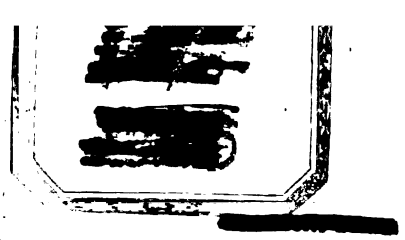
HYDROXY-ACIDS FROM CELLULOSE DECOMPOSITION

Thesis for the Degree of M. S.
MICHIGAN STATE COLLEGE
Wen Tah Tsiang
1947



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HYDROXY-ACIDS FROM
CELLULOSE DECOMPOSITION

presented by

Wen TAH Tsiang

has been accepted towards fulfillment
of the requirements for

MASTERS degree in CHEMICAL ENGINEERING

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Date May 28, 1947

M-795

HYDROXY-ACIDS FROM CELLULOSE DECOMPOSITION

By

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A THESIS

Submitted to the Graduate School of Michigan State College of Agriculture and Applied Science in partial fulfilment of the requirements for the degree of

MASTER OF SCIENCE

Department of Chemical and Metallurgical Engineering

1947

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ACKNOWLEDGEMENT

The author wishes to express to Dr. Clyde Colvin DeWitt and Dr. Richard Thurm his deepest appreciation and gratitude for their unfailing guidance and suggestions which have made this investigation possible.

INTRODUCTION

Each year, in every country many tons of cellulose material is burned or is otherwise wasted. In the present processes of rayon manufacture, large quantities of degraded cellulose find their way to waste heaps, or they are burned to recover their potential soda ash content. The same type of degraded cellulose waste material is found in the effluent solutions from the brewing industry, the cellophane industry, the ethyl-cellulose industry, the wood sugar industry, and from the manufacture of soda-pulp for paper manufacture.

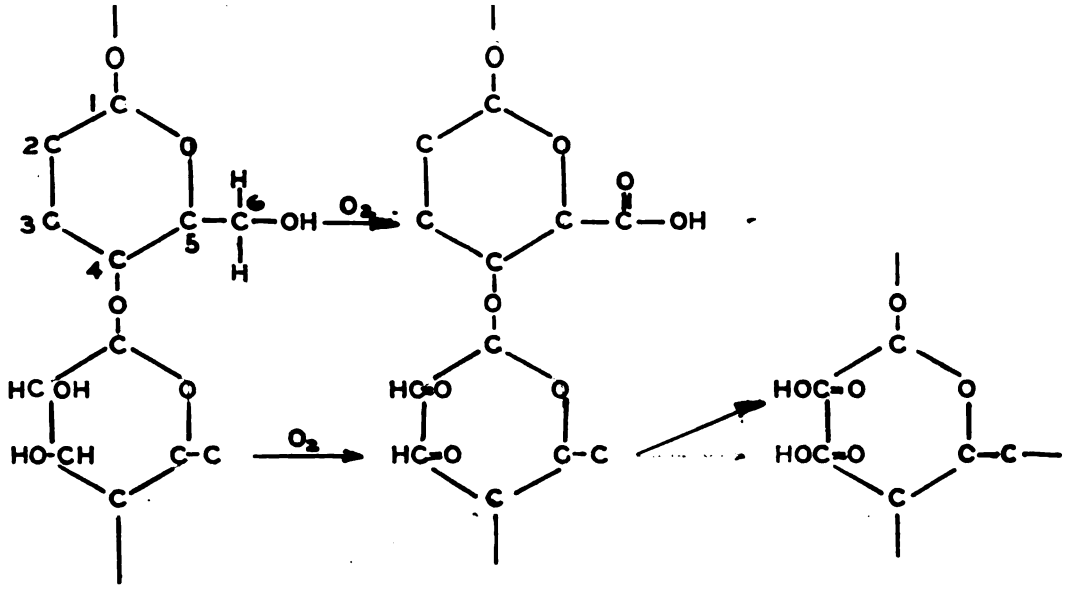
It has long been recognized that these solutions contain complex soluble mixtures of organic compounds derived from the degradation of cellulose. Such materials are most always found in the form of the sodium salts of hydroxy-organic acids, or, in the case of the brewing industry, in the form of aliphatic diols. The growing industrial importance of such compounds has quickened the efforts of many investigators toward work on their recovery.

This interest has been enhanced by the insistence of State Conservation Departments that the stream pollution formerly practiced shall be discontinued. Such efforts demand large capital expenditures; the operation and maintainence costs of such processes are likewise high. The reduction of these costs through recovery of valuable products heretofore discarded is clearly within the

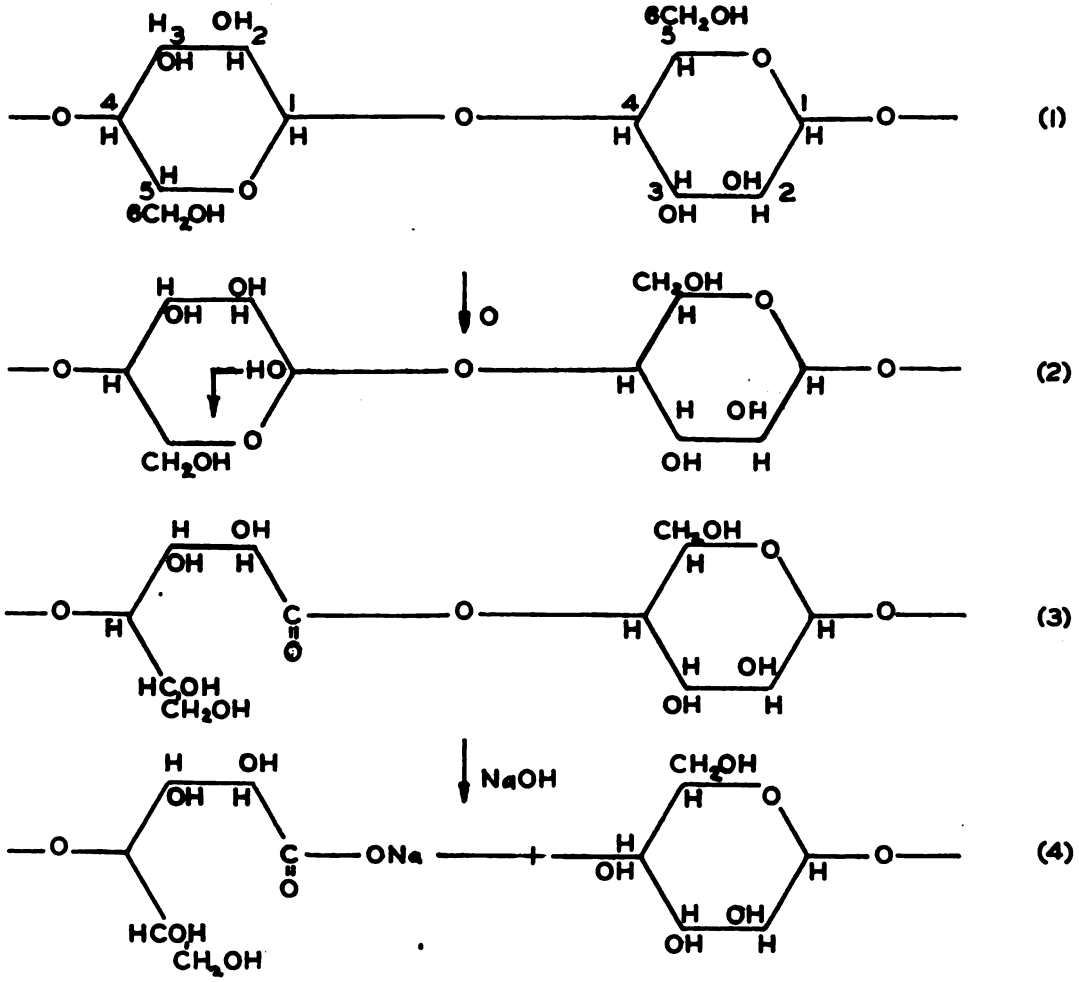
province of the chemical engineer. This thesis presents a preliminary investigation of the nature of some of the products of present industrial value that one may expect to recover from such waste solutions.

LITERATURE REVIEW

It has been known that cellulose has a stronger resistance toward alkaline solutions than acid solutions. However strong alkaline solutions at high temperatures will dissolve cellulose to an extent depending upon the alkali concentration, the temperature, and the pressure used.(1) If the cellulose is treated with strong alkali solution in the presence of air or oxidizing reagents, the cellulose will be degraded with the formation of a lower molecular weight cellulose chain. This reaction is utilized in the preparation of regenerated cellulose fibres in the rayon industry.(2) This reaction is considered to be a special kind of oxidation.(3) The chemical mechanism of the oxidative attack by strong alkali is not clearly understood. It has been explained by H. A. Rutherford and M. Harris(2) thus: "It would appear that the attack on cellulose by oxidizing reagents would be confined to three points in the anhydroglucose residue of the cellulose chain: (1) The aldehydic end groups of which there are few if any in native cellulose could be oxidized to carboxyl groups. (2) The primary alcohol groups could be oxidized to the aldehyde group or carboxylic acid depending upon the oxidizing conditions. (3) The glycol group (the 2,3 dihydroxy group) of the glucose residue could be oxidized with the formation of ketonic, aldehydic, or carboxylic groups depending upon the course of the reaction." Typical possibilities for the primary attack are formulated by H. Mark and M. Harris.(2)



In studying the ageing of alkali-cellulose in the viscose process, one of the possible explanations for the mechanism of alkaline oxidation of cellulose has been scheduled as follows:[4]



The action of strong alkali solution toward cellulose at high temperature and high pressure has been investigated by former workers.[5][6] They found that cellulose can be completely dissolved in sodium hydroxide or potassium hydroxide solutions.

In 1871 and 1889 Hoppe and Seyler[5] treated Swedish filter paper with alkali about 9 N. The cellulose went into solution at 200-240°C., with the formation of about 360 c.c. of gas per gram of cellulose. Most of this gas was hydrogen (86-8%); the solution contained formic, acetic, and other fatty acids. Later Fischer and Schrader treated filter paper with 47 grams of 4.1 N KOH and 27 grams of 5.0 N NaOH per 100 grams of cellulose at temperature 200-300°C. A quantity of CO_2 equivalent to 9.3 grams per 100 grams cellulose was obtained and about 20 grams per 100 grams cellulose was obtained as formic, acetic, and lactic acid. The hydroxy-acids have been found in larger quantities by Fischer and Schrader.[7] Oden and Lindberg[5] reported that when the mixture of cellulose and caustic soda were heated in autoclaves to 372° C, pressure at 241 atmospheres, a yellow to brown, quite transparent solution was obtained. This solution had a strong odor of methanol and mesitylene; it contained methanol, acetone, and various salts of organic acids. Oden and Lindberg[5] suggested that the first stage of decomposition was the splitting up of cellulose into glucose which is known to yield lactic acid and in turn, the lactic acid would dissociate into ketones by further reaction with caustic solution according to the following reactions:

$$2CH_3CH(OH)COONa + 2NaOH \longrightarrow (CH_3)_2CO + 2Na_2CO_3 + H_2O + CH_4$$

$$2CH_3CH(OH)COONa + 2NaOH \longrightarrow C_2H_5CH_3CO + H_2O + 2Na_2CO_3 + H_2$$

Emil Heuser[6] and his co-workers found that when soda pulp was treated with a 17% caustic soda solution at a pressure of 8-10 atmospheres, corresponding to 171-181°C, the cellulose was perfectly dissolved after 6-7 hours. From this solution lactic acid could be isolated. No detailed information is available. Heuser[6] believed that the formation of lactic acid is preceded by that of other hydroxyl carboxylic acids of greater molecular weight, such as saccharic acids, which are isomeric with glucose, a decomposition product of cellulose.[8] P. Klason[6] has found these acids in the waste liquor of the soda pulp mill.

In the soda process for the manufacture of cellulose fibre from the wood, the lignin in wood is dissolved much faster and at lower alkali concentration than cellulose. However, the comparatively low yield of cellulose-fibre by this process gives the evidence of the fact that considerable amounts of cellulose are also dissolved during the cooking period. The resulting organic acids are destroyed together with the dissolved lignin when the black liquor is burned to soda ash.

H. Kiliani[9][10] and his co-workers reported on the alkaline decomposition of the disaccharides, dextrose, and laovulose with potassium hydroxide. They found an isosaccharinic acid. When this acid was treated with $Ag(OH)_2$, acetic acid and glycolic acid were

obtained. 1,3 dihydroxy butyric and 1,2 dihydroxy butyric acids in its active forms were obtained by Nef[11][12][13] and his students in the course of their work on the effect of alkalis on the various sugars.

Evans, Glattfeld, and their co-workers [14][15][16][17][27] have done considerable work on the alkaline degradation of sugars, i.e., cellubiose, lactose, melibiose, and gentiobiose. They concluded that these sugars, when reacted with aqueous solutions of potassium hydroxide, gave lactic, acetic, and formic acids. These reactions may be explained by the endiol theory of chemical reaction in the disaccharides.

The isosaccharinic acid and dihydroxy butyric acid have also been prepared by treatment of oxycellulose with lime water. Both of these acids were obtained by Sccarachmidt and Nowak[18] by the action of nitrogen tetroxide on cellulose.

Since the cellulose contains cellubiose units, the treatment of the cellulose with acetyl bromide and glacial acetic acid has shown the existence of the cellubiose.[1][19] Therefore, all the acids which have been found in degraded disaccharides may be looked for in the alkaline solution degradation products of cellulose.

In all the previously reported work on alkaline degradation products of cellulose-like materials, the identification of these products has depended solely upon the preparation of relatively impure calcium, sodium, zinc, or silver salts. High temperature, vacuum distillation, and selective, solvent extraction have failed

to give decisive separations of the hydroxy acids such as lactic, glycolic, dihydroxy-butyric, and hydroxy-valeric acids.

Scope of Present Investigation

The object of this investigation was to prepare derivatives of these hydroxy acids from the foregoing cellulose solutions, in the hope that these derivatives of organic hydroxy acids might be separated by distillation. The identity of the compounds separated by distillation was then proven by analytical methods.

The present work indicates that the acetylation of the cellulose syrup with acetyl chloride appeared to be the most feasible way for isolating these hydroxy acids by distillation methods.

Acetylated derivatives of glycolic, lactic, and dihydroxy-butyric acids have been obtained. Primary identification has been made by boiling point range of distillates and by molecular weight determination. Barium content of respective salts has been determined. Carbon and hydrogen content of each of these acids has been checked.

The fact that the boiling points of these acetyl hydroxy acids are close to each other makes it quite difficult to prepare by distillations very pure fractions. This phase of our problem needs further attention.

EXPERIMENTAL PROCEDURE

(1) Preparation of alkaline solution of cellulose.

171.1 grams of cotton linter with 3-4% moisture content was placed in a steel autoclave previously charged with 271 grams of 25.8% caustic soda in 430 grams of distilled water. The cotton linter was thoroughly mixed with the alkali solution. The autoclave was closed and heated electrically to a temperature of 480°F. (250°C.) for six to ten hours; then cooled to room temperature. No gas was generated. All the cotton linter was dissolved. The solution had a yellowish to brownish color and possessed a characteristic odor. Different sources of cellulose, i.e., absorbant cotton, washed rugs, filter paper, and cotton linter have been used in these experiments. The same type solutions were obtained, in as far as their appearances were concerned. When the cooking temperature was lower than 350°F. (177°C.), a suspension of tiny fibres was observed. This indicated the incompleteness of cellulose dissolution. The influence of cooking time upon yields of hydroxy acids was not investigated.

(2) Treatment of cellulose solution with formaldehyde.

Murray Senkus[20] has isolated the 2,3 butanediol from beer by treating it with 50% H_2SO_4 and 36% formaldehyde. The hydroxyl groups on carbon atoms alpha and beta to each other in the butanediol react with formaldehyde to form 2,3 butanediol formal which can be distilled off over the boiling range, 97-102°C. When the cellulose was dissolved in alkali solution, the dihydroxy acids such as 2,3

dihydroxybutyric acid, dihydroxy valeric, or isosaccharinic acids, etc., were possibly formed. If any of these dihydroxy or poly hydroxy acids existed in cellulose solution, it was hoped that they might form the formal compound with formaldehyde in presence of sulfuric acid.

600 grams yellowish cotton solution from the autoclave was neutralized with 50% sulphuric acid. The evolution of gas in neutralization showed the presence of carbonate in the alkali solution. A small amount of pitch floated on the top which could easily be filtered from the cool solution. To the filtrate 20 grams Norite was added to effect decolorization. A nearly colorless filtered solution was obtained. The formic and acetic acids were separated by steam distillation. The distillation was carried on until the distillate showed but a trace of acid. (A small amount of lactic, and glycolic acid always came off with the steam.) To the residual solution, 50 c.c. of concentrated sulphuric acid and 100 c.c. of 36% formaldehyde were added. This mixture was refluxed at 100°C. for three hours, and then distilled with steam. No product was obtained.

Another batch of cotton solution was neutralized with 50% sulphuric acid, and filtered, and decolorized just as before. The clear solution was concentrated by distilling off 500 c.c. water. 200 c.c. of concentrated solution was mixed in a round bottom flask with 100 c.c. of 36% formaldehyde. The flask was provided with reflux condenser and a dropping funnel. 50 c.c. of concentrated

sulphuric acid was dropped through the funnel into the mixture. The mixture was refluxed for about five hours. Distillation of the mixture gave no product.

These experiments while negative in giving the desired separation, showed that the essential nature of the diol separation is substantially different in mechanism than the previous investigators work seemed to indicate.

(3) Acetylation of cellulose syrup with acetylchloride.

1600 grams of sulphuric acid neutralized cellulose solution in which 300 grams of cotton linter has been dissolved was decolorized with Norite, and the solids filtered. The clear solution was evaporated in a vacuum at a temperature of 70-80°C. until a yellowish syrup was formed. The syrup was extracted from inorganic salts with 99% methyl alcohol. The methanol extract was distilled on a water bath. When all solvent was driven off, several 50 gram lots of glacial acetic acid were added and distilled off under vacuum. When the density of the distillate reached that of pure glacial acetic acid, all of the water remaining in the syrup had been carried off with acetic acid vapor. 150 grams acetylchloride and 10 grams anhydrous sodium acetate were then added to the dried syrup; the mixture was refluxed gently on a water bath for about five hours. The reaction mixture was dissolved in glacial acetic acid; the undissolved solids, most of which are sodium chloride, were filtered. The filtrate was distilled in a vacuum on an oil bath at about 250° C. When all acetic acid had been distilled off, the temperature

raised suddenly, and a colorless to slight yellow liquid began to come off at 120°C. at 12 mm. The distillate of boiling point range from 120°C. to 170°C. was collected. The weight of crude oil was 53 grams. The total yields of these acetyl hydroxyl acids is about 18% based on the total weight of cotton linter charged.

The crude oil was redistilled in vacuum. Three fractions were obtained. The specific gravity of each fraction was determined (Table 2).

Hydrochloric acid in place of sulfuric acid was used in a similar neutralization of the solution of cellulose. When the same procedure noted above was used, no vacuum distilled product was obtained. In this case the acetylation was carried out with acetyl chloride in the presence of dry hydrochloric acid gas.[21)(27)

TABLE I

Run No.	Raw Material	Weight of Cellulose	Weight of NaOH	Weight of Water	Heating Time	Temperature of Cooking	Remarks
1	absorbent cotton	100 gms	200 gms 25%	300 gms	15 hrs.	350°C.	brownish solution with suspending fibres
2	"	" "	" "	" "	" "	480°C.	complete brownish solution
3	"	150 gms	300 gms 25% soln.	350 gms	16 hrs.	480°C.	" "
4	raw cotton	150 gms	75 gms solid	800 gms	8½ hrs.	480°C.	more tarry material
5	cotton linter	150 gms	75 gms solid	700 gms	21 hrs.	480°C.	lighter colored
6	"	150 gms	"	800 gms	16 hrs.	480°C.	" "
7	washed rags	170 gms	75 gms	700 gms	16 hrs.	480°C.	brown solution more oily
8	filter paper	170 gms	75 gms	700 gms	9 hrs.	480°C.	lighter colored solution
9	cotton linter	171 gms	271 gms 25.8% soln.	430 gms	15 hrs.	480°C.	" "
10	" "	171 gms	"	" "	6 hrs.	480°C.	lighter colored solution
11	" "	" "	"	" "	3 hrs.	480°C.	solution with suspending fibres
12	" "	" "	"	" "	16 hrs.	400°C.	complete solution

TABLE II

Fraction No.	Boiling temperature at 10-13 mm. vacuum	Specific gravity at 25°C.
A	128-130°C.	1.1767
B	130-145°C.	1.1771
C	145-148°C.	1.1776

ANALYSIS

(1) Preparation of barium salts.

Weigh out one gram of each acetylated hydroxy acids from the above distillation fractions. Titrate the acid with 0.37 N$Ba(OH)_2$ at a temperature, 3-5°C., using phenolphthalein as indicator. The red color of indicator will fade gradually on standing. (This may be explained as caused by the hydrolysis of the small amount of lactone existing with the hydroxy acids. When in alkali solution the lactone ring of acid opens to form the corresponding hydroxy acid.) Then to the solution, add 50 c.c. excess $Ba(OH)_2$, and reflux gently for several hours. The residue is neutralized with 0.50 N sulphuric acid, and an excess is added. Distill off the acetic acid with steam until the final distillate shows very slight acidity. Filter off the $BaSO_4$. Exactly neutralize the clear filtrate with $Ba(OH)_2$ to a point where neither barium nor sulphuric acid shows its presence. Evaporate to dryness at 100-120°C. An amophorous salt of barium is obtained. Analyze for the Ba content of this salt.

Barium Contents:

Fraction A	I	II
Weight of crucible and sample	15.5657 gms	16.4503 gms
Weight of crucible	15.1514 "	16.0479 "
Weight of sample	0.4143 "	0.4024 "
Weight of ash (as $BaSO_4$) and crucible	15.4502 "	16.3379 "
Weight of crucible	15.1514 "	16.0479 "
Weight of $BaSO_4$	0.2988 "	0.2900 "

Weight of Ba $0.2988 \times \frac{137.36}{233.42} = 0.1758$ gms

% of Ba $\frac{0.1758}{0.4143} \times 100 = 42.43$

Weight of Ba $0.2900 \times \frac{137.36}{233.42} = 0.1706$ gms

% of Ba $\frac{0.1706}{0.4024} \times 100 = 42.40$

Fraction B	I	II
Weight of crucible and sample	15.3746 gms	15.4244 gms
Weight of crucible	15.1501 "	15.1503 "
Weight of sample	0.2245 "	0.2741 "
Weight of ash ($BaSO_4$) and crucible	15.3182 "	15.3543 "
Weight of crucible	15.1501 "	15.1503 "
Weight of $BaSO_4$	0.1681 "	0.2040 "

Weight of Ba $0.1681 \times \frac{137.36}{233.42} = 0.0987$ gms

% of Ba $\frac{0.0987}{0.2245} \times 100 = 43.95$

Weight of Ba $0.2040 \times \frac{137.36}{233.42} = 0.1200$ gms

% of Ba $\frac{0.1200}{0.2741} \times 100 = 43.78$

Fraction C	I	II
Weight of crucible and sample	16.2716 gms	15.3968 gms
Weight of crucible	16.0431 "	15.1506 "
Weight of sample	0.2285 "	0.2462 "
Weight of ash ($BaSO_4$) and crucible	16.2111 "	15.3333 "
Weight of crucible	16.0431 "	15.1506 "
Weight of $BaSO_4$	0.1680 "	0.1827 "

Weight of Ba $0.1680 \times \frac{137.36}{233.42} = 0.0990$ gms

% of Ba $\frac{0.0990}{0.2285} \times 100 = 43.28$

Weight of $BaSO_4$ $0.1827 \times \frac{137.36}{233.42} = 0.1074$ gms

% of Ba $\frac{0.1074}{0.2462} \times 100 = 43.60$

(II) Determination of molecular weight - by Beckmann's Freezing Point Depression Method.

Use glacial acetic acid as solvent which has a constant 3.90.

$$M = \frac{1000\ K_f g}{\Delta T_f\ G}$$

Fraction A	I	II
G, Weight of acetic acid	23.6276 gms	28.2373 gms
g, Weight of acetyl acid	0.7630 gms	0.3687 gms
T_1	4.475 °C	2.175 °C
T_2	3.400 °C	1.732 °C
ΔT_f	1.075 °C	1.732 °C

$$M = \frac{1000 \times 3.90 \times 0.763}{1.075 \times 23.6276} = 116.9$$

$$M = \frac{1000 \times 3.90 \times 0.3687}{0.443 \times 28.2373} = 115.0$$

Fraction B	I	II
G, Weight of acetic acid	27.9000 gms	29.8543 gms
g, Weight of acetyl acid	0.3985 "	0.4120 "
T_1	2.132 °C	2.012 °C
T_2	1.750 °C	1.643 °C
ΔT_f	0.382 °C	0.369 °C

$$M = \frac{1000 \times 3.90 \times 0.3985}{0.382 \times 27.9000} = 146.1$$

$$M = \frac{1000 \times 3.90 \times 0.4120}{0.369 \times 29.8543} = 145.9$$

Fraction C	I	II
G, Weight of acetic acid	31.4060 gms	29.9745 gms
g, Weight of acetyl acid	0.5093 "	0.4372 "
T_1	2.070 °C	2.125 °C
T_2	1.630 "	1.725 "
ΔT_f	0.440 "	0.400 "

$$M = \frac{1000 \times 3.90 \times 0.5093}{0.440 \times 31.406} = 143.7$$

$$M = \frac{1000 \times 3.90 \times 0.4372}{0.4000 \times 29.9745} = 141.1$$

(III) Determination of carbon and hydrogen contents by combustion method

Fraction A

The acetyl group in the lower hydroxy acid is apt to be hydrolyzed when it stands a long time at room temperature. The carbon, hydrogen determination of the first distillation fraction is determined on the barium salt instead of the oily acetyl liquid.

Weight of sample and boat	3.7101 gms
Weight of boat	3.6277 gms
Weight of sample	0.0824 gms
Weight of Ascarite tube after combustion	63.6766 gms
Weight of Ascarite tube before combustion	63.6242 gms
Weight of CO_2	0.0524 gms
Weight of Dehydrite tube after combustion	56.2213 gms
Weight of Dehydrite tube before combustion	56.2005 gms

Weight of H_2O 0.0208 gms

$$\% H = \frac{0.0208 \times 0.1119}{0.0824} \times 100 = 2.82$$

$$\% C = \frac{0.0524 \times 3}{0.0824 \times 11} \times 100 = 17.47^{*}$$

Weight of sample and boat	3.8146 gms
Weight of boat	3.7236 gms
Weight of sample	0.0910 gms
Weight of Ascarite tube after combustion	63.7340 gms
Weight of Ascarite tube before combustion	63.7261 gms
Weight of CO_2	0.0579 gms
Weight of Dehydrite tube after combustion	56.2652 gms
Weight of Dehydrite tube before combustion	56.2411 gms
Weight of H_2O	0.0241 gms

$$\% H = \frac{0.0241 \times 0.1119}{0.0910} \times 100 = 2.96$$

$$\% C = \frac{0.0579 \times 3}{0.0910 \times 11} \times 100 = 17.35$$

Fraction B (Determined by oily acetyl acid)

Weight of sample and boat	3.9016 gms
Weight of boat	3.7281 gms
Weight of sample	0.1735 gms
Weight of Ascarite tube after combustion	62.5428 gms
Weight of Ascarite tube before combustion	62.2534 gms

* The correction for $BaCO_3$ is negligible.

Weight of CO_2 0.2894 gms

Weight of Dehydrite tube after combustion 56.3817 gms

Weight of Dehydrite tube before combustion 56.2944 gms

Weight of H_2O 0.0873 gms

$$\% H = \frac{0.0873 \times 0.1119}{0.1735} \times 100 = 5.65$$

$$\% C = \frac{0.2894 \times 3}{0.1735 \times 11} \times 100 = 44.96$$

Weight of sample and boat 3.9155 gms

Weight of boat 3.7238 gms

Weight of sample 0.1917 gms

Weight of Ascarite tube after combustion 62.8581 gms

Weight of Ascarite tube before combustion 62.5444 gms

Weight of CO_2 0.3137 gms

Weight of dehydrite tube after combustion 56.4026 gms

Weight of dehydrite tube before combustion 56.3136 gms

Weight of H_2O 0.0890 gms

$$\% H = \frac{0.0890 \times 0.1119}{0.1917} \times 100 = 5.19$$

$$\% C = \frac{0.3137 \times 3}{0.1917 \times 11} \times 100 = 44.63$$

Fraction C (Determined by oily acetyl acid)

Weight of sample and boat 3.9301 gms

Weight of boat 3.7287 gms

Weight of sample	0.2014 gms
Weight of Ascarite tube after combustion	47.4811 gms
Weight of Ascarite tube before combustion	47.1380 gms
Weight of CO_2	0.3431 gms
Weight of Dehydrite tube after combustion	56.5814 gms
Weight of Dehydrite tube before combustion	56.4717 gms
Weight of H_2O	0.1097 gms

$$\% H = \frac{0.1097 \times 0.1119}{0.2014} \times 100 = 6.09$$

$$\% C = \frac{0.3431 \times 3}{0.2014 \times 11} \times 100 = 46.46$$

Weight of sample and boat	3.8348 gms
Weight of boat	3.6261 gms
Weight of sample	0.2087 gms
Weight of Ascarite tube after combustion	47.8079 gms
Weight of Ascarite tube before combustion	47.4501 gms
Weight of CO_2	0.3578 gms
Weight of Dehydrite tube after combustion	56.7889 gms
Weight of Dehydrite tube before combustion	56.6718 gms
Weight of H_2O	0.1171 gms

$$\% H = \frac{0.1171 \times 0.1119}{0.2087} \times 100 = 6.28$$

$$\% C = \frac{0.3578 \times 3}{0.2087 \times 11} \times 100 = 46.71$$

DISCUSSION

From all the facts available it appears improbable that at the low temperatures employed for the dissolution of cellulose by caustic solutions any deep pyrolytic decomposition of cellulose will take place. Evolution of gases indicating such violent and unpredictable decomposition are only encountered if the reaction temperature exceeds 275°C. to 300°C. But, when the cellulose is treated with a caustic solution at a temperature around 200°C. to 250°C. in a closed vessel, the cellulose completely goes into solution. A small amount of pitch and a light color of cellulose solution may indicate that rather smooth and normal reactions take place during the cooking. The mechanisms of these reactions is not yet clear. The dissolution of cellulose involves:

(1) The cellulose molecules are first hydrolyzed into simple cellubiose or glucose units.

(2) These cellubioses or glucoses formed may be immediately oxidized into acids or decomposed into lower-carbon acids by intra-oxidation.

(3) Intramolecular rearrangement would take place resulting in the formation of hydroxy acids.

The theoretical equations which may represent the formation of hydroxy acid from cellulose solution are suggested as following: (22)

$$(1)\ \underset{\text{cellulose}}{(C_6H_{10}O_5)} - H_2O \longrightarrow \underset{\text{acetic acid}}{3CH_3COOH}$$

(2) $(C_6H_{10}O_5) + H_2O \longrightarrow 2CH_3CH(OH)COOH$
Lactic acid

(3) $(C_6H_{10}O_5) + H_2O \longrightarrow CH_3CH(OH)CH(OH)COOH + CH_3COOH$
dioxybutyric acid acetic acid

(4) $(C_6H_{10}O_5) + H_2O \longrightarrow CH_2CH(OH)CH(OH)CH(OH)CH_2COOH$
isosaccharinic acid

(5) $(C_6H_{10}O_5) \longrightarrow CH_3CH_2CH(OH)CH_2COOH + CO_2$
mono-oxy valeric acid

(6) $(C_6H_{10}O_5) \longrightarrow CH_3CH_2CH(OH)CH(OH)COOH + HCOOH$
dioxy-valeric acid formic acid

(7) $(C_6H_{10}O_5) \longrightarrow HOOCCH_2CH(OH)CH_2CH_2COOH$
mono-oxy adipic acid

(8) $2(C_6H_{10}O_5) + 2H_2O \longrightarrow 3CH_3CH(OH)CH(OH)COOH$
di-oxy butyric acid

(9) $(C_6H_{10}O_5) + H_2O \longrightarrow CH_2(OH)COOH + CH_3CH_2CH(OH)COOH$
glycolic acid mono-oxy butyric acid

All reactions proposed above may take place at the same time. It seems reasonable at this time to believe that under the different conditions used in the solution of cellulose, i.e., temperature, strength of alkali, cooking time etc., different reactions might take place, or a particular reaction or group of reactions may dominate the overall result so that the formation of a particular hydroxy acids will be favored.

From all results obtained in the work reported here, three hydroxy acids have been found, namely glycolic acid, lactic acid, and di-hydroxy butyric acid. All these acids were recovered as acetyl compounds.

Although the molecular weight, carbon and hydrogen contents, and barium content of each salt from each fraction have been determined, a more accurate result will depend primarily on better techniques of separation of the acetylated acids. The following facts are of significance:

(1) The boiling points of these acetyl compounds are very close to each other. Therefore the obtaining of a very pure compound by vacuum distillation is quite difficult.

(2) The calculated value of carbon and hydrogen content in each of the acetyl derivatives are likewise close to each other. Any analytical error would lead a wrong interpretation.

(3) All these compounds have almost the same appearances, i.e. colorless oily liquids, pleasant odor, etc. They have almost the same specific gravity.

Therefore the method used for identification of hydroxy acids in this report can only be considered as a preliminary step which should be followed by further experimental work.

In comparison with the experimental results with all constant available, the first distillation fraction is principally acetyl glycolic acid (CH_3COOCH_2COOH). The molecular weights determined from this experiment are a little lower than that of calculated value. This may show the presence of a very small quantity of acetic acid which has decomposed from its acetyl compound.

Fraction A:

	Experimental	Theoretical
Molecular weight	116.9, 115.0	118
Ba content of free oxy acid	42.43, 42.2%	47.7%
Carbon content in Ba salt	17.35, 17.47%	16.7%
Hydrogen content in Ba salt	2.96, 2.82%	2.1%
Boiling point	128 - 130°C.[12]	145°C.[12]*
Density	1.1767 at 25°C.	1.0993 at 17°C.*

* based on R. Anschutz's experiment[23]

The fraction B which has boiling point range 130-145°C. at 10-12 mm. vacuum has been found to be a mixture of acetyl lactic acid and acetyl dioxybutyric acid. And the percentage of each of these acids is interpreted based on their molecular weights. About 85% of acetyl lactic acid and 15% of acetyl dioxybutyric acid are found in this fraction.

Fraction B:	Experimental	Theoretical		
		Pure Aceto Lactic	Pure Aceto Dioxybutyric	Mixture**
Molecular weight	143.7, 141.1	132	204	142
Ba content of salt free acid	46.1, 45.6	43.6	36.5	42.6
Carbon content	44.96, 44.63	45.42	47.1	46.35
Hydrogen Content	5.65, 5.19	6.06	5.90	6.02
Boiling point	130-145°C.[12]	127°C[11][24]	127°C.[4][25]	----
Density	1.1771 at 25°C.	-------	------	-----

** Calculated as 85% acetolactic acid and 15% diacetyl dihydroxy-butyric acid.

The fraction C also contains acetyl lactic acid and diacetyl dihydroxy - butyric acid, with about 80% of the former and 20% of the latter.

Fraction C

	Experimental	Theoretical		
		Pure Aceto Lactic	Pure Aceto Dioxybutyric	Mixture**
Molecular weight	146.1, 145.9	132	204	146
Ba content of salt free oxy acid	43.28, 43.60	43.6	36.5	42.2
Carbon content	46.46, 46.71	45.42	47.1	45.7
Hydrogen content	6.09, 6.28	6.06	5.9	6.02

**Calculated as 80% acetyl lactic acid and 20% diacetyl dihydroxy - butyric acid.

The results listed in the above tables are estimates which are based on the known presence of the compounds in question. The boiling points of all the aceto-hydroxy acids under investigation are so close to one another that a given fraction may contain more than two hydroxy acids. Therefore, it seems quite probable that the higher hydroxy acids, other than dihydroxy-butyric acid may be found in the distillation residue which begins to polymerize and decompose at a temperature above 148°C. Better vacuum distillation

techniques are indicated as a possible solution for this problem.

Future work in this field may well be confined to the waste solutions obtained from the soda pulp paper industry which daily discards hundreds of pounds of the hydroxy acids in the form of an alkaline solution.

It is possible to replace the hydroxy groups by hydrogen atoms through reduction with hydriodic acid.[9][10] This reduction has been reported [28] using sodium ammalgam. Phosphorous iodide likewise has been used for this purpose.[26] These methods of reduction were not used in the present investigation because it was felt that large operations would not be feasible with such reagents.

The results of the present investigation indicate that Aushutz[23] data on the boiling point of acetyl glycolic acid is in error. He reported for this compound a lower boiling than that of acetyl lactic acid.

SUMMARY

(1) When cellulose is treated with 10% sodium hydroxide solution and heated to a temperature about 250°C. in an autoclave, it will completely go into solution.

(2) When the clear and dried cellulose syrup is acetylated with acetyl chloride in presence of anhydrous sodium acetate, a colorless, oily-like compound is obtained by vacuum distillation of the reaction mixture. It has a boiling point range from 120°C. to 148°C.

(3) The molecular weights, barium content, carbon and hydrogen contents of each distillation fraction of these compounds have been determined.

(4) Glycolic acid (hydroxy-acetic acid), lactic acid (hydroxy propionic acid) and dihydroxy butyric acid have been found in the alkaline solution of cellulose.

(4) The contents of each distillation fraction are estimated by interpretation of their average molecular weight, the barium content of the barium salts, the carbon hydrogen content of the barium salt of the lower boiling fraction, and also of higher boiling fractions of the oil-like acetyl compounds.

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Hydroxy-acids from cellulose decomposition

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