Studies on the Alcoholization of Cellulose Materials.
Part IV.
On the Saccharified Solution of Mulberry-tree.

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The components of the saccharified solution of a wood which are produced by diluted acid at high temperatures and pressures are the decomposed products of the components of a wood and their secondary products. Up to the present, many experiments on this problem have been carried out, but probably because of their complication, there are few reports published. It seems that the components of the saccharified solution of a wood are different not only according to the condition of the saccharification but the kind of wood.

The author will make clear the components of the saccharified solution of the mulberry-tree which is prepared by Scholler's method for various fermentative industries.

Method of Experiment

The saccharified solution used was the same as described in the report on the saccharification of the mulberry-tree by Scholler's method (7500 c.c. of the saccharified solution obtained from 500 g of the mulberry-tree.) The sample was analysed as follows. The saccharified solution is thoroughly neutralized with barium hydroxide, the precipitate produced is filtered off, and the solid substances, ashes and reducing sugars in the filtrate are measured. After distilling the same filtrate with steam until the acetic acid anilin reaction is negative and pH 6.5, the acidity of the distillate is titrated with N/10 natrium hydroxide. As for the volatile acid salts obtained from the evaporation of a part of the neutralized distillate, formic, acetic and lavulinic acids are tested and determined. In another part of the neutralized distillate, furfurol and oxymethylfurfurol are tested and determined. The residue from the steam distillation is neutralized and extracted with ethyl ether. Part of the residue extracted with ethylether, after having been evaporated to dryness, is used for the measurement of solid substances and ashes, and the other part is concentrated under
low pressures. Absolute ethyl alcohol is added to the concentrated solution until the concentration of the alcoholic solution produced is 80%. The yellowish brown precipitate produced at the same time is filtered, washed with 80% ethyl alcohol, dried up in a sulfuric acid desiccator and measured. Dissolving this precipitate in hot water, the water solution produced is tested. Concentrating this 80% alcoholic solution under low pressures, the ethyl alcohol contained is removed. The concentrated solution is diluted with water and neutralized with diluted sulfuric acid. The barium sulfate produced being filtered off, the filtrate is tested.

Experimental Results

As for the saccharified solution the weight of the solid substances contained are 186.00g — 37.33% to the raw materials, that of ashes 17.25g — 5.45% and that of reducing sugars 167.75g — 33.55%. The ethyl ether extracts are very small in amount. The natrium-nitro-prusside reaction to aceton is negative. At the first stage of the saccharification the saccharified solution is rich in furfurol, but it gradually reduces furfurol and at the end shows a trace of it. The concentration of furfurol is on an average 0.01g per 100 c.c. saccharified solution — 0.82% to the raw materials. It seems that the production of furfurol is dependent on the temperature, the hour and the acid concentration of the saccharification. The concentration of oxymethyl-furfurol is on an average 0.00028g per 100 c.c. saccharified solution — 0.021% to the raw materials. Formic, acetic and lavulinic acids are surely found as the volatile organic acid and the concentration of their acids is on an average 0.2165g per 100 c.c. saccharified solution as the acetic acid — 3.25% to the raw materials. The ferric chloride reaction to the distilled solution with steam is negative.

The saccharified solution, from which sulfuric acid, volatile substances and other soluble materials, have been removed, contains 162g solid substances and the concentration is 2.16g per 100c.c. — 32.4% to the raw materials. After concentrating this sacharified solution under low pressures, absolute alcohol is added until the concentration of the alcoholic solution produced is 80% and simultaneously the yellow precipitate is produced so-called fumin substance. The weight of this precipitation dried up is 58.04g. The dried precipitate being washed with hot water, the water solution produced contains barium, which

is removed surely with sulfuric acid. The following tests have been carried out. (1) Reducing the Fehling solution. (2) Producing brown precipitate on adding lead acetate. (3) Not forming hydrazone and osazone. (4) Uncertainty examining glucose by the potash-saccharic acid method, galactose by the mucic acid method and uronic acid by the naphthoresorcin method. (5) Producing ethyl alcohol by the yeast, the ability of the fermentation being 61.32%.

The 80% ethyl alcohol solution, filtrated off the precipitate, is concentrated under low pressures, diluted with distilled water and the precipitate is not produced on adding lead acetate to it. Therefore, it seems that this solution is considerably pure as a sugar solution. The following examinations on the monosaccharides have been carried out. Solid materials in the solution is 101.17g—20.23% to the raw materials. The solution is coloured slightly, but not completely decolourized with active carbon. It seems that other substances are slightly contained because the ferric chloride reaction is black and the acetic acid anilin reaction is red. Pentose is found surely because the Phloroglucin reaction and the Orucin are positive. By the potashsaccharic acid method the crystal of glucose derivative is slightly produced—m.p. 130—132°C, and the presence of galactose by the mucic acid reaction is negative. The presence of ketose by Seliwanoif's method is remarkable. Regardless of producing d-fructose-α-methyl-phenyl hydrazone with methyl phenyl hydrazone, a substance crystallizes—m.p. 173—174°C and is unknown. This crystal seems to be the decomposed or condensed products of glucose—fumin substance, etc.

The test of various sugars which are surely contained by the phenyllosazone method is as follows. From the solution, with phenylhydrazine a crystal comes out, and melts at 188°C—d-mannose-phenylhydrazone and with excess phenylhydrazine no crystal comes out. Next with diphenylhydrazine a crystal comes out and melts at 204—205°C—1-arabinose-phenylhydrazone. A crystal formed with methyl phenyl hydrazine has been mentioned above and with p-Br-phenylhydrazine a crystal comes out and melts at 160°C—1-arabinose-p-Br-phenyl-hydrazone. Producing ethyl alcohol by the yeast, the ability of the fermentation is 80.50%.

Conclusions

The author studied on the components of the saccharified solution.
of Mulberry-tree. The presence of furfurol and the like which obstruct the alcoholic fermentation is plain enough, but it seems that the amount of them is not harmful. There is fumig substance and it complicates the components of the saccharified solution. Mannose, arabinose and glucose are surely detected, but glucose only is not isolated. 80% of sugars separated from the saccharified solution is fermentative.

**Literature**


2) H. Katagiri, C. Tatsumi: Reports of Institute for Chem. Research of Kyoto University, 15, 67 (1946), 16, 46 (1947).