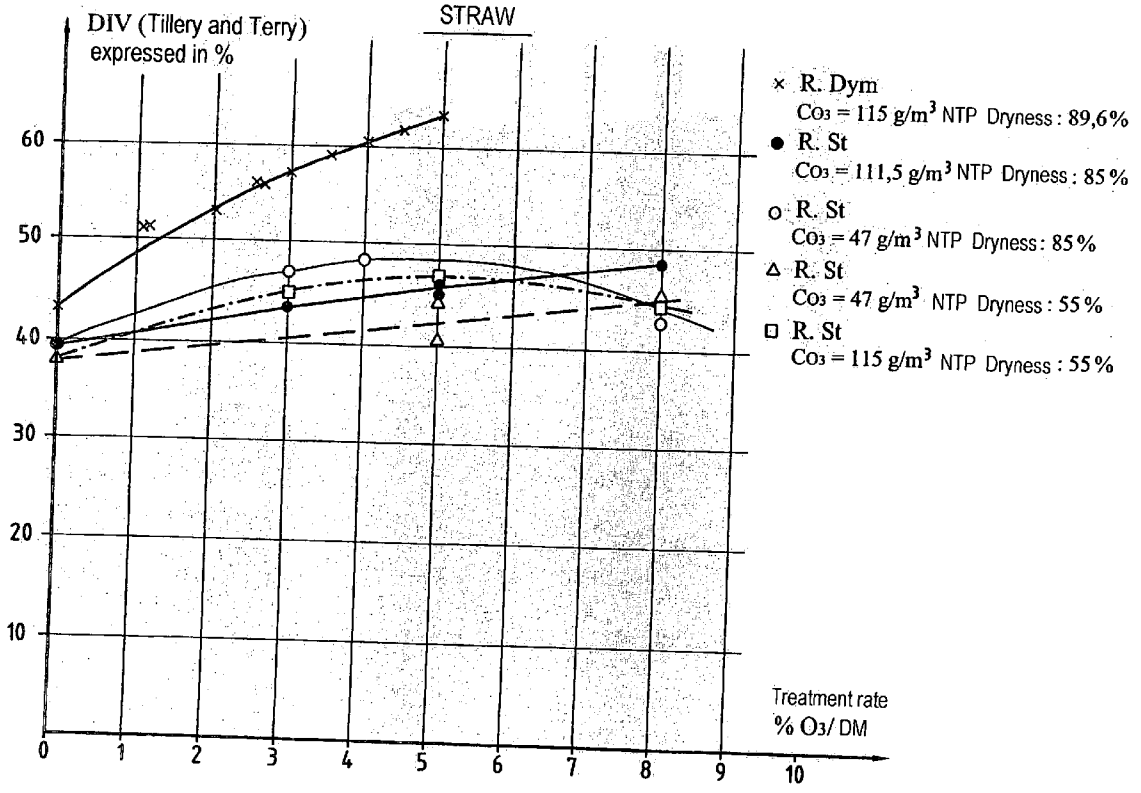
(57) ABSTRACT

The invention relates to a process for the preparation of lignocellulosic substrates having a high digestibility. This process consists in bringing said lignocellulosic substrates, which have been ground beforehand and optionally moistened in the case of dry substrates, in a stirred reactor, into contact with ozone produced from a carrier gas, the ozone being present in the carrier gas in a concentration of between 80 and 200 g/m^3 NTP, with a residence time of between 8 and 40 min in said reactor.

The invention further relates to the lignocellulosic substrates treated in this way.



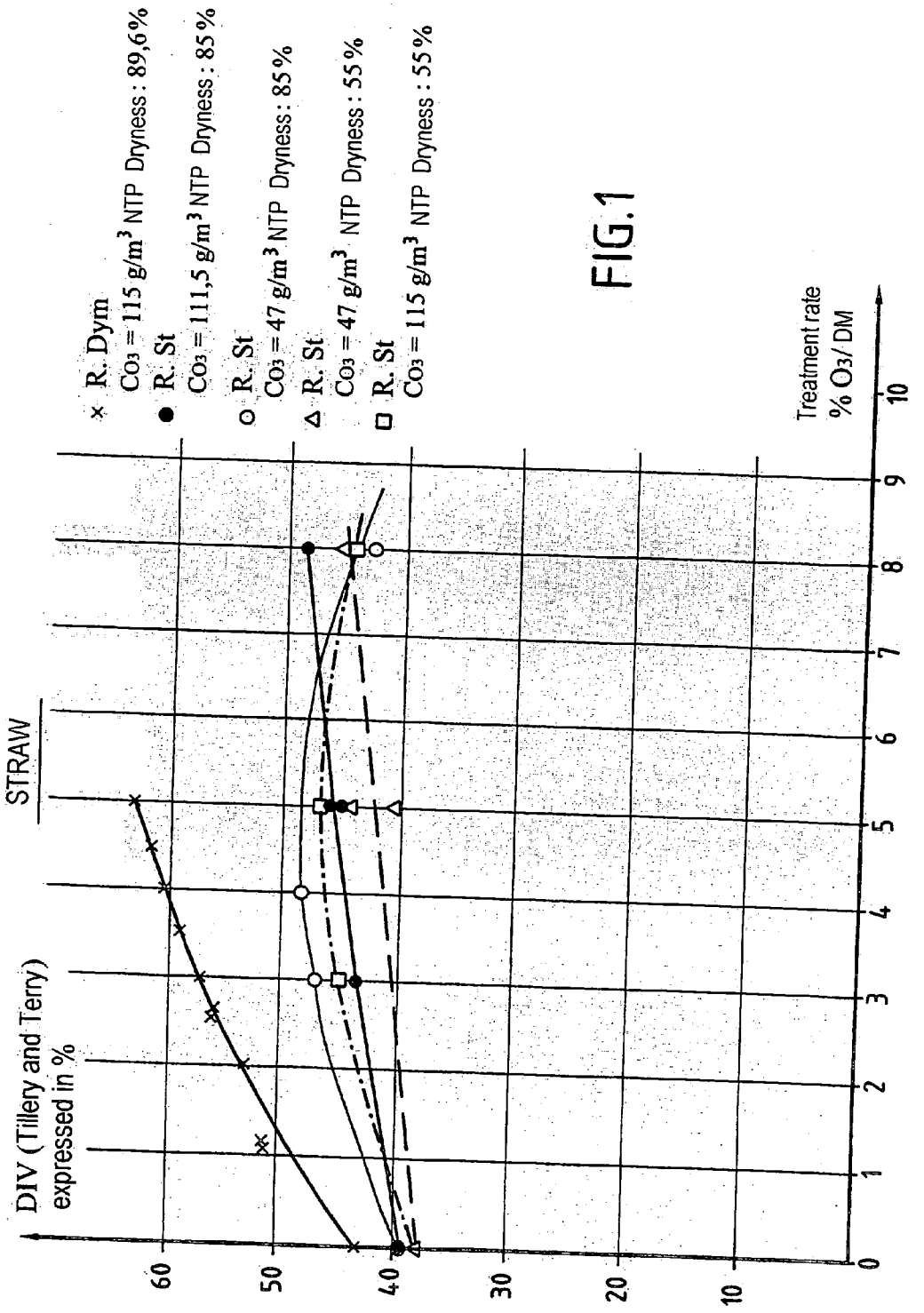

× R. Dym
Co3 = 115 g/m3 NTP Dryness : 89,6%
● R. St
Co3 = 111,5 g/m3 NTP Dryness : 85%
○ R. St
Co3 = 47 g/m3 NTP Dryness : 85%
△ R. St
Co3 = 47 g/m3 NTP Dryness : 55%
□ R. St
Co3 = 115 g/m3 NTP Dryness : 55%
STRAW
DIV (Tilley and Terry) expressed in %
60
50
40
30
20
10
0
1
2
3
4
5
6
7
8
9
10
Treatment rate % O3/ DM

FIG.1

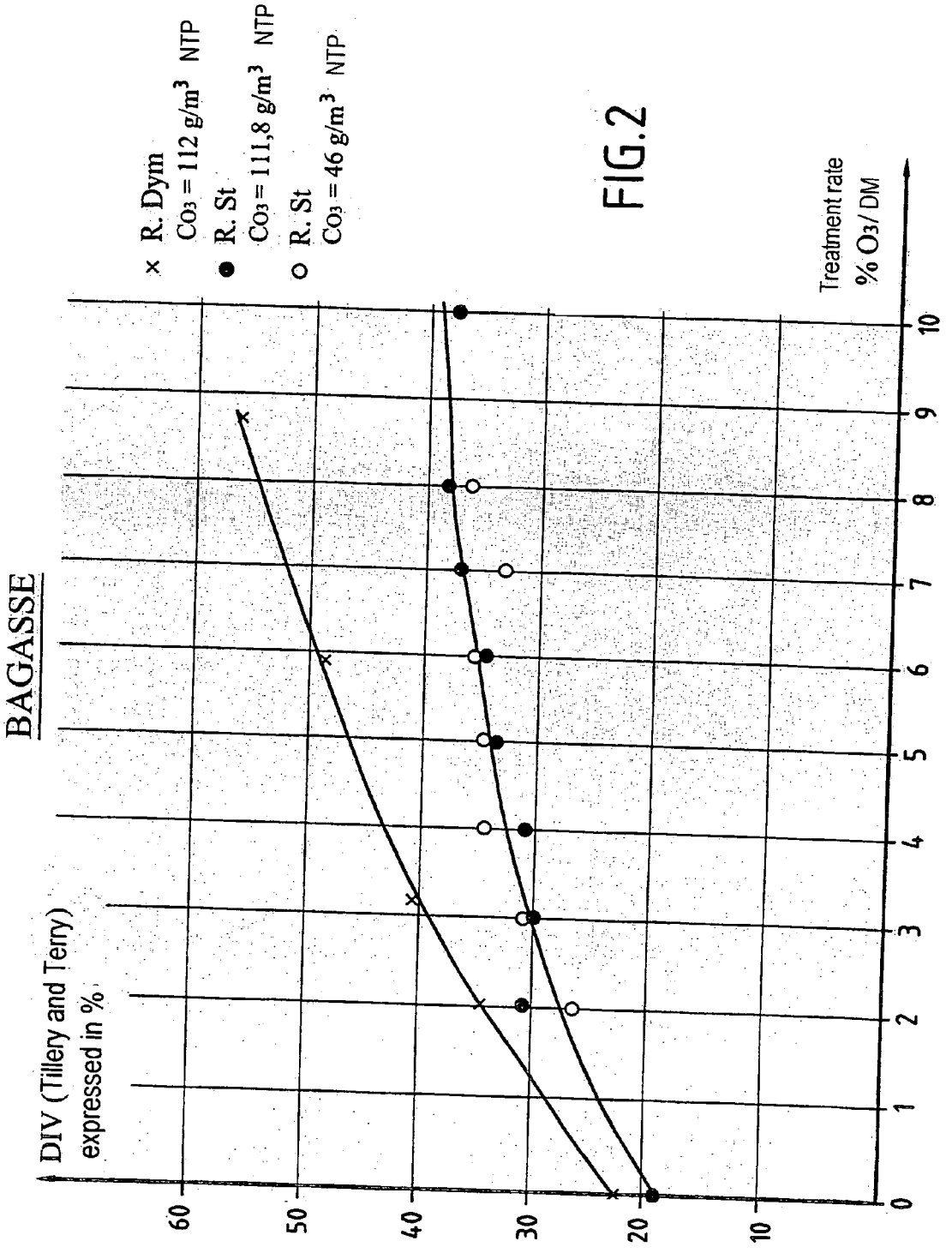

BAGASSE
DIV (Tilley and Terry) expressed in %
60
50
40
30
20
10
0
1
2
3
4
5
6
7
8
9
10
Treatment rate % O3/ DM
× R. Dym CO3 = 112 g/m3 NTP
● R. St CO3 = 111,8 g/m3 NTP
○ R. St CO3 = 46 g/m3 NTP

FIG.2

TREATMENT OF LIGNOCELLULOSIC SUBSTRATES WITH OZONE

[0001] The present invention relates to a novel process for the preparation of lignocellulosic substrates for animal nutrition which have a high digestibility.

[0002] It further relates to the lignocellulosic substrates obtainable by carrying out this process.

[0003] The invention applies especially to the field of the treatment of products originating from agriculture and the agri-foodstuffs sector, and to the industrial manufacture of animal feedingstuffs.

[0004] Lignocellulosic substrates as such are rather unsuitable for animal nutrition because of their low digestibility due to the presence of lignin.

[0005] Various processes have been proposed for increasing their digestibility, two examples being hydrolysis under the action of pressurized steam (STAKE process) and attack with hydrogen peroxide in the presence of cyanamides (FR-A-2 560 898). However, these processes have practical difficulties and are expensive, which explains why they have not yet been exploited industrially.

[0006] Patent application FR-A-2 603 775 proposes the treatment of cereal straws and other ground, dry lignocellulosic materials with a gas containing ozone in a sufficient amount for between 10 and 40 grams of ozone to be absorbed per kilogram of dry straw. The process described in said document consists in passing said gas through a bed of straw or other lignocellulosic substrate, thereby making it possible to increase the digestibility with an upper limit of about 10%. By way of comparison and according to patent application FR-A-2 603 775, the process applied to an aqueous suspension of straw (moisture content of 500%) affords a very small increase in digestibility, being of the order of a few percent.

[0007] However, the process described in patent application FR-A-2 603 775 has the following disadvantages:

[0008] the digestibility of the dry straw does not exceed a certain upper limit and decreases even when the degree of ozonization is greater than 25 milligrams of ozone per gram of dry straw;

[0009] the relatively small increase in digestibility has to be compensated by the addition of a nitrogen compound;

[0010] the process seems to be suitable only for the treatment of a small amount of lignocellulosic substrate;

[0011] the use of a fixed bed reactor does not allow the substrate, finely divided though it is, to present a maximum surface area to the chemical reaction;

[0012] the use of an amount of ozone determined solely by the amount which reacts with the lignocellulosic substrates does not afford good control over the operating conditions; and

[0013] the poor yield of the system gives rise to an overconsumption of ozone for a limited result.

[0014] Canadian patent no. 1 169 794 proposes a process for the treatment of lignocellulosic substrates with ozone which comprises grinding said substrate to a size of at most 4 mm, mixing said ground substrate with water in a ratio of 1:10 to 10:1 and then exposing the resulting mixture to ozone, the concentration of ozone in the carrier gas being between 0.75 and 6.8%.

[0015] When used on small amounts of substrate in the order of 20 g, this process affords an acceptable increase in digestibility. However, it has the following two disadvantages:

[0016] on the one hand the residence time in the ozone treatment reactor has to be at least one hour and preferably 16 hours, which amounts to a relatively long time for an industrial process; and

[0017] on the other hand the amount of water used is such as to produce a suspension of material, so the finished product has to be subjected to a subsequent drying treatment in order to be in an acceptable form for the animals for which these finished products are intended.

[0018] It is interesting to note the divergence of results between these two patents, the one advocating the treatment of dry substrates with ozone and the other advocating the treatment of aqueous suspensions of substrates with ozone.

[0019] The Applicant has now found, surprisingly, that the above disadvantages can be overcome by a process that consists in treating lignocellulosic substrates, which have been ground beforehand and optionally moistened (without creating an aqueous suspension) when the substrate is dry, e.g. straw, in a stirred reactor, with ozone produced by a carrier gas, the ozone being present in the carrier gas in a given concentration, with a greatly reduced residence time in said reactor.

[0020] Thus, according to a first feature, the invention relates to a process for the preparation of lignocellulosic substrates having a high digestibility, which consists in bringing said substrates, which have been ground beforehand and optionally moistened when the substrate is dry, in a stirred reactor, into contact with ozone produced from a carrier gas, the ozone being present in the carrier gas in a concentration of between 80 and 200 g/m^3 NTP and preferably of between 140 and 160 g/m^3 NTP, for a residence time of between 8 and 40 min and preferably of between 15 and 30 min in said reactor.

[0021] This process makes it possible for the first time, and in an entirely satisfactory manner, to solve the problem of insufficient and limited digestibility of relatively dry lignocellulosic substrates in a greatly shortened reaction time, and to obtain hitherto unavailable lignocellulosic substrates having an acceptable moisture content for storage and animal nutrition and a high digestibility.

[0022] According to a second feature, the invention relates to the lignocellulosic substrates obtainable by the above process.

[0023] By way of example, with the process of the invention applied to wheat straw (moisture content of 4-5%), which normally has an initial digestibility of about 40%, it is possible to increase this digestibility by 20% or more by means of a treatment with ozone in an amount of 3 kg of ozone per tonne of straw at an ozone concentration of 115 g/m^3 NTP, for a contact time of 20 to 30 min. Likewise, for sugar cane bagasse, which has a mean digestibility of 20% in the natural state, it is possible to raise this digestibility to 40% or more by means of a treatment with ozone in an

amount of 3 kg of ozone per tonne of bagasse, and to 60% for a treatment rate of 9 kg of ozone per tonne of bagasse, at an ozone concentration of 122 g/m^3 NTP, for a contact time of 20 to 30 min.

[0024] In the process of the invention, the concentration of ozone in the carrier gas is between 80 and 200 g/m^3 NTP (Normal Temperature and Pressure) and preferably between 140 and 160 g/m^3 NTP. If this concentration is below 80 g/m^3 NTP, the digestibility of the ozonized substrate is not sufficiently high to be of value for direct animal nutrition. If the ozone concentration is above 200 g/m^3 NTP, it is possible to observe a degradation of the lignocellulosic substrate such that it becomes difficult to transport and use. The carrier gas advantageously consists of oxygen. The carrier gas can also be produced from ambient air which has been filtered, compressed and dried at the dew point of between −50 and −70° C. In another alternative, the carrier gas can consist of a mixture in any proportions of pure oxygen and filtered, compressed and dried air.

[0025] According to one particular characteristic, the relative pressure of the ozonized carrier gas when it is brought into contact with said substrates is between 0.6 and 1.5 bar and preferably between 0.6 and 1.2 bar. If the pressure is below 0.6 bar, the problem of poor penetration of the ozone into the lignocellulosic substrate may arise, resulting in an imperfect treatment and a small increase in digestibility. On the other hand, if the pressure is above 1.5 bar, the following problems may arise:

[0026] as regards the generation of the ozone: industrial ozonizers do not operate at pressures above 1.5 bar;

[0027] as regards the treated substrate: above this pressure, the ozone penetrates the lignocellulosic material very deeply and, because of its reactivity, almost completely destroys the structure of the material to be treated.

[0028] The lignocellulosic substrates used in the present invention include any substrate originating from the agri-foodstuffs sector. The substrates can be classed in two categories, namely dry substrates and moist substrates. Examples of dry substrates include rye, wheat and alfalfa straws, sugar beet cossettes and cereal grains, and examples of moist substrates include sugar cane bagasse, sorghums, ray grasses and hays.

[0029] The amount of lignocellulosic substrate treated can be as much as several tens of tonnes per hour because of the high concentration of ozone used and the specificity of the process developed, so the process of the invention is suitable for use on an industrial scale.

[0030] If the substrate is dry, it has to be moistened to optimize the result. This moistening consists in spraying with water or ozonized water in an amount of between 1 and 6% and preferably of between 1 and 5%, based on the dry matter. If the moisture content is greater than 6%, the digestibility will be reduced.

[0031] The substrate also has to be ground before being treated with ozone. This operation makes it possible to improve the packing of the reactor, avoiding preferential passages, to increase the reactive surface area of the substrate and to favor the homogeneity of mixing. The grinding is carried out by processes well known to those skilled in the art, before moistening and before the substrate enters the stirred reactor.

[0032] According to one particular characteristic, the ground substrates have a size of between 5 mm and 20 mm, the range from 10 to 20 mm being particularly preferred. If the size is less than 5 mm, the substrate can be in the form of powder in the case of dry materials and in the form of slurry in the case of moist substrates, these forms being unacceptable. If the size is greater than 20 mm, treatment is difficult and it is possible to observe preferential passages and voids in the packing.

[0033] The treatment with ozone is carried out in a stirred reactor, which will hereafter be referred to as an ozonization reactor. This reactor can be of vertical or horizontal type.

[0034] In general, the ozonization reactor used can consist of a cylindrical body comprising a device for introducing the ground lignocellulosic substrate, such as a hopper, and an internal device for mixing the lignocellulosic substrate and assuring its residence time in the reactor so as to optimize the treatment with ozone. The ground lignocellulosic substrate can be brought into contact with the ozonized carrier gas continuously or batchwise in said ozonization reactor.

[0035] The residence time in the ozonization reactor is between 8 and 40 min and preferably between 15 and 30 min. If this residence time is less than 8 min, the treatment with ozone is insufficient. If it is greater than 40 min, degradation of the lignocellulosic structure is observed.

[0036] Thus, in contrast to the known processes of the prior art, the process of the invention makes it possible to treat an amount of lignocellulosic substrate that is suitably large for use on the industrial scale, in a very rapid reaction time.

[0037] The constituent materials of the body of the ozonization reactor will be chosen so as to assure abrasion resistance and resistance to the oxidation generated by the presence of ozone in high concentration. Such a material can be e.g. a stainless steel known to those skilled in the art.

[0038] The mixing device with which the ozonization reactor is equipped can be any device known to those skilled in the art. This device must allow homogeneous mixing of the ground substrate while at the same time allowing its transport towards the outlet of the ozonization reactor or its internal recycling, depending on whether the reaction is being carried out continuously or batchwise.

[0039] The speed of rotation of said mixing device and the dimensions of the reactor used will be calculated by those skilled in the art as a function of the amount of material to be treated, the ozone concentration used and the intended residence time. In one preferred embodiment, to treat 3 tonnes of ground lignocellulosic substrates with an ozone concentration of 150 g/m^3 NTP in a reactor having a diameter of 1.20 m and a total height of 4.60 m, the speed of rotation is in the order of 100 to 120 rpm.

[0040] Examples of mixing devices include an Archimedean screw, a conical screw or a drive shaft on which blades are mounted.

[0041] If this last type of device is used, namely a drive shaft and blades, the distance between the last blades and the bottom of the ozonization reactor must be sufficient to prevent the mass to be treated from building up at the bottom of said reactor. Those skilled in the art will be capable of determining such a distance as a function of the density of

the reacting mass. In the case of vertical ozonization reactors, a scraping and mixing device can be added at the conical end.

[0042] In the case of horizontal ozonization reactors, the mixing device is centered in said reactor. It is advantageous to use a drive shaft carrying alternate sets of blades of two different dimensions, locked at 120° on the horizontal shaft. Each set of blades consists of 3 blades of the same length and of large diameter, the following set consisting of 3 blades of the other length (smaller diameter), offset by 60° relative to the blades of the first set. These small blades can carry a mixing device, inclined by a few degrees to the vertical axis, so as to ensure that the substrate undergoes a helical rotational movement during treatment. This movement further ensures that the material to be treated undergoes a horizontal translational movement with permanent renewal of the interface.

[0043] In the case of vertical ozonization reactors, the mixing device is either centered on the vertical axis of said reactor, or offset relative to this axis and driven with a gyratory movement around this vertical axis. In the latter case, it is preferable to use a conical screw. The axis of rotation of the screw is at an angle relative to the vertical axis of the ozonization reactor. The upper part of the screw is connected to a drive device via gearboxes and the lower part is centered on the vertical axis at the end of said reactor. The screw rotates about itself to assure mixing and rotates about the vertical axis to cover the total volume of substrate to be treated. Depending on the speed of rotation of the screw about the vertical axis of the ozonization reactor, the movement described can be likened to a simple cycloid or to a hypocycloid of shortened pitch.

[0044] The mixing device is driven by an electromechanical device, making it possible to adjust the speed of the mixing device so as to assure the intended residence time in the ozonization reactor with precision. Preferably, the mixing device is driven by a variable-speed motorized step-down gear unit.

[0045] The electromechanical device itself possesses one or two centering and sealing devices well known to those skilled in the art.

[0046] In the case of dry lignocellulosic substrates requiring moistening, the ozonization reactor is also equipped with a device for moistening the reacting mass. An example of such a device comprises spray nozzles. The moistening rate will be determined as a function of the amount of water necessary to achieve the chosen moisture content. Those skilled in the art will easily be capable of determining such a rate.

[0047] The ozonization reactor is also equipped with one or more devices for injecting the ozonized carrier gas, said gas itself being produced from an ozonizer well known to those skilled in the art. The device(s) for injecting the ozonized carrier gas are designed so as to ensure the distribution of the gas in said ground substrate with a sufficient injection rate to assure a good penetration of said gas into said substrate. Injection nozzles are examples of such devices. In general, the injection rate of the ozonized carrier gas is between 30 and 60 $m.s^{-1}$.

[0048] In the case of horizontal ozonization reactors possessing a single device for injecting the ozonized carrier gas, said device is placed in the upstream part of said reactor, just behind the device for introducing the ground substrate and the moistening device. If this type of reactor has several devices for injecting the ozonized carrier gas, said devices can be placed over the whole length of the mixing device, for example between the blades. In general, these injection devices will be arranged at a distance of between 0.08 d and 0.15 d, where d is the diameter of the reactor. The number of injection devices will be chosen so that the injection rate falls within the range indicated above. Such an arrangement affords better control over the ozone concentration used.

[0049] In the case of vertical ozonization reactors, the devices for injecting the ozonized carrier gas are placed in the lower part of said reactor so that their action is of the countercurrent type.

[0050] The ozonization reactor is also generally equipped with a device for discharging the ozonized carrier gas after the reaction to the upper part of the ozonization reactor (residual ozone present in the carrier gas after the reaction) and with a pressure measuring device, both said devices being well known to those skilled in the art.

[0051] Finally, the ozonization reactor is equipped with a device for discharging the treated product, located opposite the device for introducing the ground ligno-cellulosic substrate. This discharging device can consist e.g. of apertures in the flat end opposite the feed. In the case of a continuous reaction, the device for discharging the product and the device for introducing the ground lignocellulosic substrate must be leaktight. An alveolar slide valve is an example of such a device.

[0052] Furthermore, as the ozonization reaction is of exothermic type, the body of the ozonization reactor is usually equipped with a temperature control device and a cooling device for maintaining a constant temperature inside said reactor and in the reaction medium, without a vertical or radial temperature gradient, for the requisite reaction time.

[0053] This efficient cooling of the ozonization reactor favors the safe operation of said reactor and affords precise control over the ozonization reaction.

[0054] The cooling device can be located on the outside or inside of the ozonization reactor. It can be fed e.g. with cold water under pressure or via a circuit of iced water produced by a refrigerating set. The body of the ozonization reactor is advantageously cooled by means of an external cooling device, which can consist e.g. of a conventional device of the water jacket type or a circuit made up of half-shells that captures the heat flux originating from the reaction mass and dissipates it to the outside.

[0055] The lignocellulosic substrate treated with ozone in the ozonization reactor will be collected e.g. in a hopper and then passed on for bagging, weighing or any other packaging operation prior to distribution. This gives a ready-to-use finished product with a high digestibility, so there is no need for complements, said product being intended for animal nutrition and especially for feeding cattle, sheep and poultry.

[0056] The invention will be understood more clearly from the Examples and attached diagrams, which are given solely by way of illustration and without implying a limitation. In said diagrams:

[0057] **FIG. 1** is a curve showing the variability of the digestibility in vitro as a function of the treatment rate of the moistened, dry lignocellulosic substance (straw) with ozone in a dynamic (stirred) reactor and in a static reactor; and

[0058] **FIG. 2** is a curve showing the variability of the digestibility in vitro as a function of the treatment rate of the moist lignocellulosic substrate (bagasse) with ozone in a dynamic (stirred) reactor and in a static reactor.

EXAMPLE 1

Comparison of the Modification of the Digestibility of Straw Treated in a Dynamic Reactor and in a Static Reactor

[0059] Wheat straw was ground to a size of the order of 13 mm. Said ground straw, having various moisture contents as a result of prior moistening, was then treated with an ozonized carrier gas, either in a static reactor (R. St), i.e. a reactor containing a fixed bed of straw through which a stream of ozone borne by the oxygen carrier gas was passed from bottom to top, or in a dynamic (or stirred) reactor (R. Dym), i.e. a vertical or horizontal reactor in which the mixing device was a shaft and blades (horizontal reactor) or a central screw with recirculation (vertical reactor), the residence time in the reactors being 20 to 30 min.

[0060] 5 experiments with the following characteristics were performed:

[0061] x: ozone concentration (CO_3) of 115 g/m^3 NTP, straw dryness of 89.6%, dynamic reactor,

[0062] ●: ozone concentration of 111.5 g/m^3 NTP, straw dryness of 85%, static reactor,

[0063] ○: ozone concentration of 47 g/m^3 NTP, straw dryness of 85%, static reactor,

[0064] ▽: ozone concentration of 47 g/m^3 NTP, straw dryness of 55%, static reactor, and

[0065] ?: ozone concentration of 115 g/m^3 NTP, straw dryness of 55%, static reactor.

[0066] After treatment, the digestibility in vitro (DIV) was determined by the method of Tillery and Terry in percent as a function of the treatment rate with ozone, itself expressed in percent of ozone relative to dry matter (3% means that 30 g of ozone were used to treat 1000 g of substrate).

[0067] The results of these tests are given in the form of curves in **FIG. 1**.

[0068] The results obtained lead to the following two conclusions:

[0069] Firstly, in the case of static reactors, increasing the ozone concentration, in the present case from 47 g/m^3 to 115 g/m^3, with a dryness of 55%, brings about only a very small variation in the digestibility of the straw, which is in agreement with the results obtained according to patent application FR-A-2 603 775.

[0070] Secondly, when using a dynamic reactor and a high ozone concentration (115 g/m^3), the digestibility results improve as a function of the treatment rate applied.

[0071] These results eloquently prove the increase in digestibility provided that the operating parameters are perfectly controlled.

EXAMPLE 2

Comparison of the Modification of the Digestibility of Bagasse Treated in a Dynamic Reactor and in a Static Reactor

[0072] The procedure of Example 1 was repeated except that the lignocellulosic substrate used was bagasse and the following 3 experiments were performed:

[0073] x: ozone concentration of 112 g/m^3 NTP, dynamic reactor,

[0074] ●: ozone concentration of 111.8 g/m^3 NTP, static reactor,

[0075] ○: ozone concentration of 46 g/m^3 NTP, static reactor.

[0076] The results of these tests are given in the form of curves in **FIG. 2**.

[0077] The results obtained lead to the same conclusions as those indicated in Example 1.

EXAMPLE 3

Improvement in the Digestibility of Wheat Grains Treated with Ozone

[0078] The digestibility of wheat grains treated with ozone was analyzed on cockerels by measuring the metabolizable energy (ME) in accordance with farming procedures SVDC 03 and SVDM 01. The method applied is the rapid method of measuring metabolizable energy developed by Mr Lessire of INRA and the method of determining the viscosity of aqueous extracts (Viscometer method, standard NFV 03749).

[0079] Groups of 9 cockerels each were fed for 8 days with 4 different batches of untreated wheat grains or wheat grains treated with ozone, as follows:

[0080] batch 1: untreated grains

[0081] batch 2: grains treated with 3 g of ozone per kilogram of grains (85 g/m^3 NTP) with a moisture content of 4%

[0082] batch 3: grains treated with 4 g of ozone per kilogram of grains (85 g/m^3 NTP) with a moisture content of 4%

[0083] batch 4: grains treated with 5 g of ozone per kilogram of grains (85 g/m^3 NTP) with a moisture content of 4%

[0084] The wheat grains corresponded to 97% of the food ration.

[0085] The raw results are given in the Table below, in which:

[0086] UV denotes useful viscosity,

[0087] RE denotes raw energy,

[0088] DM denotes dry matter.

TABLE

	Sample 1	Sample 2	Sample 3	Sample 4
Moisture content (%)	12.6	15.5	15.5	15.4
Raw protein (%)	10.32	9.92	10.04	10.09

TABLE-continued

	Sample 1	Sample 2	Sample 3	Sample 4
Fats (%)	1.38	1.36	1.33	1.42
Raw cellulose (%)	2.06	1.96	1.76	1.75
Minerals (%)	1.49	1.43	1.38	1.38
Starch (%)	60.39	58.81	58.14	58.01
Sugars (%)	2.19	2.75	2.75	2.88
Wall (%)	10.54	9.54	9.59	8.91
Spec. visc. (cPs/g sec)	0.30	0.40	0.50	0.40
UV pentosan (Log/sec)	1.80	2.40	2.40	2.20
RE (kCal/kg DM)	4369	4354	4369	4347
ME (kCal/kg DM)	3604 ± 26	3597 ± 26	3578 ± 12	3618 ± 14
ME/RE (%)	82.5	82.6	81.9	83.2

[0089] Analysis of the Results

[0090] In the context of poultry nutrition, two parameters are to be considered: viscosity and metabolizable energy (ME). Viscosity is considered to be a disadvantage and represents a good factor for analyzing the digestibility.

[0091] The effect of treating the grains with ozone was to cause a few small but significant variations in composition: a slight degradation of the raw cellulose and of the starch composition and the walls, together with an increase in the free sugars.

[0092] This degradation is verified by both the specific viscosity and the pentosan viscosity. In fact, a slight degradation of the polysaccharides, specifically the pentosans, initially causes an increase in the viscosity due to solubilization of the pentosans and the short cellulose fragments.

[0093] If the oxidation is increased, a drop in viscosity can be anticipated. This drop appears as from 5 g of ozone per kg of grains.

[0094] This analysis is confirmed by the fact that the ME increases in real terms as from 5 g of ozone per kg of grains, i.e. as from sample 4.

1. A method for preparing lignocellulosic substrates having high digestibility, comprising the steps of:

grinding said lignocellulosic substrates,

moistening the lignocellulosic substrates in the case of dry substrates, and

bringing the lignocellulosic substrates in a stirred reactor, into contact with ozone produced from a carrier gas, the ozone being present in the carrier gas in a concentration of between 80 and 200 g/m^3 NTP,

wherein the residence time in said reactor is between 8 and 40 min, and

wherein the moisture content of said substrates is between 1 and 6% based on the dry matter.

2. A method according to claim 1, wherein the residence time is between 15 and 30 min.

3. A method according to claim 1, wherein the concentration of ozone in the carrier gas is between 140 and 160 g/m^3 NTP.

4. A method according to claim 1, wherein the moisture content of the lignocellulosic substrates is between 1 and 5%, based on the dry matter.

5. A method according to claim 1, wherein the size of the ground lignocellulosic substrates is between 5 mm to 20 mm.

6. A method according to claim 1, wherein the relative pressure of the ozonized carrier gas when it is brought into contact with said substrates is between 0.6 and 1.5 bar.

7. A method according to claim 1, wherein the lignocellulosic substrates are selected from the group consisting of dry substrates and moist substrates.

8. A lignocellulosic substrate obtainable by the method according to claim 1.

9. A method according to claim 1, wherein the size of the ground lignocellulosic substrates is between 10 mm to 20 mm.

10. A method according to claim 1, wherein the relative pressure of the ozonized carrier, gas when it is brought into contact with said substrates is between 0.6 and 1.2 bar.

11. A method according to claim 7, wherein the dry substrates are selected from the group consisting of rye, wheat and alfalfa straws, sugar beet cossettes and cereal grains.

12. A method according to claim 7, wherein the moist substrates are selected from the group consisting of sugar cane bagasse, sorghums, ray grasses and hays.

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