We, GEORGE N. VALKANAS, DEMETRIUS G. ECONOMIDIS, and EMMANUEL G. KOUKIOS, of 14 Constantinopoleos Street, Amaroussion, 7 Agiouthoma Street, Amaroussion, and 14 Ilision Street, Athens, all of Greece, respectively, hereby apply for the grant of a Patent for an invention entitled: "PRODUCTION OF PULP" which is described in the accompanying Complete Specification.

This Application is a Convention Application and is based on the Application numbered 49197 for a Patent or similar protection made in Greece on 24th October, 1975.

Our address for service is:

SHELSTON WATERS,
55 Clarence Street,
Sydney, N.S.W. 2000.

DATED this 15th day of October, 1976

GEORGE N. VALKANAS, DEMETRIUS G. ECONOMIDIS
AND EMMANUEL G. KOUKIOS

by

Fellow Institute of Patent Attorneys of Australia
of SHELSTON WATERS

To: The Commissioner of Patents,
WODEN, A.C.T.

D.B.381
mg

Fee: $116.00
COMMONWEALTH OF AUSTRALIA
Patents Act, 1952-1962
DECLARATION IN SUPPORT OF A CONVENTION
APPLICATION FOR A PATENT

In support of the Convention Application numbered 18,810/76 made by George N. Valkanas, Demetrius G. Economides and Emmanuel G. Koukios for a patent for an invention entitled:

"PRODUCTION OF PULP"

We, the said George N. Valkanas, Demetrius G. Economides, and Emmanuel G. Koukios, respectively of 14 Constantinopoleos Street, Amaroussion, Greece; of 7 Agiouthoma Street, Amaroussion, Greece, and of 14, Ilision Street, Athens, Greece, do solemnly and sincerely declare as follows:

1. We are the Applicants for the Patent.

2. The basic Application as defined by section 141 of the Act was made in Greece on the 24th October 1975 by George N. Valkanas, Demetrius G. Economides, Emmanuel G. Koukios and Con/na G. Valkanas.

3. We are the actual inventors of the invention, together with Con/na G. Valkanas, deceased; and I, George N. Valkanas am the legal representative of the said Con/na Valkanas.

4. The basic Application referred to in paragraph 2 of this Declaration was the first Application made in a Convention country in respect of the invention, the subject of the Application.

DECLARED at Athens, Greece
this 22nd day of DECEMBER, 1978

George N. Valkanas
Demetrius G. Economides
Emmanuel G. Koukios
COMMONWEALTH OF AUSTRALIA
Patents Act, 1952 - 1962

DECLARATION IN SUPPORT OF A CONVENTION
APPLICATION FOR A PATENT

18810/76

In support of the Convention Application made by
George N. VALKANAS, Demetrius G. ECONOMIDIS and Emmanuel G. KOUKIOS
for a patent for an invention entitled:

"PRODUCTION OF PULP"

We, the said George N. Valkanas, Demetrius G. Economidis, and
Emmanuel G. Koukios, of 14 Constantinopoleos Street, Amaroussion,
Greece; of 7 Agiouthoma Street, Amaroussion, Greece, and of 14,
Ilision Street, Athens, Greece,
do solemnly and sincerely declare as follows:

1. We are the Applicants for the Patent.

2. The basic Application as defined by section 141 of the Act was
made in Greece on the 24th October 1975 by George N. Valkanas,
Demetrius G. Economidis, Emmanuel G. Koukios and Constantina
G. Valkanas.

3. We are the actual inventors of the invention, together with
Constantina G. VALKANAS, deceased; and I, George N. Valkanas
am the personal representative of the said Constantina Valka-
nas.

4. The basic Application referred to in paragraph 2 of this Decla-
ration was the first Application made in a Convention Country
in respect of the invention, the subject of the Application.

DECLARED at Athens
this 12th day of October 1976

George N. VALKANAS
Demetrius G. ECONOMIDIS
Emmanuel G. KOUKIOS
HYDROLYSING A CEREAL STRAW.

VALKANAS, G.N., ECONOMIDIS, D.G., KOUKIOS, E.G.

VALKANAS, G.N., ECONOMIDIS, D.G., KOUKIOS, E.G., & VALKANAS, C.G.

CLAIM 1. A process of hydrolysing a cereal straw to produce monosaccharides and a cellulosic residue rich in cellulose suitable for processing to chemical pulp and to pure cellulose comprising: subjecting the cereal straw to acid hydrolysis at temperatures between 100-160°C, the acid being present at a concentration of 0.1 - 1% by weight, for a reaction time between 10-120 minutes, for hydrolysis monosaccharides representing 15-23% by weight of the initial untreated straw, and to a cellulosic residue representing 68-76% by weight of the initial untreated straw, the cellulosic residue comprising 52-58% alpha-cellulose by weight calculated on dry residue, wherein the acid hydrolysing reactant is selected from at least one of the following: H₂SO₄, sulphurous acid, HCl, HNO₃, H₃PO₄, HClO₄, ClCH₂COOH or 2-CH₃-C₆H₄-SO₃H.
The following statement is a full description of this invention, including the best method of performing it known to me/us:

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**PRODUCTION OF PULP**

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This invention relates to a new method for the profitable utilisation of cellulosic agricultural by-products. It refers particularly to a new method for the profitable utilisation of straw to produce useful products such as pulp, cellulose of desirable purity and fermentable sugars. The present invention relates especially to a process for producing the cellulosic product (pulp or pure cellulose) and the fermentable sugars simultaneously, that is by making from each part of the raw material a product of optimal quality and yield. Thus, the utilisation of straw is substantial and much needed materials are produced, such as pulp for making paper, grades of cellulose and fermentable sugars suitable for use in the cultivation of microbes for the production of single cell proteins for cattle feed and human use. The present invention apart from its technological value has considerable economic and social importance, since about 60 - 70% by weight, of the annually produced agricultural products are cellulosic by-products.

In a large number of these agricultural by-products, the cellulose is of the type which can be used in several industrial applications (for example for the production of chemical pulp) and according to the present process can be obtained in a high yield and purity or in the form of widely used industrial products together with the other non-cellulosic constituents it contains. If the present process was used on a wide scale, agricultural by-products could become a more important source of valuable materials.

The present invention relates to a process for the substantial utilisation of cellulosic agricultural waste
which comprises subjecting the cellulosic waste to a selective hydrolysis treatment in the presence of one or more acid hydrolysing reactants, wherein the easily hydrolysable constituents of the waste such as pentosans, starch and hemicelluloses are converted substantially into monosaccharides, and wherein a residue rich in cellulose is obtained which is suitable for processing to chemical pulp and to pure cellulose.

All the percentage figures given herein are used on a weight basis, unless otherwise indicated.

Cereal straws form a main part of the annually produced agricultural by-products, being produced in approximately twice the quantity by weight, of cereal grains. Of main interest, for use in this present invention, and for other reasons which will become evident below, are varieties of straw from wheat, barley and rice which have the composition shown in the following table.

<table>
<thead>
<tr>
<th></th>
<th>Wheat</th>
<th>Barley</th>
<th>Rice</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pentosans</td>
<td>22 - 25</td>
<td>25 - 27</td>
<td>23 - 26</td>
</tr>
<tr>
<td>Hemicelluloses</td>
<td>19</td>
<td>15</td>
<td>-</td>
</tr>
<tr>
<td>Alpha-Cellulose</td>
<td>38 - 41</td>
<td>40 - 41</td>
<td>42 - 44</td>
</tr>
<tr>
<td>Lignin</td>
<td>15 - 17</td>
<td>17 - 18</td>
<td>12 - 14</td>
</tr>
<tr>
<td>Ash</td>
<td>6 - 7</td>
<td>3 - 5</td>
<td>14 - 16</td>
</tr>
</tbody>
</table>

According to the present process, the pentosans in the straw is subjected to a partial or complete hydrolysis, in such a way, that the hydrolysis product essentially consists of pure monosaccharides and of a solid residue which is
suitable for the production of high quality chemical pulp or cellulose of high grades. The partial hydrolysis, being combined with the production of chemical pulp, has to satisfy several requirements. The cellulosic hydrolysis product should comprise a pulp of high quality suitable for use in the paper industry, and this, which is well known to the specialists in the field, depends on many, mostly controversial, factors. Thus, the quality of pulp basically depends on the structure of the cellulosic fibres but also on the presence of hemicelluloses which substantially improve the pulping properties. In the case of pulp from straw, the presence of hemicelluloses is also of fundamental importance for preserving the structure of the fibres since the hemicelluloses contribute to the protection of the fibres from the chemicals generally used in pulping. It is known that straw fibres are rather short, having a mean length of 1-1.5 mm compared to a mean length of 4-5 mm for wood fibres. On the other hand, straw fibres show better orientation and cohesion, qualities which, in the presence of hemicelluloses, compensate for the shortness deficiency and therefore a pulp of high quality can be produced.

Broadly, the present invention provides a method of hydrolysing cereal straw to produce monosaccharides and a cellulosic residue rich in cellulose suitable for processing to chemical pulp and to pure cellulose comprising: subjecting the cereal straw to acid hydrolysis at temperatures between 100-160°C., the acid being present at a concentration
of 0.1 - 1% by weight, for a reaction time between 10-120 minutes, for hydrolysis to monosaccharides representing 15-23% by weight of the initial untreated straw, and to a cellulosic residue representing 68-76% by weight of the initial untreated straw, the cellulosic residue comprising 52-58% alpha-cellulose by weight calculated on dry residue, wherein the acid hydrolysing reactant is selected from at least one of the following: H₂SO₄, sulphurous acid, HCl, HNO₃, H₃PO₄, HClO₄, ClCH₂COOH or p-CH₃-C₆H₄-SO₃H.

The cereal straws are known to be rich in pentosans which, if they remain in the final pulp, adversely affect its quality. Thus, the pentosans should be removed before pulping but at the same time ensuring the cellulosic residue is of the desired quality, as indicated above. Additionally, the pentosans should be quantitatively hydrolysed to monosaccharides which are sufficiently free from inhibiting compounds so as to be suitable for fermentation processes. According to the above the hydrolysis treatment should be selective in that the easily hydrolysable constituents of the straw are converted mainly into monosaccharides. This is one of the fundamental features of the present invention. According to the present method, the selective hydrolysis is catalysed by one or more acids and is performed preferably under pressure at a temperature above 100°C. The concentration of the acid hydrolysing reactant is kept low and the temperature selected so that the hydrolysis treatment is for 10-120 minutes. Suitable acid hydrolysing reactants
are strong inorganic and organic acids for example, sulphuric acid (H₂SO₄), hydrochloric acid (HCl), nitric acid (HNO₃), perchloric acid (HClO₄), phosphoric acid (H₃PO₄), sulphurous acid (H₂SO₃), chloroacetic acid (CICH₂COOH), p-toluene sulphonica acid (p-CH₃-C₆H₄-SO₃H), of the above catalysts, HCl, H₃PO₄, and HNO₃ and mixtures thereof give better results as regards the quality of the
hydrolysis sugars obtained. Phosphoric acid is a nutrient in the fermentation of sugars while nitric acid is useful because during fermentation it is converted to a nitrogeneous nutritive salt and because when it is used as an acid hydrolysing reactant, partial oxidation of sugars and lignin occurs, the traces of partial oxidation products formed being useful in the fermentation process. The concentration of the acid catalysts is kept between 0.1 - 1% and the temperature between 100 - 160°C preferably between 130 - 150°C.

The acids used as hydrolysing reactants in the hydrolysis behave as usually happens in these types of reactions, according to their molarity and not to their normality. If the action of HCl is compared with that of H₂SO₄ (and also with other acids having a higher molecular weight), it can be seen that smaller amounts of HCl are required to produce the same effect. Furthermore, it is more preferable to have chlorides than sulphates in the sugar solution during its subsequent fermentation. The yield of the proteinic mass produced from the microbial growth when the yeast Candida utilis for example, is used, amounts to 60 - 65% by weight based on the sugars consumed in the substrate. The highest yields are obtained when one of the acids HCl or HNO₃ or H₃PO₄ is used as the hydrolysing reactant in the hydrolysis.

Using the present process, not only are fermentable sugars produced, but also a cellulosic residue of high quality. Thus, the present process is continuous and bi-directional in that two distinct operations, which were previously considered to be contradictory (namely the
production of fermentable sugars and the production of chemical pulp) may be efficiently carried out. Since both these products are economically important the fact that the process is bi-directional is very important. Paper pulp of high quality can be produced, using as raw material the cellulosic residues from hydrolytic pretreatments, which have already produced 15 to 25% by weight based on the initial straw of monosaccharides. Since these sugar solutions are also useful products the maximum possible sugar yield should be preferred each time. Other factors which influence the hydrolysis are the temperature and the pressure at which the process occurs. Hydrolysis treatment at a temperature between 120 - 140°C is completed in a short time of 10 - 60 minutes and because of that and the treatment under pressure, the structures of the cellulosic fibres and of the hemicelluloses are preserved. The yields of sugars after the hydrolysis treatment as above are independent of the processing temperature, and are as follows: xylose 67 - 75%, arabinose 10 - 18%, mannose 1.2 - 5%, glucose 5 - 12% and galactose 2 - 4% all the percentages being by weight. This sugar mixture is a very suitable nutrient for microbes used for the production of protein feeds, the monosaccharides apart from arabinose, being completely consumed. Arabinose is exceptional because although it resists fermentation, it does not act in any way as an inhibitor. Under the above conditions, some furfural is produced together with the sugars in a concentration of 0.02 - 0.25 g/lit in the final sugar solution. The above monosaccharides are the complete hydrolysis products of the pentosans and to a small extent...
the hydrolysis products of hemicelluloses. The hydrolysis solution has the sugar composition: xylose 67 - 75%, mannose 1.2 - 5.0%, arabinose 10 - 18%, glucose 5 - 12, galactose 2 - 4% by weight. The cellulosic residue composition: alpha - cellulose 52 - 54%, hemicelluloses 11 - 13%, lignin 21 - 23%, extractables 10 - 13%, ash 5 - 6% and a degree of polymerization of 790 - 830 glucose units. All percentages being by weight.

We have also discovered that the cellulosic residue can be successfully used, under specified conditions, in the production of chemical pulp. In particular, we have developed methods for the production of all basic commercial types of pulp, that is kraft, sulphite, and modified kraft which are characterised by high mechanical strength, suitability in paper making and compatibility in paper making with the same or different types of wood pulp. Our methods are substantially different from the processing and the technology used in pulp production from wood, and according to our knowledge, they have not been used before in that form or in such a relation for the production of pulp from this special quality of prehydrolysed straw. The hydrolysed straw, which is the starting material for pulp production according to the present invention, as stated before, is an entirely different material to wood and a substantially different material to straw, and to some types of straw subjected to pretreatments of a hydrolytic character before the production of rayon viscose, or low quality paper, according to the literature.

In our new starting material the cellulose fibers are
kept in their natural state without fragmentation of the cellulose molecules and disturbances in the orientation of the fibers.

Thus, the present invention also relates to a process for the production of chemical pulp wherein the cellulosic residue of the straw hydrolysis in which the yield of sugars was 17 - 20% by weight, is treated with an alkaline solution of sulfite salts, and then heated within two hours up to 150 - 160°C and maintained at that temperature for 5 - 6 hours.

The alkaline solution of sulphite salts preferably contains 255 kg Na$_2$SO$_3$ and 85 kg NaOH per ton of dry pulp.

The present invention also relates to a process for the production of kraft pulp wherein the cellulosic residue of the straw hydrolysis in which the yield of sugars was 15 - 19% by weight is treated with a kraft pulping solution containing Na$_2$S and NaOH and with a pulping solution in which Na$_2$S and NaOH are partially replaced by Na$_2$SO$_3$ and then heated up to 150 - 160°C and maintained at that temperature for 4 - 6 hours.

The kraft pulping solution preferably contains 125 kg Na$_2$S and 260 kg NaOH per ton of dry pulp.

Preferably, the pulping chemicals Na$_2$S and NaOH are partially replaced by Na$_2$SO$_3$ in a quantity of 0.1 - 30% by weight. Our hydrolysis treatment is very successful in that the hydrolysed product has a degree of polymerisation similar to that of the starting straw of 800 - 820 glucose units compared with a degree of polymerisation of 500 - 600 glucose units obtained when a non selective straw hydrolysis treatment is used. The cellulose and lignin contents are...
substantially higher, amounting to 50 - 54% and 22 - 24% by weight respectively, while other constituents such as hemicelluloses are present in about normal amounts. Thus, in pulp production conditions are required which preserve the qualities and the quantities of alpha-cellulose and hemicelluloses. The prior art methods of pulping are therefore not suitable for use in the present case in the form they are used for wood but, as shown in the examples of this invention can be substantially revised. A high quality paper pulp can be produced according to the kraft method from a hydrolysis residue after only comparatively mild hydrolytic treatment of straw, that is, after the production of no more than 15 - 18% by weight, based on the straw. This is the result of the high penetration efficiency of the chemicals used in this method, together with the absence of a great part of the hemicelluloses from the cell walls. On the other hand, paper pulp, of exceptional quality can be produced from hydrolysis residues according to the sulpite and modified kraft (Example 12) methods, after a stronger hydrolytic treatment of straw, wherein upto 20% of monosaccharides by weight of the straw, have been produced.

This difference can be explained on the basis of the greater selectively of delignification presented by the latter two methods.

The present invention also relates to a process for the production of pulp from our hydrolysed straw, using a chlorine method which is entirely different from the other chlorine methods for pulping and from the well-known "POMILIO" method for the production of pulp from straw.
According to the present method, the chlorine treatment is subsequent to the useful acidic prehydrolysis and does not require an alkali wash in between. Thus, the present chlorine method has fewer steps of treatment and in spite of the very simplified procedure gives impressive results in yield and quality of pulp. The hydrolysed straw obtained that is, the residue of a hydrolytic treatment whereby 15 - 23% monosaccharides by weight of the straw were produced after pressing and draining off of the sugar solution, with moisture between 60 - 100% of dry matter, is directly subjected to chlorine treatment with chlorine gas. The chlorine is absorbed readily in quantities between 18% and 23%, by weight, of the hydrolysed straw in a reaction which, although exothermic, is readily controlled at a temperature between 30° and 40° C.

The absorption of chlorine leads to the formation of pink coloured chlorolignins, the coloration of which at the end of the reaction is spread homogeneously all over the chlorinated mass. The development, thus, of the pink coloration can be used to follow the chlorination procedure. Another significant advantage of using this method of pulping hydrolysed straw, is that even after a hydrolysis producing 20 - 23% monosaccharides by weight of the initial untreated straw, (that is, a yield not permissible when using conventional methods of pulping) the residue can be easily chlorinated and gives a pulp of exceptional quality.

Delignification by chlorine is very effective and as it was developed by Pomilio and others, a special method for the pulping of straw. These chlorine pulping methods, however,
are impaired by the liberation of substantial quantities of hydrochloric acid which makes the processing acidic in nature, in which the hydrophobic straw is much more resistant and can stand these conditions better than the prehydrolysed straw. The present case, therefore, requires different utilisation of the chlorine reagent for selective delignification without damaging the structure of the fiber and the hemicelluloses. After extensive studies on existing possibilities in procedures of treatment, we were successful in developing a special method and condition of processing satisfying all the above requirements. Our special method consists of introducing the chlorine into horizontal slowly rotating reactors or vertical slowly reactors containing the residue from a straw hydrolysis, as described before, having produced 15 - 23% and preferably 20 - 23% monosaccharides by weight of straw until up to 20% by weight of chlorine, based on the hydrolysis residue treated is absorbed. The product is then washed with water and alkaline solution until neutral. Generally, to obtain a pulp of improved colour quality, the residue from straw hydrolysis, is washed with a 1 - 3% solution of NaOH before pulping.

After obtaining a satisfactory and uniform chlorination, the processed mass may be washed successively with water, 2% sodium hydroxide solution and again water. Generally, the chlorination lasts 30 - 60 minutes and the subsequent washings should preferably be fast, using large volumes of water. The residue from the straw hydrolysis may be introduced into the chlorination reactors in the form of a compressed hydrophilic mass and does not require a prewashing with
dilute sodium hydroxide as in industrial practice for straw when the Pomilio process is used. The yield in dry pulp is between 50 - 51% based on the initial straw.

Although it is preferred to use horizontal or vertical reactors for chlorine delignification it is also possible to use chlorination towers in which the chlorine gas passes in a direction counter-current to that of the moist residue from the straw hydrolysis which is introduced at the top of the reactor. We have calculated that the time required for the hydrolysed straw to fall from the top to the bottom (i.e. the time of straw-chlorine contact) should be reduced considerably with respect to that required using the known towers used in the Pomilio process. On the other hand, the instruction of chlorine needs special care and dilution with air. In the line of such improvements the pulp obtained is satisfactory both in quality and yield.

The types of pulp produced in accordance with the above treatment show satisfactory mechanical and paper making properties compared with the best such qualities produced from wood. In addition, high purity pulps are obtained which may be decolorised with calcium hypochlorite in a mild treatment resulting in a weight loss of only 2 - 3% by weight. This may be compared with losses of 6 - 10% by weight for Pomilio straw pulp and 5 - 8% by weight for pulp from wood. Thus, the yield in pulp improves favourably between straw and hydrolysed straw. In the following Table are given certain results after testing the paper making characters and the mechanical properties of the pulps obtained from
prehydrolysed straw according to our process.

The present process is not only of technological success but also substantially decreases the costs of production. This is because both fermentable sugars, and a cellulosic residue suitable for chemical pulp formation are produced, and furthermore, there is a reduction in the industrial installations required.

TABLE

<table>
<thead>
<tr>
<th>Pulping method</th>
<th>Kraft</th>
<th>Alkaline Sulfite</th>
<th>Chlorine</th>
</tr>
</thead>
<tbody>
<tr>
<td>Freeness (SR₀)</td>
<td>40</td>
<td>60</td>
<td>40</td>
</tr>
<tr>
<td>Breaking length</td>
<td>5800</td>
<td>6500</td>
<td>6000</td>
</tr>
<tr>
<td>Burst factor</td>
<td>30</td>
<td>56</td>
<td>28</td>
</tr>
<tr>
<td>Tear factor</td>
<td>70</td>
<td>52</td>
<td>65</td>
</tr>
<tr>
<td>Folding number</td>
<td>450</td>
<td>990</td>
<td>500</td>
</tr>
</tbody>
</table>

The production of pulp from wood or straw, because of the starting material used and the volume of the wastes produced, generally requires large industrial installations, which are expensive. Additionally, in most countries, it is necessary to use installations for the purification and disposal of the wastes produced and for the recycling of cooling and processing water. This substantially increases the cost of processing and of the installations themselves.

By using the process of the present invention, there are not such pressing problems. The industrial waste formed from both lines of processing, that is the hydrolysis and pulping lines, amounts to about 30% of the organic matter. Using
the prior art processes, however, about 60% of the organic matter is lost as waste. In addition to this, the organic wastes produced by this method contain 60 - 70% lignin, that is, they have a high thermal value so that by condensing to 50% solids, they burn easily in ordinary incinerators. In our chlorine method, lignin can be easily precipitated by acidification from the waste liquors of the alkali extraction following chlorination. The yield of the lignin is about 80% by weight of the theoretical yield, and the lignin is suitable for a variety of uses according to known methods.

Thus, in accordance with the present invention relating to the utilisation of straw, there is obtained at the end, a successful separation to its three partial constituents, that is, the pentosans, the pulp and the lignin. Thus, straw utilisation can be optimised, whilst overall pollution may be decreased.

As is specified, by using the present invention, the basic machinery required for pulping is substantially reduced since the starting material is condensed by 25 - 30% and the time for processing reduced by 35 - 40%. Thus, the industrial installations required are reduced in volume by about 50% as compared with those needed for the previously used wool pulping methods. In addition, water can be significantly economised because the effluents of the sugar fermentation plant contain 1 - 3% of organic matter which is an acceptable purity for utilising these effluents in pulp washings. One of the advantages of the present invention in the utilisation of cereal straws is the reduced cost of processing and the reduced cost of the installations.
The prehydrolysis treatment may be carried out in a vertical reactor which is loaded by a known method, for example, the procedure of loading wood for pulping. Alternatively, horizontal reactors may be used through which is passed a line of loaded carriages, so that loading and unloading the reactor is a fast operation hence enabling the reactor to be used more efficiently. After the prehydrolysis treatment, the prehydrolysed straw may be brought into a tank to drain the sugar solution and is then placed in another tank to be washed with water. This is usually followed by compressing at a pressure of 20 - 30 atm from which the prehydrolysed straw is obtained advantageously in bales having a retained moisture content of 40 - 50% by weight. The compressed product may be directly utilised for pulping. In the case of chlorine pulping an alkali wash with 1 to 3% NaOH solution before pressing may sometimes be advantageous for improving the colour of the finished pulp.

In one embodiment of the process according to the present invention, the cellulosic residue, after the prehydrolysis treatment is washed with water and/or with a 1 - 3% sodium hydroxide solution and thereafter is compressed to a product having a moisture content of 40 - 50% by weight.

In the hydrolysis procedure water is used in a quantity of 5 - 8 times the weight of the straw. A yield of from 15 to 23%, of sugars are obtained from the hydrolysis which after the necessary washing of the cellulosic residue make solutions containing some 1.2 - 5% sugars. If the sugars are to be used for fermentation purposes, higher sugar
concentration (between 4 - 6%) are desirable. We have found that the sugar solutions can be recycled to concentrations of 6 - 8% by weight without any significant losses in sugars or destruction of the sugar composition.

In the prehydrolysis installations, all surfaces contacting the sugar solution should be resistant to the acidity of the solutions because metallic impurities such as Fe, Ni, Co, and Mn, when in solution inhibit fermentation of the sugar used as a substrate by microbes for producing single cell proteins. All metallic surfaces in contact with the solution must therefore be covered or lined with ceramics or with a plastics material suitable for the purpose.

In a partly different adaptation of the prehydrolysis procedure, the cellulosic residue, after processing in batch reactors, is pressed to produce a sugar solution of high sugar concentration (up to 5%, by weight). The pressed mass is subsequently washed with hot water and the new resulting dilute sugar solution, obtained after pressing, is recycled as the process solution. Using such a sequence, production of a concentrated solution of sugars is possible.

Under stronger conditions of temperature or time of processing, the hydrolysis of straw proceeds to a higher degree which is characteristic and at which the reducing sugars produced amount to 29 - 31% of straw weight. The cellulosic residues after this severe hydrolysis show a certain resistance to further hydrolysis and appear to have attained a stable structure which on analysis was found to have the composition: alpha-cellulose 57%, hemicellulloses 10%, lignin 22%, other constituents 11%. The sugar solution
obtained had the composition: xylose 70, 3%, mannose 2,1%, ribose 1,4%, arabinose 17, 6%, glucose 6,8% and galactose 1,8% and it was especially suitable as a fermentation substrate for microbes for producing proteins. The cellulosic residue thus obtained is not very suitable for processing alone to pulp of good paper making characteristics. Using mixtures, however, of that pulp with mechanical wood pulp 50 : 50 (w/w), products having excellent paper making properties are obtained. On the other hand, this pulp prepared under selective conditions, may have a high alpha-cellulose content, that is, 95 - 96%, by weight, which makes its quality very suitable for the production of rayon, of Cellophane ("Cellophane" is a Registered Trade Mark) and substituted cellulose products.

According to the present method, the end products obtained are pulp and protein cultures in approximate yields of 43 - 51% and 18%, respectively, both of which are known to be basic market products of high value and which represent a utilisation of straw of 59 - 69% by weight. This utilisation of straw is higher than could be obtained by other previously known methods. If lignin is also considered, the maximum total yield of useful products is 85% by weight, based on the initial dry straw.

The invention is illustrated by the following Examples:

EXAMPLE 1

Prehydrolysis of wheat straw was carried out in an apparatus, lined internally with Teflon ("Teflon" is a Registered Trade Mark) the apparatus being capable of working under pressure and being equipped with recording instruments
for temperature and pressure. The apparatus consisted of a 5
lit reactor, a preheating unit used to heat up the process
water solution, and following the reactor, the pressure and
flow regulating valve system and a graphite heat exchanger.
The following methods were used:
a) 0.8 kg of dry straw was introduced into a cage of Teflon
in the reactor. Through this were introduced 10 lit of 0.3%
aqueous HCl, under a pressure of 5 – 5.5 atm. at a
temperature of 145°C and at a flow rate of 0.55
litres/minute. The reactor was then drained with dry steam
(i.e. supersaturated vapour was used to drain the material)
filled with hot water at a temperature of 120 – 130°C and
drained again with dry steam. After that, the residue was
taken out and pressed at 25 kg/cm² to form a product having
a moisture content of 45 – 50% by weight. From the apparatus
and the press were collected a total of 13.4 litres of
solution containing 1.34% by weight monosaccharides, equal to
a yield during straw hydrolysis of 23% by weight. The sugar
solution had the composition: xylose 74.3% mannose 5.2%
arabinose 11.8% glucose 5.9% galactose 2.9% and furfural 0.16
g/lit. The cellulosic residue had a dry weight of 0.545 kg,
that is a yield of 68.2% by weight and had the following
composition: alpha-cellulose 53.1% hemicelluloses 12.6%
lignin 22.1% ash with extractables 12.2% and a degree of
polymerisation of 805 glucose units.
b) 0.8 kg of dry straw was placed into the reactor of the
apparatus and subjected to a hydrolysis treatment as
described above, using a solution containing 0.5% HCl at a
temperature of 145°C introduced at a flow rate of 0.95 lit
minute. After draining with steam, washing with hot water, draining again with steam, and pressing the residue, there were collected 13.5 litres of solution containing 1.32% by weight of monosaccharides corresponding to a yield during straw hydrolysis of 22.7% by weight. The cellulosic residue had a dry weight of 0.550 kg, that is, a yield of 69.4% by weight of the original straw and a degree of polymerisation of 792 glucose units.

c) in a hydrolysis treatment of 0.8 kg dry straw as described above using a 0.3% HCl solution, at a temperature of 145°C and a flow rate of 1.0 lit/minute there were collected: a sugar solution containing 1.09% monosaccharides, by weight, that is a yield during hydrolysis of 18% by weight of the straw, the solution having the following composition: xylose 74% mannose 2.9% arabinose 10.5% glucose 9.7% galactose 2.8% and furfural 0.15 g/lit and a cellulosic residue having a dry weight of 0.565 kg that is, a yield of 70.7% by weight of the original straw, a composition: alpha-cellulose 52.0% hemicelluloses 13.8% pentosans 5.0% lignin 21.8% and others 12.4% and a degree of polymerisation of 820 glucose units.

EXAMPLE 2

a) 0.8 kg of wheat straw was placed in a Teflon cage in an apparatus comprising a 5 lit reactor, a system to heat up the process water solution, and in line, a system to regulate flow and pressure and an efficient exchanger. 10 litres of HNO₃ (0.3% solution) were introduced at a pressure of 5 - 5.5 atm., at a temperature of 145°C, and at a flow rate of 0.48 lit/minute. The solution kept in the reactor was
drained with steam, followed by washing with water of 120 - 130°C and again draining with steam. There were collected 13.6 litres of solution containing 1.30% monosaccharides, by weight, which corresponds to a yield during hydrolysis 22.8% by weight, and a residue of 0.540 kg dry weight. The sugar solution after filtration and stripping with steam to remove the furfural it contained, had the composition: xylose 71.2%, mannose 1.7%, arabinose 12.8%, glucose 11.0%, and galactose 3.2%. This sugar solution to which were added the necessary nutrients, was used in the production of protein by a culture of *Candida utilis*. In a cycle of growth of 16 hrs, there was obtained a yeast yield of 65%, dry weight, based on the consumed sugars.

b) After a treatment as described above, in which a solution of sulfuric acid (0.5%), at a flow rate of 0.8 litre/minute was used for the hydrolysis, there were obtained 13.5 litres of sugar solution containing 1.29% monosaccharides, by weight, or a yield during hydrolysis of 22.6%, by weight, and a solid residue of 0.540 kg of dry weight. Under the same conditions of hydrolysis, but using a 0.3% solution of sulfuric acid, there were obtained yields of 18.5% in monosaccharides and of 70.5% in cellulosic residue, having a degree of polymerisation of 830 glucose units.

**EXAMPLE 3**

0.8 kg of wheat straw was placed in apparatus as described above and hydrolysed using 10 litres of 0.5 HCl solution at a temperature of 140°C, and at a flow rate of 0.55 litre/minute. This was followed by draining with steam, washing with hot water at 120 - 130°C and again draining.
with steam. There were collected from the reactor and the pressing of the residue a total of 13.6 litres of solution having a concentration of monosaccharides of 1.3%, by weight, corresponding to a yield during hydrolysis of 20.7%. The cellulosic residue had a dry weight of 0.550 kg, that is a yield of 68.8% by weight based on the straw. Under the same processing conditions, except for the flow rate of the solution which was 0.92 lit/minute, were obtained yields of 15.5% of monosaccharides and 74.0% of cellulosic residue. A sugar solution produced as described above was filtered, treated with steam to remove the furfural it contained, and used as a nutrient for a culture of *Candida utilis*. The cycle of growth was 16 hrs and the yield in dry protein was 64.5% based on the consumed sugars.

**EXAMPLE 4**

In apparatus as described above was placed 0.8 kg of dry wheat straw, partially hydrolysed according to Example 1a by using the sugar solution obtained in this Example (13.4 litres) as a processing solution, after an adjustment of its HCl concentration to 0.3% HCl. The solution at 80 - 85°C was quickly heated to 145°C and introduced at a flow rate of 0.56 lit/hour. Proceeding as described in Example 1a, there were obtained 15 lit of a solution containing 2.28% monosaccharides, by weight, and a solid residue of 0.580 kg dry weight. After recycling twice more, the solution containing above 2.28% monosaccharides which leaving the exchanger each time at 80 - 85°C, was heated up to 145°C, and used for the hydrolysis of 0.8 kg of dry straw, there were finally obtained 20 litres solution of 4.65%
monosaccharides content by weight. The cellulosic residue was obtained in yields of 72.2% and 73.5%, respectively and both were found to be of the desired composition. A quantity of the above concentrated sugar solution was diluted to 2.3% monosaccharides, filtered, stripped with steam to remove furfural, and was used as a nutrient for a culture of protein-producing, Candida utilis. The cycle of growth was 15 hrs, the yield in dry yeast 64.5% and approximately 90% of the sugars were consumed.

EXAM I LE 5

a) In an autoclave of capacity 5 litres, lined with Teflon and equipped with an agitator and internal cooling coil, were placed 0.5 kg of dry wheat straw and 4 litres of 0.5% HCl solution. The whole was heated, with stirring, to 130°C in 20 minutes and kept at that temperature for 20 minutes with stirring, and then cooled quickly. The product of the autoclave was drained from the solution and the solid part was washed with 2 litres of hot water at 60 - 70°C, drained again and then pressed at 25 kg/cm². In total, 5.5 litres of solution containing 2.0% monosaccharides, by weight, were collected or a hydrolysis yield of 21% and 0.355 kg of dry cellulose residue, that is, 70.0% of the original straw, by weight. The sugar solution had the composition: xylose 74.3%, mannose 5.2%, arabinose 11.8%, glucose 5.9%, galactose 2.9 1%, by weight, and furfural 0.13 gr/litres.

b) In the above autoclave were placed 0.8 kg of straw and 4 litres of 0.3% HCl solution. The whole was heated up to 135°C in 20 minutes and kept at that temperature for 20 more minutes. The product was pressed at 25 kg/m² to
produce, in total, 3.5 lit. of solution containing 3.2% of simple monosaccharides (representing a yield in hydrolysis of 16%). The pressed product was washed with 4 litres of hot water (70°C), with stirring and pressed at 25 kg/m². 3.6 litres of dilute sugar solution were obtained which contained 0.9% of monosaccharides.

c) In accordance with a treatment as described above, the autoclave was charged with 0.8 kg of dry straw and the 3.6 lit. of dilute sugar solution of Example 5b, after adding 0.5 lit. of water, and hydrochloric acid solution so that the process solution contained 0.3% HCl by weight. After heat processing at 135°C, as described above, the product was pressed at 25 kg/m² producing 3.6 litres of sugar solution with 4.25% monosaccharides (hydrolysis 16%). The solid residue was washed with 4 litres of hot water (70°C) with stirring, and was pressed again at 25 kg/m² to produce 3.8 litres dilute sugar solution containing 1.00% monosaccharides. This dilute solution after recycling gave concentrated sugar solutions.

EXAMPLE 6

Using the autoclave of Example 5, a series of hydrolysis runs were performed, using 0.5 kg of dry wheat straw, each time under different processing conditions, with the following results:

a) The hydrolysis treatment was performed using 4 litres of 0.5% H₂SO₄ solution at 130°C, according to a procedure of heating up to 130°C in 20 minutes and keeping at that temperature for 60 minutes with stirring. After draining the solution, washing and pressing the solid residue, there were
obtained 5.65 litres of a solution with 2.05% monosaccharides, by weight, and a solid product of 0.330 kg, dry weight, having a moisture content of 40 - 45%, by weight. Processing as described in Example 6a in all respects except for the catalytic strength of the solution, which was reduced to 0.3% in H₂SO₄, gave a solution containing 1.30% monosaccharides and a cellulosic residue having a dry weight of 0.352 kg, and a moisture content of 45 - 50%, by weight. A quantity of the above sugar solutions containing 1.8% of monosaccharides, was used as nutrient in the production of a microbe culture which produced protein. The cycle of growth was 18 hrs and the yield in dry yeast was 61% based on the consumed sugars of which 87% were utilised.

b) The hydrolysis treatment was performed using 4 litres of 0.5% HClO₄ solution but in all other respects according to Example 6a. There were obtained 5.63 litres of sugar solution containing 2.03% monosaccharides and 0.350 kg of dry cellulosic residue having a moisture content of 40 - 45%, by weight, and a degree of polymerisation of 825 glucose units.

c) The hydrolysis treatment was performed using 4 litres of a 0.35% HNO₃ solution but in all other respects in accordance to Example 6a. There were obtained 5.6 litres of solution containing 2.08% monosaccharides and a cellulosic residue having a dry weight of 0.340 kg, a moisture content of 50%, by weight, and a degree of polymerisation of 810 glucose units.

d) The hydrolysis treatment was conducted using 4 litres of 0.5 M phosphoric acid solution, but otherwise as described in Example 6a. There were obtained 5.6 litres of sugar solution
containing 2.05% monosaccharides and a cellulosic residue having a dry weight of 0.340 kg dry weight, a moisture content of 50%, and a degree of polymerisation of 825 glucose units.

EXAMPLE 7

Into each of 5 flasks of 5 litres capacity, with reflux condensers, designated as I, II, III, IV, V, were placed 0.5 kg of wheat straw and 4 litres of processing solution. The type and concentration of catalysts used were: flask I, HCl 0.5 M; II H₂SO₄ 0.25 M; III H₂SO₄ 0.5 M; IV HClO₄ 0.5 M; and V HNO₃ 0.5 M. All were heated up to boiling and at the 2nd and 3rd hour samples were taken (I-2, I-3 etc., where the numbers 2 and 3 indicate the hours of boiling when the sample was taken) and examined for the sugar content from which it was concluded that the degree of hydrolysis, based on the initial straw (%) was:

I-2 17.8% II-2 7.3% III-2 16.7% IV-2 17.1% V-2 17.9%
I-3 23.9% II-3 19.9% III-3 23.1% IV-3 22.9% V-3 23.4%

With the above results it was shown, as was also observed in the hydrolysis treatment at higher temperatures (Examples 1, 2 and 5), that the acid catalysis is of the molecular type, that is, its effect depends on the molecular concentration of the acid and not on the hydrogen ion concentration. The sugar solutions according to their time of boiling and the resultant degree of solubilisation had the composition found in the preceding examples. The catalytic strength of the acids H₃PO₄, C₁CH₂COOH and p-CH₃-C₆H₄-SO₃H was also studied and it was found that of the 3 hours of boiling, the degree of hydrolysis was
23.0, 22.2 and 21.9% respectively. Using a 0.5 M SO\textsubscript{2} solution in a run, in the autoclave at 100\degree C, for 3 hrs, sugars were produced corresponding to 22.0% of hydrolysis.

**EXAMPLE 8**

In the autoclave used in Example 5, following the procedure described in that Example, barley straw was subjected to hydrolysis under the following conditions and with the following results:

0.5 kg of barley straw were subjected to a hydrolysis treatment using 0.5% HCl solution at 130\degree C under conditions such that the heating to 130\degree C took 20 minutes and the solution was kept at that temperature with stirring for 30 minutes. After draining, washing and pressing the solid product there were obtained 5.7 litres of solution containing 1.90% monosaccharides, by weight, equal to a yield of 21.6% of hydrolysis, and a cellulosic residue having a dry weight of 0.335 kg and a moisture content of 45% by weight. The cellulosic residue had the composition: alpha-cellulose 52.3%, hemicelluloses 13.4%, lignins 24.0%, ash and extractables 10.3%. The sugar solution was found suitable for the growth of protein-producing microorganisms.
weight of 0.325 kg and the following composition:
alpha-cellulose 50.8%, hemicelluloses 13.1%, lignin 25.0%,
ash and extractables 11.1%. The sugar solution examined was
found to be very suitable for fermentation by proper
producing microorganisms.
c) 0.5 kg of alfalfa (dry weight), were hydrolysed using 4
litres of 1.5% H₂SO₄ at 100°C. After boiling for 3
hrs, the solid residue was drained, washed with 2 litres of
hot water and compressed to a cellulosic product having a dry
weight of 0.330 kg. The alpha-cellulose content of that
residue was 50.8%, by weight.

EXAMPLE 9

0.5 kg of wheat straw were placed in the autoclave
subjected to hydrolysis to produce a resistant stable solid
product. This was achieved using 4 litres of 0.5% H₂SO₄
solution which was heated to 150°C in 25 minutes, and kept
at that temperature for 20 minutes with stirring, followed by
fast cooling. After draining, washing with 2 litres of hot
water and compressing the solid residue at 25 kg/cm², there
were obtained 5.6 litres of solution containing 2.67%
monosaccharides, by weight, corresponding to a yield of
30.0%, and a solid residue having a dry weight of 0.310 kg or
62% of the charged straw, by weight. The sugar solution had
the composition: xylose 67.0%, mannose 1.1%, arabirrose
18.0%, glucose 11.7%, galactose 2.2% and fufural 0.243
gr/litres. The solid product had the composition:
alpha-cellulose 57.0%, hemicelluloses 10.9%, lignin 22.1%,
ash and extractables 11.0%. By prolonging the time of
heating at 150°C, the following results were obtained:
after 10 minutes - hydrolysis sugars 29.2% and cellulosic residue 63% based on the charged straw; after 30 minutes - hydrolysis sugars 30.6% and cellulosic residue 61.2% based on the charged straw. The cellulosic residue, by prolonging the time of heating at 150°C from 0 to 30 minutes, showed a small change in yield which decreased only by 1.8%. Thus, it had attained a somewhat stable structure which was resistant to hydrolysis. Under the above variation in processing conditions, the composition changes were:

alpha-cellulose 57.5% → 57.0%, hemicelluloses 11.6% → 10.8%, extractables 7.4% → 7.2%, lignin 22.5% → 23.0%, ash 5.2% → 5.8%.

**EXAMPLE 10**

In an autoclave of 5 litres capacity were charged 0.8 kg of hydrolysed straw (produced by a hydrolysis which resulted in a 18% yield in sugars; Examples 1 and 2) together with 4 litres pulping solution having the composition: 0.120 kg Na₂SO₃, and 0.040 kg of NaOH, for the production of an alkaline sulfite pulp. The hydrolysed straw was kept within two plates having holes for the circulation of the solution, in such a way that the pulp was permanently fully covered with solution. The whole was then heated in 2 hours to 160°C and kept for 6 further hours at this temperature. After cooling the pulp was separated and washed with excess water, and then subjected to beating in a mill to separate the fibers. It was then passed through a diaphragm to separate the unprocessed parts, representing 3% by weight, which after collection were recycled. The pulp was obtained in a yield of 42% based on the initial straw or a yield of
59% based on the hydrolysed straw and had a permanganate number of 15.0 corresponding to a lignin content of 3.6%, by weight. After testing, the pulp was found to have very good mechanical and paper making properties. The production of pulp according to the above, but with heating to 150°C within 2 hrs and keeping at that temperature for 8 hrs, gave a pulp of very satisfactory paper making properties at a yield of 43.2% and having a permanganate number of 17.0 corresponding to a lignin content of 4.2%, by weight.

The pulps of the above quality are self sufficient to make paper of satisfactory properties. By increasing or decreasing the amount of chemicals and temperature and time of processing, there are obtained pulps containing higher or lower than optimum quantities of lignin and consequently in higher or lower yields. These qualities are not always self sufficient, but after mixing produce paper of satisfactory quality. In general, self sufficient quantities of pulp prepared as above have a permanganate number of 10 - 20, that is, contain lignin in quantities of 2 - 5%. The alkaline sulfite pulps obtained according to the above procedure are usually of good colour quality. To improve the colour quality they are decolorised with calcium hypochlorite, for example at 30°C for 2 hours, in a solution containing 9.0% of chlorine, by weight. This treatment results in a pulp of excellent colour and having very satisfactory paper making properties, with a weight loss of only 3.0% (based on the initial straw). The pulps of the above type mixed with 10 - 15% by weight of mechanical wood pulp, give a product for paper of improved writing properties.
EXAMPLE 11

In the autoclave of capacity 5 litres used in Example 10 were placed 0.8 kg of hydrolysed straw having a moisture content of 50% (produced by a hydrolysis resulting in a 16% yield of sugars) between two plates having holes and subjected to kraft pulping using 4 litres of solution having the composition: 0.110 kg NaOH and 0.05 kg of Na$_2$S, by heating at 100°C for 3 hours. After cooling, the pulp was separated from the solution, washed with excess of water, and beaten in a mill to separate the fibers. It was then passed through a diaphragm to separate the unprocessed parts, representing 5% by weight, which were collected and recycled. A pulp of the kraft type was obtained in a yield of 42%, based on the initial straw, or 55.0% based on the prehydrolysed straw, having a permanganate number of 14.0 corresponding to a lignin content of 2.5% by weight, based on the pulp. The pulp had a satisfactory colour and good mechanical properties, with characteristics of a kraft type wood pulp. A treatment as described above, but with heating to 145°C for 5 hours, gave a pulp having satisfactory properties as above with a permanganate number of 16.5 corresponding to a lignin content of 4.0%, by weight, based on the pulp.

Pulps of satisfactory kraft characteristics obtained from the treatment as described above are those having a permanganate number of between 10 to 20 which correspond to a lignin content of 2 - 6% by weight, based on the dry pulp. Smaller or greater quantities of chemicals and longer or shorter times of processing than normal, give pulps which
can not produce good quality paper, in either lower or higher yields depending on how low or high is the amount of lignin present. Those having a low content in lignin are suitable for the production of regenerated cellulose whereas those having a high content in lignin are good for wrapping and packaging. To improve the colour of the good quality pulps they are decolorised using a solution of calcium hypochlorite. With 70 gr of chlorine per kg dry pulp in the decolorising solution and treatment at 300C for 2 hrs, there are obtained pulps of satisfactory colour quality. The decolorising causes a weight loss in the pulp of 2.2% by weight (based on the initial straw).

EXAMPLE 12

In the autoclave used in Example 10 was placed successively 0.8 kg of dry weight hydrolysed straw which was subjected to kraft pulping with processing solutions, where the Na2S and NaOH are artially replaced by Na2SO3. In four such runs, the effect of the degree of substitution by Na2SO3 on the yield and the quality of the pulp was examined. The following solutions and conditions of treatment were used:

a) A solution of Na2SO3 0.040 kg, Na2S 0.112 kg and NaOH of 0.233 kg, per kg of dry pulp, processing at 1600C for 3 hours.

b) A solution of Na2SO3 0.080 kg, Na2S 0.100 kg and NaOH 0.205 kg, per kg of dry pulp and processing at 1600C for 3.5 hrs.

c) A solution of Na2SO3 0.20 kg, Na2S 0.088 kg and NaOH 0.177 kg, per kg of dry pulp, processing at 1600C for
4 hours.

Progressing from a→c the pulps obtained showed a yield improvement of from 42 to 44% and also a colour improvement. There was observed in the results obtained from a→c, a progressing change in the kraft characteristics. The lignin content was in a) 4.8% and in c) 2.5% by weight. All these pulps were of satisfactory mechanical and paper making properties.

EXAMPLE 13

A flask of 5 litres capacity was used which was equipped with a stirrer a system for introducing chlorine and external cooling with running water into this flask was placed 0.4 kg of hydrolysed straw (dry weight) obtained by a hydrolysis which resulted in a 23% yield by weight of sugars. The hydrolysed straw had a moisture content of 5% by weight. After slow and careful agitation, the mass became homogeneous and then chlorine gas was introduced at a flow rate of 2 litres/minute and at a constant temperature of 30°C. After 10 minutes of chlorine flow, the hydrolysed straw had become homogeneously pink in colour. An absorption of 0.35 kg of Cl₂ per kg of dry pulp was recorded. To complete the chlorination, the mixture was agitated for 60 minutes and after this, it was poured into 10 litres of water. The solid residue was drained and washed with a 3% NaOH solution, followed by water washing until it was neutral. The pulp was thus delignified to the right extent and was of a quality suitable for use. It was obtained in a yield of 48 - 51% by weight based on the initial straw, and had a lignin content of 4.3% by weight. The colour of the pulp was very
satisfactory but after a mild decoloration treatment, improved further. The weight loss on decoloration was 3% by weight, based on the initial straw. By changing the quantity of absorbed chlorine, by 20%, the lignin content was further lowered by 50 - 60% and the yield dropped by 2 - 2.5%. On the other hand, by reduction of the absorbed chlorine by 20%, the lignin content was further increased by 100 - 150% and the yield in pulp increased by 2 - 3% units. With the above examples it is shown that delignification with chlorine is a special treatment for pulping the prehydrolysed straw of this invention and that the improved results in quality and in yield of pulp are determined by treatment conditions which are narrowly defined.

EXAMPLE 14

Hydrolysed straw resulting from a hydrolysis which produced a yield of less than 23% of sugar was successfully used in the production of pulp under the following conditions:
a) Hydrolysed straw, resulting from a hydrolysis which produced a yield of 19% of sugars was pulped according to Example 10 with an alkaliel sulfite solution to give a pulp which, after decolorising, was obtained in a yield of 41.5% based on the initial straw. This pulp had satisfactory paper making properties.
b) Hydrolysed straw resulting from a hydrolysis which produced a yield of 15.6% of sugars was pulped according to Example 11, to kraft pulp. A pulp of satisfactory colour and mechanical properties containing 2.6% lignin was obtained.
After mild decolorising, it was shown to be suitable for making paper of good quality.

EXAMPLE 15

a) The cellulosic residue obtained from the hydrolysis treatment of barley straw described in Example 8 was pulped to produce a sulfite pulp according to Example 10. After mild decolorising, the pulp was obtained in a yield of 40% based on the initial straw, having a lignin content of 1.5% and satisfactory paper making properties.
THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:-

1. A process of hydrolysing a cereal straw to produce monosaccharides and a cellulosic residue rich in cellulose suitable for processing to chemical pulp and to pure cellulose comprising: subjecting the cereal straw to acid hydrolysis at temperatures between 100-160°C, the acid being present at a concentration of 0.1 - 1% by weight, for a reaction time between 10-120 minutes, for hydrolysis to monosaccharides representing 15-23% by weight of the initial untreated straw, and to a cellulosic residue representing 68-76% by weight of the initial untreated straw, the cellulosic residue comprising 52-58% alpha-cellulose by weight calculated on dry residue, wherein the acid hydrolysing reactant is selected from at least one of the following: H₂SO₄, sulphurous acid, HCl, HNO₃, H₃PO₄, HClO₄, ClCH₂COOH or p-CH₃-C₆H₄-SO₃H.

2. A process as claimed in claim 1 wherein the hydrolysis treatment is performed under pressure.

3. A process as claimed in claim 1 or claim 2 wherein the cellulosic residue, after the hydrolysis treatment, is washed with water and/or with a 1 - 3% sodium hydroxide solution and thereafter is compressed to a product having a moisture content of 40 - 50% by weight.

4. A process as claimed in claim 3 wherein the solution obtained after hydrolysis and the washing solution and the compressing solution are mixed to form a solution having a concentration of 1.2 - 5.0% in sugars, by weight which
adjusting to the original acid strength is recycled as a whole or partly as hydrolysis solution until a final concentration of 6 - 8% in sugars by weight, is obtained and 90 - 95% of the sugars in the final concentrated solution are monosaccharides.

5. A process as claimed in claim 2 wherein the composition of the monosaccharides in the hydrolysis solution is:

- xylose 67 - 75%
- mannose 1.2 - 5.0%
- arabinose 10 - 18%
- glucose 5 - 12%
- galactose 2 - 4%

and the cellulosic residue composition is:

- alpha-cellulose 52 - 54%
- hemicelluloses 11 - 13%
- lignin 21 - 23%
- extractables 10 - 13%
- ash 5 - 6%

all the percentages being by weight, and a degree of polymerisation of 790 - 830 glucose units.

6. A process for the production of chemical pulp wherein the cellulosic residue of the straw hydrolysis process defined in claim 1 or claim 2, in which the yield of monosaccharides was 17 - 20% by weight, is treated with an alkaline solution of sulfite salts, and then heated within two hours up to 150 - 160°C and maintained at that temperature for 5 - 6 hours.

7. A process as claimed in claim 6 wherein the alkaline solution of sulfite salts contains 255 kg Na₂SO₃ and 85 kg NaOH per ton of dry pulp.

8. A process for the production of kraft pulp wherein the cellulosic residue of the straw hydrolysis process defined in claim 1 or claim 2, in which the yield of sugars was 15 - 19% by weight, is treated with a kraft pulping solution containing Na₂S and NaOH and with a pulping solution in
which \( \text{Na}_2\text{S} \) and \( \text{NaOH} \) are partially replaced by \( \text{Na}_2\text{SO}_3 \), and then heated up to 150 - 160°C and maintained at that temperature for 4 - 6 hours.

9. A process as claimed in claim 8 wherein the kraft pulping solution contains 125 kg \( \text{Na}_2\text{S} \) and 260 kg \( \text{NaOH} \) per ton of dry pulp.

10. A process as claimed in claim 8 or 9 wherein the pulping chemicals \( \text{Na}_2\text{S} \) and \( \text{NaOH} \) are partially replaced by \( \text{Na}_2\text{SO}_3 \) in a quantity of 0.1 to 30% by weight.

11. A process as claimed in claim 1 or claim 2 wherein the cellulosic residue of straw hydrolysis, after hydrolysis to 20 - 23% by weight, in monosaccharides, is treated with chlorine in a horizontal slow rotating reactor or a slowly agitated reactor of the vertical type, until up to 20% by weight of chlorine based on the hydrolysis residue treated is absorbed, and is subsequently washed with water and alkaline solution until neutral.

12. A process as claimed in claim 1 or 2 wherein to obtain a pulp of improved colour quality the residue from the straw hydrolysis is washed with a 1 - 3% solution of \( \text{NaOH} \) before pulping.

13. A process as claimed in claim 11 wherein the pulp obtained is decolorised with calcium hypochlorite in a mild treatment resulting in a weight loss of only 2 - 3% by weight.

14. A process as claimed in any one of claims 1, 2, 6, 8 and 11 wherein alfalfa or rice straw is subjected to the hydrolysis treatment for the production of a cellulosic residue.
15. A process as claimed in any of claims 1 to 14 wherein in the hydrolysis there are obtained sugars in quantities up to 23%, dry pulp up to 51% and lignin up to 13% by weight, based on the initial untreated straw.

16. A process as claimed in claim 1 substantially as herein described with specific reference to any one of Examples 1, 2, 3, 4, 5, 6, 7 and 8.

17. A process for the production of a chemical pulp from a cellullosic residue obtained by the process defined in claim 1, substantially as herein described with reference to any one of Examples 10, 11, 12, 13, 14 and 15.

DATED this 3rd day of August, 1979.

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