1921

Glucose from corn cobs

Barney Nudelman

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GLUCOSE FROM CORN COBS

By

B. NUDELMAN

A

THESIS

submitted to the faculty of the
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MASTER OF SCIENCE IN CHEMISTRY

Rolla, Mo.

1921

Approved by

W. D. Turner

Head, Department of Chemistry
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- 00000 -
The efforts of American chemists in recent years have been devoted largely to the utilization of our waste products. This was particularly true during the war and will, no doubt, continue to be true in the years to come as our natural resources become depleted. Corn cobs offer a particularly inviting field for research along this line on account of the large supply of cobs available and the variety of substances obtainable from them. One of the leaders in this branch of investigation is Dr. F. B. LaForge of the Chemistry Division of the Bureau of Agriculture, who has contributed numerous papers on the subject. In one of these,* in collaboration with C. S. Hudson, he describes, among other things, the preparation of glucose, but recognizes the commercial limitations of the process on account of the cost of the large amount of sulfuric acid used. It was in the hope that the conversion of cellulose to glucose might be accomplished using weaker acid under moderate temperatures and pressures, thus making the process commercially possible, that the present work was undertaken. While the results were disappointing, the hope has not been entirely

* "The Preparation of Several Useful Substances from Corn Cobs" - Journal of Industrial & Engineering Chemistry, X 925 (1918)
abandoned, because lack of time and suitable apparatus prevented as thorough an investigation of the subject as was desired. The writer wishes to express his indebtedness to Dr. LaForge for helpful information and Dr. J. D. Turner and Mr. H. L. Dunlap for kindly suggestions.
It was decided to run several batches of cobs by the method described by LaForge and Hudson before attempting any hydrolyses under elevated temperatures. Five hundred grams of shredded cobs were placed in a small enamel-lined steam-jacketed Elyria autoclave and covered with four liters of water. The temperature was gradually raised during an hour to a maximum of 150\degree C. During the digestion, the material was thoroughly stirred by means of an automatic stirrer driven by a one-fourth horsepower motor. After cooling below the boiling point of water, the autoclave was opened and the contents removed and filtered on a suction filter, after which the residue was pressed in a powerful screw press. The filtrate from this operation, on being concentrated, yields a brown adhesive which can be used in fiber board and paper box manufacturing. About thirty per cent. of the weight of the dry cobs is extracted as adhesive by this treatment. The residue is returned to the autoclave, covered with an excess of 1.8% sulfuric acid and heated to 130\degree C. This treatment liberates xylose and acetic acid together with some furfural. The yields of xylose and acetic acid are comparatively small, being about five and three
per cent. respectively, so that in commercial practice it would be more efficient to use the solution containing them to digest succeeding batches until their concentration had been built up to a desired degree. The contents of the autoclave are treated as before to separate the liquid from the residue, which is the crude cellulose from which the glucose is to be obtained.

To this point in the process our results conform with those of LaForge and Hudson, but in the treatment of the cellulose cake we are unable to agree. They claim to grind the residue to a fine powder and mix it intimately with an equal weight of 75% sulfuric acid "considering the small amount of moisture left in the cake after the pressing operation" when calculating the amount of acid to be added. From the very nature of corn cobs we would expect them to retain considerable moisture even when subjected to high pressures. As shown in the table on page 6, four different samples analyzed 72, 75, 61 and 72½ moisture.
<table>
<thead>
<tr>
<th>Number</th>
<th>Per Cent. moisture in residue from dilute acid treatment</th>
<th>Per cent. cobs extracted by water and dilute acid treatment</th>
<th>Weight 75% acid used expressed as % weight of crude cellulose</th>
<th>Glucose expressed as per cent. dry cobs</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>100</td>
<td></td>
<td></td>
<td>3.14</td>
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<tr>
<td>2</td>
<td>72</td>
<td>61</td>
<td>100</td>
<td>Fermented</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2.84</td>
</tr>
<tr>
<td>3</td>
<td>75</td>
<td>56</td>
<td>100</td>
<td>2.84</td>
</tr>
<tr>
<td>4</td>
<td>61</td>
<td>60</td>
<td>315</td>
<td>1.67</td>
</tr>
<tr>
<td>4a</td>
<td></td>
<td></td>
<td>150</td>
<td>0.48</td>
</tr>
<tr>
<td>5</td>
<td>72</td>
<td>57</td>
<td>250</td>
<td>3.89</td>
</tr>
<tr>
<td>5a</td>
<td></td>
<td></td>
<td>100</td>
<td>0.75</td>
</tr>
</tbody>
</table>
The press employed consisted of a cylinder of six-inch iron pipe with numerous eighth inch holes drilled through it, resting on a solid wooden base and having an iron plate to fit snugly in it. Pressure is applied to this plate by means of a screw, thus forcing the solution out through the holes.

It is of course obvious that with so large a percentage of moisture it is impossible to add a weight of 75\% acid equal to the weight of the dry cobs, so the residue was carefully dried on a steam-heated sand-bath to avoid charring, to a point where the moisture content was low enough to avoid reducing the acid concentration below 75\%. It was observed that when the residue was dried to this extent, an equal weight of 75\% acid was not sufficient to even moisten all of it. A communication was addressed to Dr. LaForge asking for figures on the amount of moisture left in his crude cellulose cake after pressing. His reply merely stated that the cake was partially dried and the amount of moisture left in it considered when making up the acid.

For the first three batches an equal weight of acid was all that was used, an effort being made to get as intimate contact as possible between acid
and cellulose. For the fourth, twice the weight of 75\% acid was used and the residue from this treatment subjected to further action with twice its weight of the same strength of acid. The fifth batch was treated with three times its weight of strong acid and the residue with its own weight for the second treatment.

In the case of these first five batches, the stiff dough of acid and cellulose was permitted to stand seven hours at room temperature at the end of which time seven or eight volumes of water were added and the mixture boiled for an hour. It was then filtered, using strong suction and the residue washed thoroughly with hot water. The filtrate was neutralized with lime and the resultant precipitate of calcium sulfate removed by filtration. The solutions resulting from this treatment were yellow to brown. Enough of the coloring matter could be removed by boiling with charcoal to make titration possible. In each case the volume of the solution was measured and the amount of glucose in it determined by measuring the amount necessary to precipitate the copper from a given quantity of Fehling's solution.
The Fehling's solution was prepared according to directions given in "Methods of Analysis" Bulletin 107 of the Bureau of Chemistry, and carefully standardized against chemically pure glucose. Four determinations showed that one c.c. of Fehling's solution would be reduced by .00481, .00478, .00480, and .00483 of glucose.

The second batch fermented making titration impossible, while the others gave the results tabulated.
TABLE II

<table>
<thead>
<tr>
<th>Number</th>
<th>Volume of final solution</th>
<th>Volume used to precipitate 20 cc. of Fehling's solution</th>
<th>Weight of sugar</th>
<th>Weight of dry cobs</th>
<th>Per cent. sugar</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2310</td>
<td>16</td>
<td>15.85</td>
<td>457</td>
<td>3.14</td>
</tr>
<tr>
<td>3</td>
<td>4050</td>
<td>30</td>
<td>12.95</td>
<td>457</td>
<td>2.84</td>
</tr>
<tr>
<td>4</td>
<td>6440</td>
<td>40.7</td>
<td>15.2</td>
<td>913</td>
<td>1.67</td>
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<tr>
<td>4a</td>
<td>4000</td>
<td>87.1</td>
<td>4.41</td>
<td>913</td>
<td>0.48</td>
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<tr>
<td>5</td>
<td>3050</td>
<td>11</td>
<td>26.65</td>
<td>685</td>
<td>3.89</td>
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<tr>
<td>5a</td>
<td>2770</td>
<td>52</td>
<td>5.12</td>
<td>685</td>
<td>0.75</td>
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</tbody>
</table>

EXPLANATION: Since each c.c. of Fehling's solution corresponds to .004805 grams glucose, twenty c.c. corresponds to .0961 gm. Taking No. 1 for an example

\[
\frac{2310}{16} \times 0.0961 = 13.85 \text{ gms. of sugar obtained.}
\]

This is 13.85 or 3.14\% based on the weight of dry cobs. For one, two and three 500 gms. of cobs were used, for four 1000 gms. and for five 750 gms. In each case the 8.63\% moisture is deducted.
These figures do not compare very favorably with the 25% claimed by LaForge and Hudson. They say that an additional 12% yield is obtainable by treating the residue with an equal weight of 75% acid a second time or a total of 37% based on the weight of dry cobs. The results given under 4a and 5a are those obtained by treating the residues from 4 and 5 respectively, a second time.

There appears to be no relationship between the quantity of acid used and the amount of sugar formed. It might be expected that a deficiency of acid would cause a low yield because all the cellulose did not have a chance to react, or that a large excess would cause charring. As a matter of fact, charring occurred in each case suggesting the probability that 75% acid is too strong.

It was next decided to study the effect of weaker acid at moderate temperatures. Two more batches were run in the same manner as the preceding five to the point where the crude cellulose is obtained. The residue from the sixth was treated with twice its weight of 50% sulfuric acid, heated in the autoclave for three hours between 95 - 115°
and then boiled at atmospheric pressure with four
liters of water for an hour. The seventh was treated
with three times its weight of 35% acid for three
hours between 100 - 140° and then boiled with excess
of water for an hour.

After the residue had been removed and the
acid neutralized with lime these two solutions were
so dark as to render titration impossible. Boiling
with charcoal was tried but proved of no avail. Basic
lead acetate was then added to precipitate the color-
ing matter and the excess of lead removed by addition
of sulfuric acid. While this procedure decolorized
the solution thoroughly, it is quite likely that it
also extracted the sugar mechanically on account of
the numerous filtrations necessary, even though each
precipitate was carefully washed five to ten times.
On adding these solutions to Fehling's solution the
only effect was to reduce the blue color to green in-
dicating a trace of sugar.

Due to numerous difficulties of manipulation,
there remain several additional problems for future
investigation.
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Chemical Age XXVIII (1920)

Preparation of Xylose From Corn Cobs

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Preparation of Xylose From Corn Cobs

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Journal of the American Chemical Society XLI - 1002 (1919)
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C.A. VI 3340  U.S. 1,037,185 (1912) Gallagher and Mork
Making fermentable sugars from lignocellulose

C.A. VII. U.S. 1,056,161 (1913) Gallagher and Mork
Chlorinating cellulose, then digesting with steam under pressure with $H_2SO_4$.

C.A. VIII 3364  Canada 156,539 (1914) Gallagher and Mork
Use of sulfite liquor for hydrolysis. Treating with hydrolyzing agent until considerable has dissolved, then continuing digestion at lower temperature. Spent residue subjected to further treatment with $H_2SO_4$ and a soluble metal chloride under pressure.

C.A. VII 2321. Sweden 33,876 (1910) P.G. Ekstrom
Cellulose or sulfite back-water boiled five hours with 70 - 80% $H_2SO_4$.

Same as above.

Fermentable sugar from cellulose. Cellulose is treated with chlorine in conjunction with sulfuric acid or other hydrolyzing acid. Steam under pressure may also be used.

C.A. IX 2124. Germany 279,991. Standard Alcohol Co. (1913)
Fermentable sugar from cellulose.
   Same as above.

   Sugar from cellulose. Cellulose containing material boiled under pressure with sulfite lye, which before hydrolyzing is acidified by addition of a strong acid, to release the weaker acid SO₂, which is the active hydrolyzing agent.

   Adhesive from cobs. Digesting cobs with hot 1% NaOH and concentrating the resultant liquid.

C.A. XIII 252 U.S. 1,285,247 (1919) F. B. LaForge
   Adhesive from cobs. Corn cobs are heated under pressure with water to cause separation and solution of colloidal matter, and the colloidal solution separated from the residue of insoluble materials by pressing and then concentrated to a thick syrup, which is adapted for use as an adhesive. Dedicated to the public for free use.
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