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A STUDY OF "BLACK LIQUOR" FROM SODA PULP

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A Thesis submitted to the Graduate Faculty of the University of Maine in partial fulfillment of the requirements for the degree of Master of Science in Chemical Engineering.

By

Chen Chi Pan.

S. B., Ch. E., M. I. T., 1918.

June 1920.
Orono, Maine.

FORWARD

To Doctors C. W. Easley and H. F. Lewis, to whose patient help and unfailing kindness, whatever is good in this thesis is due.

66,571

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INTRODUCTION

At the present time, practically all of the soft easy bleaching pulps used for the manufacture of high class book, magazine, general printing and cheaper writing paper are made by the Soda Process. Although, the sulphite and mechanical process and to a less extent the Sulphate Process - predominate, the Soda Pulp is remarkably well adopted for producing Pulp Fibres from any kind of wood or other fibrous material, no matter how resistant to chemical attack it may be.

Because of this above fact and since Soda Pulp is considered an important supply of fibre, a general outline of its manufacture perhaps will not be out of place.

The Soda Process (1)

In reality the Soda Process is a modification of the old Watt and Burgess Process and is probably the oldest commercial method for producing chemical pulp from wood.

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(1) - Bulletin of U. S. Department of Agriculture, No. 80.

It originally consisted in digesting suitably prepared wood in a large boiler with a strong solution of caustic soda under a pressure of about ninety pounds per square inch for ten to twelve hours. The wood was then washed to remove the alkali and treated with chlorine gas or an oxygen compound of chlorine. The partially digested wood was washed to free it from the hydrochloric acid formed and again treated with a small quantity of caustic soda solution. The pulp so produced was washed, bleached and beaten in a beating engine. After which it was ready for paper machine.

The modification of this process as employed at the present time dispenses with the intermediate oxidation with chlorine compounds. Different cooking conditions are also used, the details of which together with a brief description of the manner of preparing wood are given below.

The bark is first removed and the wood is then cut diagonally with the grain into slices of one-half to three-fourth inch thick by the "Chipper" and further broken up by the disintegrator or "shredder." The resulting chips are dusted and conveyed to the storage bin usually above the digester. The knots and decayed portions are not removed as the cooking liquor has strong solvent power.

The digester may vary in shape and size but the present tendency is towards stationary, vertical, cylindrical digesters, heated by live steam which enters at the bottom of the digester in such a manner as to carry the cooking liquor through a pipe to the top of the vessel and spray it over the chips. This insures good circulation. The chips and cooking liquor are charged through a man-hole at the top of the digester, the bottom of which is provided with a blow off pipe and valve for discharging the pulp after the cooking is complete. The size of the digester varies from seven to ten feet in diameter and twenty-five to fifty feet in height. The pressure is maintained from three to eight hours at around one hundred and ten pounds.

After the digestion process is complete, the pulp is forced out under pressure into a blowpit or ballon whence it is transferred to large washing pans. Here it is drained as free as possible from the strong spent cooking liquors called "Black Liquors" and washed thoroughly first with hot, weak black liquors from last washings of preceding cooks and lastly with fresh hot water.

The first draining and washings which contain the greater part of the alkali cooking chemicals and the complex organic compounds derived from hydrolysis of wood are run to evaporators, concentrated and later calcined in furnaces. The ash formed is called "Black Ash" and is leached with water, and the alkali in form of sodium carbonate is dissolved. The resulting solution is treated with quick lime (CaO) which changes the carbonate to caustic soda. Modern practice recovers from 88 to 92 per cent of the alkali charged into the digester.

The process itself is of nothing more than hydrolysis (1) in which the complex molecules are gradually broken down with the formation of acid products which combine and neutralize the alkali leaving the cellulose in form of isolated fibre.

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(1) - De Cew, J. S.C. I. 26, (1907), 561-3.

These acid radicals are produced from compound cellulose such as Lignocellulose. The extent of hydrolysis depends upon its caustisity, pressure, circulation of liquor, time of cooking and nature of wood.

The Black Liquor

Up to 1876, the liquor was ~~now~~ run to waste. But since the River Pollution Act, it is treated to recover the soda, as mentioned. If we look a little more carefully into the liquor, we can draw a comparison in the destructive distillation of wood for coke and the hydrolysis for fibre. We see that the former gives us the pyroligenous acid which contain various other chemical products while in the latter the liquor is produced.

It is known(1) that upon distillation of simple cellulose, no chemicals like those from pyroligenous acid are obtained, so it is the compound celluloses which furnishes these chemicals in wood distillation and it is the black liquor which contains the hydrolysed products of compound celluloses in Soda Pulp Manufacture.

It is also interesting to note the resemblance of organic matter obtained by precipitating from the black liquor with an acid to the type of humic acids found in the soil and in great amounts in certain deposits,

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(1) - Klason, Z. Ang. Chem. 23, (1910) 1252-7.

such as may be found in parts of Florida and New Mexico and to which reference may be found in geological literature. This same type of deposite has been found to be the cause of bad mortar when the mortar has been made from sands containing the deposite. The presence of those phenolic bodies obtained from the alkaline digestion of wood and possessing similar color reactions and solubilities mentioned above offer food for thought in connection with the possible similarity in the formation of these compounds from same parent substance, namely wood under possibly similar conditions of alkalinity and pressure.

In 1890, Benedickt and Banberger (1) digested the black liquor with hydriodic acid and obtained a yield of methyl alcohol from 4.38 to 6.52% of the weight of wood. Strut (2) showed this to be between 5.78 to 5.98%. Bergstrom and Fagerlind (3) determined by indirect process that 1.3% of the weight of pulp or 0.65% of the weight of wood is converted to alcohol in cooking. The dried soda liquor

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(1) - Monatshefte 11 (1890) 260-7.
(2) - Dissertation Gottingen (1890).
(3) - Papier Fabrikent 7 (1909) 27-32, 78-82, 104-6, 129
8 (1910) 970-1.
12 (1914) 214.

(dried by radiant heat), has 5000 B. T. U. per pound. If carbonized, 1 pound shrinks to 0.55 pound and has 3800 B. T. U. per pound.

S. D. Well (1) partially purified the black liquor and used it over again but as soon as the organic matter increases beyond a certain point, the process is of no value. Hoffman (2) concentrated the Black Liquor to 35-38° Be, then distilled it. He obtained both an aqueous and an oily portion. To the latter belong most of the phenolic compounds.

White and Rue (3) succeeded in recovering methyl alcohol and acetone by distillation. This was done by slowly feeding the liquor into a preheated inclined retort. The charred carbon has a good catlytic effect. They obtain chiefly 145# methyl alcohol and 2.6# acetone per thousand gallons of black liquor of 40° Be. They also investigated the loss of alcohol and acetone on the relief valves and found that an average of 1.32% by volume of alcohol and 0.06% acetone could be recovered.

Rinham carbonized the liquor from Esparto Grass in a conical retort. The liquor flew down the sides in films and carbonized

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(1) - Paper XXII (1918) 24.
(2) - Paper XXIII (1919) 19.
(3) - paper XIX (1917) 23. M.S.Patent 1748,2405,1544,

mass was scraped off. He obtained methyl acetone in nearly the same amount as White & Rue. He showed that a maximum yield was obtained around 255-300°C. Heat circulation was controlled by injecting steam. He also obtained a wax from the tar.

These references in addition to the patents and the literature bearing definitely on the subject matter of this thesis presented later on complete the previous study of the subject. Scanty as they are, it points directly to the scientific neglect of the subject. The present method of evaporation, ignition and caustizing with elaborate equipments offers opportunity for improvement in the recovery process the demand of such organic chemicals as methyl alcohol, acetic acid, acetone, etc. warrents the study of their possible production from black liquor wastes.

The difficulty of this problem lies in its complexity. An attempt has been made in this study to obtain some information of the action of various decomposition agents on the organic constituents of the black liquor.

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(1) Paper XX (1917) 6.

A brief outline of the work done is given below:

A- Lime Treatment

1. Drying by CaO.

   Factors:

   1. Temperature
   2. Concentration.

2. Extraction.

3. Destructive Distillation.

B- Acid Treatment.

1. Sulphuric Acid.

Distillation with insufficient acid.

Factors:

1. Concentration.

Distillation with Excess acid.

Factors:

1. Concentration.

Long time Hydrolysis at the boiling point of the solution.

Factors:

1. Temperature.
2. Time of Hydrolysis
3. Concentration.
4. Presence of Oxidizing agent

Hydrolysis under Pressure.

Factors:

1. Temperature and pressure.
2. Time.
3. Concentration.
4. Presence of Oxidizing agent

Precipitation by Carbonic Acid.

Factors:

1. Concentration.
2. Temperature.
3. Salting out effect.
4. Time of passing carbon dioxide.

Elaborate as the outline may look to be the writer regrets that he had only enough time to carry out a series of general experiments, rather more a preliminary study than a thorough investigation of the subject. The literature in connection with any part of the work besides those mentioned is not very extensive, but such as it is, it will be described as the discussion of the work proceeds.

The black liquor was obtained through the courtesy of the Penobscot Chemical Fibre Company in Great Works, Maine. Its specific gravity is 1.35. Analysis showed as follows:

Water	40%
Solid	60%
Sodium Hydroxide	1.17%
Sodium Carbonate	0.115%.

Information from the same source gave:

Moisture in wood used 50%.
Black Liquor (70° Tw or Sp. Gr. 1.35) per cord of wood, 3635# or 306 gallons.

Since no two days runs are exactly the same in soda mills, the above figure is the average of the month of July, 1919. For convenience of figuring, the above figures will be used.

LIME TREATMENT

General

Specifically, concerning the time treatment, Rinham (1) found that if liquor is evaporated, mixed with lime or soda and destructively distilled in a special designed retort in presence of steam at 400°C, he obtained:

Fuel gas 400-500 Klo/ton cellulose produced
Acetone 4% solution.
Insoluble oil.
Charcoal and alkali.

Recently S. A. Mohood and D. E. Cable (2) fused sawdust with alkali. They obtained 17-20% Acetic acid, and 50% oxalic acid of the weight of dry wood, in addition to some methyl alcohol. At low temperature both formic and acetic acids can be recovered.

V. Dreaven (3) patented the treatment of the liquor by caustic and lime to obtain acetic acid or by steam distillation for acetone and volatile products. If the mixture is treated with moist carbon dioxide, sodium acetate is produced.

Experimental:

It is apparent that although the liquid can not be evaporated to dryness, yet if a dehydrat-

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(1) Paper-Fabrikant 10, (1912) 39-41, 101-4.
(2) J. I. E. C. XI (1919) 651.
(3) M.S.P. 1298478, 1298479, 1298480, 1298481.
U?

ing agent is mixed with it, it can be handled much more easily. Lime is chosen because if its predominating property as a dehydrating agent as well as cheapness.

At a temperature lower than 70°C, a little lime will make a thick paste with the liquor and no more lime could be stirred in. However, at a temperature of 70-80°C which is the temperature of the liquor when it comes out from the last effect of the multiple evaporator, lime can be mixed in easily. A moderate heat is desired on mixing. The product is a sand like mass not entirely dry. If further heat is applied the whole mass is charred and apparently all the organic matter is burned off.

The product is leached with 2000 cc. water to obtain the soluble salt. The color of the solution being reddish yellow. Two 50 cc. samples are evaporated to determine total soluble salt while another two 50 cc. samples are titrated for sodium hydroxide using phenolphthalein as indicator. The average results of two experiments are as follows:

For 100 cc. black liquor at 72°C, 120 g. CaO is stirred in and dried as indicated.

(a) Dried over moderate heat.

56 g. soluble salt per 100 cc. liquor.
6.2 g. Na_2O as hydroxide per 100 cc liquor

(b) Dried over red heat for 5 minutes with evolution of gas.

40 g. soluble salt per 100 cc. liquor.
3.8 g. Na_2O as hydroxide per 100 cc. liquor.

To ascertain the volatile acid radical or radicals, a 100 c.c. portion of the aqueous extract from the lime dried black liquor is acidified with sulphuric acid and distilled. Out of the distillate, a Duclaux constant is determined. The values obtained were 9.93 and 8.77 in this case presumbly indicate that it is a mixture of formic and acetic and this conception will be taken for all volatile acids obtained throughout the experiments.

There is also a change in color in acid and alkali solutions of the extraction. The color is yellow in acid and depp red in alkali probably due to a change in structure or structures of the compound or compounds.

If the aqueous extract is evaporated and fused with sodium carbonate then distilled from concentrated sulphuric acid solution, some high strength acetic acid is obtained. There ~~is~~ are also unsaturated compound or compounds containing the linkage of the type represented by $Co-Ch_2$. The presence of oxalic acid has not be established.

The residue of the lime dried black liquor after extraction is destructively distilled. About 10% is obtained as tarry heavy liquor of a similar appearance to pyroligenous acid, while the residue remaining consists of carbon and calcium carbonate.

From the experiment, it is apparent that relative amount of CaO and liquor to be used is very nearly a constant value. Excess CaO is not desired nor necessary, while with less CaO the liquor will not be dry. The only questions left are the temperature of mixing with lime and temperature of distillation. To the former, it is practically fixed too as low a temperature as will ~~not~~ allow lime to be stirred in, while a high temperature which will destroy the organic material is avoided

ACID TREATMENT

The acid treatment is not a new idea. In 1844, Hoffman evaporated the liquor on heated plate and treated with acid, he got 14% acetic acid. W. H. Higgins (1) patented a process for the production of sodium acetate from the liquor of straw and esparto boiling by evaporating the liquor on hot plate and subsequently treating with acid. Patents also have been registered for the production of organic acids from waste pulp liquor (2).

M. P. Cram (3) acidified the liquor with hydrochloric acid precipitating the organic matter (100 cc. sp. gr. 1.25 liquor with 300 cc. 1.18 HCl gave 14 g. prectipitate). He suggested that the coagulated mass may be used for following purposes:

1. Sizing of paper.
2. Stain and varnish for wood.
3. A sulphur dye after fusion with potassium sulphide at 185-200°C.

He distilled the filtrate and got a small amount of acetic acid.

C. I. Buddle (4) investigated the liquor from esparto cooking. He got some acetic acid, a special kind of wax and a solution. To the latter if sulphuric acid is added, the resinous matter will be precipitated. If nitric acid is added, oxalic acid and a yellow dye are formed.

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(1) Eng. P. 13408 (1891).
(2) U.S.P. 99951, 1217218.
(3) J. I. E. C. 6, (1914) 896.
(4) Paper XVIII (1916) 22.

The acid treatment may be conveniently divided into two kinds, strong acid and weak acid and any mineral acid will be classed with the former while carbonic acid is used in the latter case.

SULPHURIC ACID

Experimental

In the same manner as humus, the organic constituent of black liquor is an acid and naturally will be precipitated by stronger acid. The coegulated matter is of molasses nature which is completely precipitated on acidifying the liquid and is not affected by further addition of acid. The precipitate is very hard to filter.

If the coagulated mass is distilled, a liquid is obtained which resembles very much the distillate from lime treatment.

The following work was carried out in order to get some idea of the products of acid hydrolysis of this organic matter.

Prolonged hydrolysis with sulphuric acid under a reflux condenser was tried. Then such oxidizing agents as mercuric oxide, lead peroxide, permanganate were also added in order to determine the possible effect of such agents.

The product was first distilled for volatile acids. The experiments were rather disappointing. They all showed the presence of formic and acetic to the extent of 6-7% of the weight of the liquor figuring all as acetic. It seems certain that a third organic acid was present but efforts to identify the acid failed. The distillate obtained by a steam distillation of the hydrolysis mixture indicates the absence of simple phenol although both ferric chloride and bromic test point to the presence of the higher phenols.

Hydrolytic decomposition under Pressure.

A series of experimants were first tried in a bomb furnace varying the amount of sulphuric acid with constant temperature and time. A heterogenous reaction product was obtained. The liquid portion contains sodium sulphate, organic acids and a sugar in solution. The solid portion is insoluble in acid, but completely soluble in alkali consisting most probably of higher phenols. From the experiments, conclusion was reached that the production of volatile acids increase as the amount of mineral acid for hydrolysis increases, while the amount of sugar is more nearly constant.

It was desired to study the last process more in detail, so the reactions were carried out in a small autoclave of about two gallons capacity equipped with pressure gauge and thermometer stand. Unfortunately the autoclave had a copper lining, thus making a study of acid hydrolysis directly in the autoclave impossible. The first experiment was carried out in a lead tube suspended in the autoclave. As sulphuric acid has a high boiling point, the water vaporizes first, thus building up the pressure and the boiling point of sulphuric acid, increases as the pressure increases making a good digestion.

The undecomposed part sticks to the bottom and is hard to remove in the lead tube so, consequently, a similar capacity test tube is used with fairly satisfactory results although it broke occasionally.

The autoclave was heated by a direct flame. Both the temperature and pressure were registered, as was the time, amount of sulphuric acid, the liquor and water.

The resultant hydrolysis mixture was filtered and diluted to 500 cc. The total acid was titrated, the volatile acid distilled according to Allen's Commercial Organic Analysis 1, 509 (4th ed) and titrated. The reducing sugar was determined by the use of Fehling's solution. The results are tabulated as follows:

As the amount of volatile acid is still small the separation of Formic and Acetic by mercuric oxide is not done. Instead, the equivalent of grams of sodium hydroxide is experessed.

Black Liquor in Grs	H_2SO_4 in Grs.	Water in cc.	Strgth of acid in %	Pressure in lbs. sq. in.	Temp. in oC	Time in hrs.	Total Acid in G.NaOH	Volatile Acid in G.NaOH	Sugar in Gms.
20	2.5	150	16.29	47.5-48.5	193-141	4	.222	.153	.480
"	"	"	"	" "	"	6	.157	.131	.322
"	"	"	"	" "	"	8	.159	.142	.192
"	"	"	"	90	165-170	4	.164	.142	.415
"	"	" "	"	" "	"	6	.169	.142	.444
"	"	"	"	" "	"	8	.179	.131	.706?
"	3.0	"	19.55	105-110	160-165	2	.654	.501	.322
"	3.5	"	22.80	"	"	"	.850	.555	.262
"	4.0	"	26.06	"	"	"	1.130	.605	.354
"	5.0	"	32.58	"	"	"	1.740	.644	.486
"	6.0	"	39.10	"	"	"	2.420	..555	
"	7.0	"	45.61	"	"	"	2.790	.447?	
"	8.0	"	52.13	"	"	"	3.260	.686	
"	5.0	"	32.58	"	"	4	1.220	.700	.491
"	5.0	"	32.58	"	"	"	1.330	.817	.366
"	10	"	65.16	"	"	"	3.760	.625	

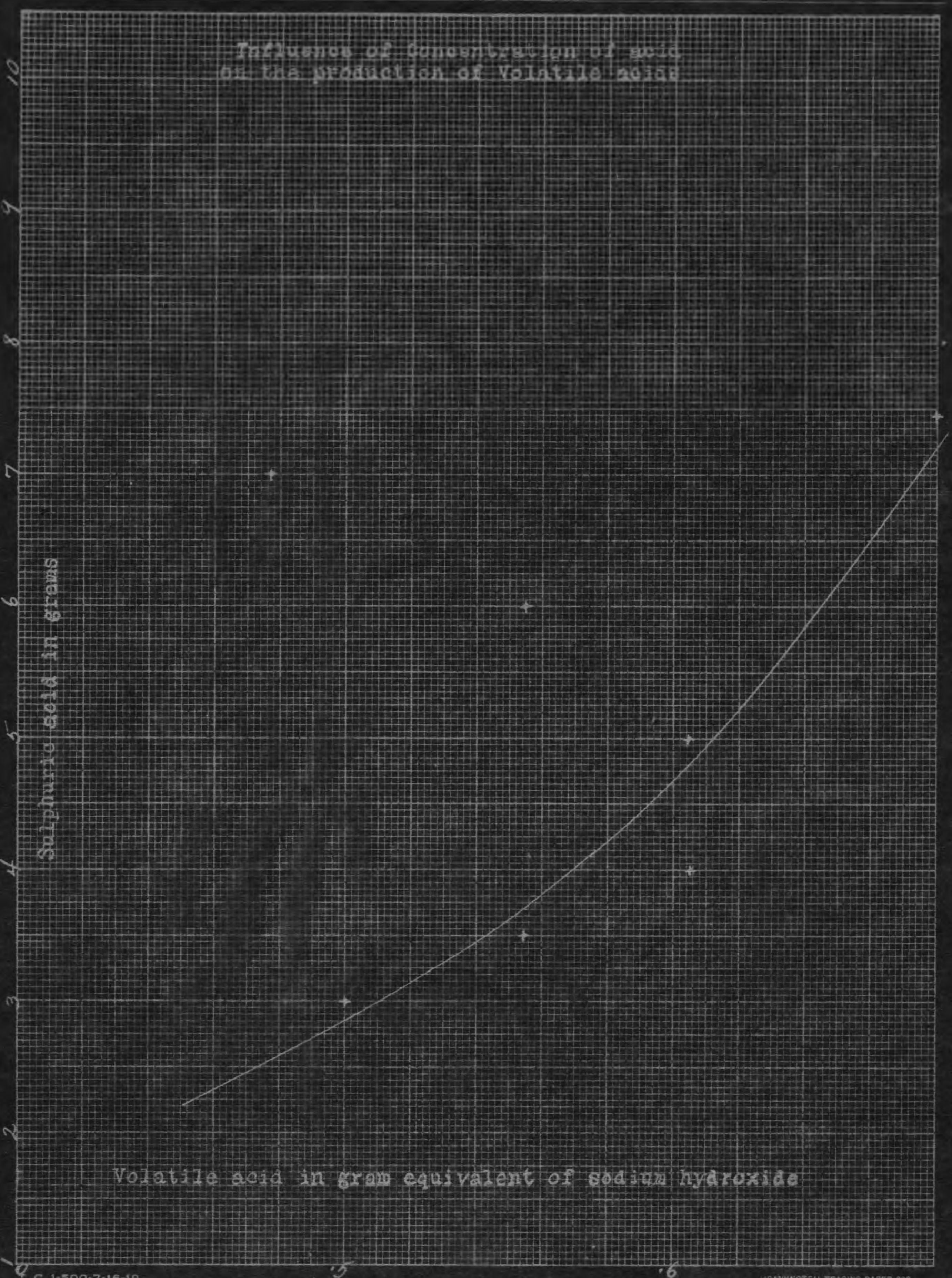
From the foregoing table, the following comparisons may be drawn.

I. Influence of concentration of acid on the production of volatile acids and sugar at constant pressure, temperature and time.

Pressure	105-106#/□"
Temperature	160-165°C
Time	2 hours.

Sulphuric Acid in Grams	Volatile Acid in Gms. equivalent of sodium hydroxide	Sugar in Gms.
3.0	.501	.332
3.5	.555	.262
4.0	.605	.354
5.0	.604	.486
6.0	.555	
8.0	.686.	

It is apparent that the hydrolysis will go further with the increase of acid concentration, thus producing more volatile acids and sugar.


Influence of Concentration of acid on the production of Volatile acids

T. C. 1-500-7-16-19.

"BANKNOTE" TRACING PAPER 203
K & E CO., N.Y.

II. Influence of time factor on hydrolysis, with constant temperature, pressure and concentration of acid.

Table I.

Sulphuric Acid - 2.5 grams.
Temperature 129-141°C.
Pressure 47.5-48.5 #/□

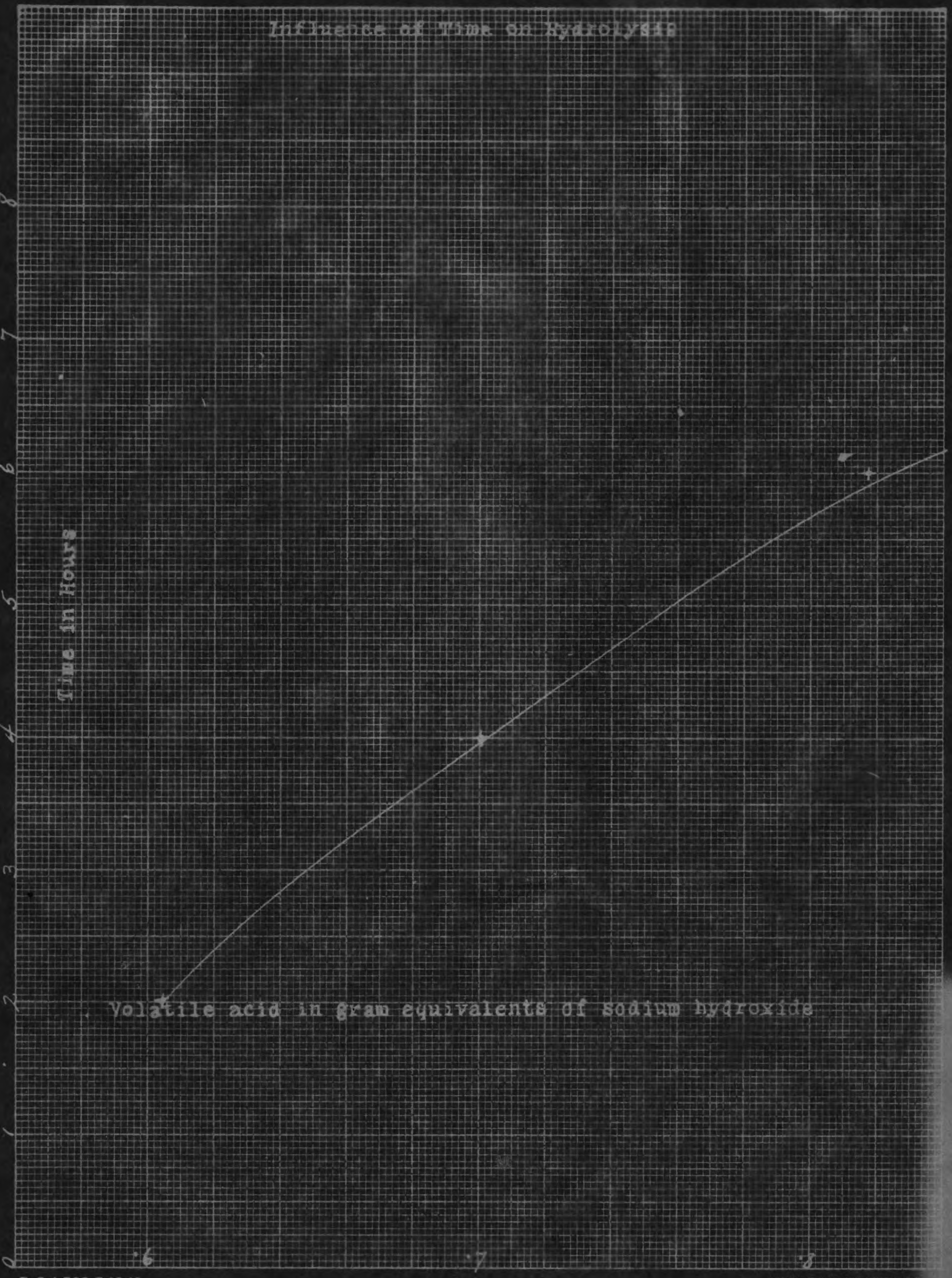
Time in hours	Volatile acid in Grams equivalents of NaOH.	Sugar in Grams.
4	.153	.480
6	.131	.322
8	.142	.193

Table II.

Sulphruic Acid 5 grams.
Temperature 160-165°C.
Pressure 105-110°/□

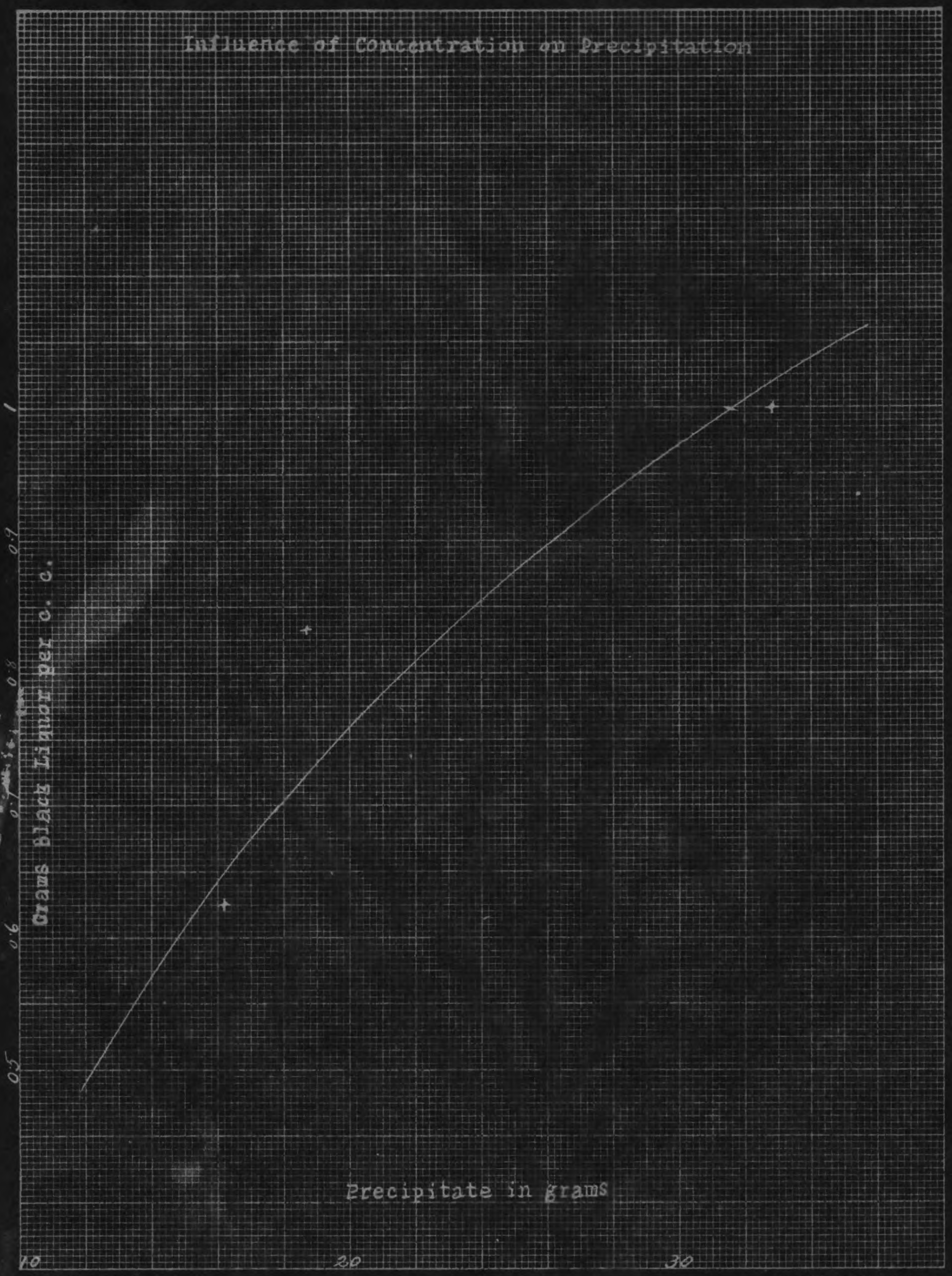
Time in hours	Volatile Acid in Gram equivalent of sodium hydroxide	Sugar in Grams.
2	.604	.486
4	.700	.491
6	.817	.366

Longer time gives slightly more volatile acid and less reducible sugar,


Influence of Time on Hydrolysis

T. C. 1-500-7-16-19.

"BANKNOTE" TRACING PAPER 208
K & E CO., N.Y.



Influence of Concentration on Precipitation

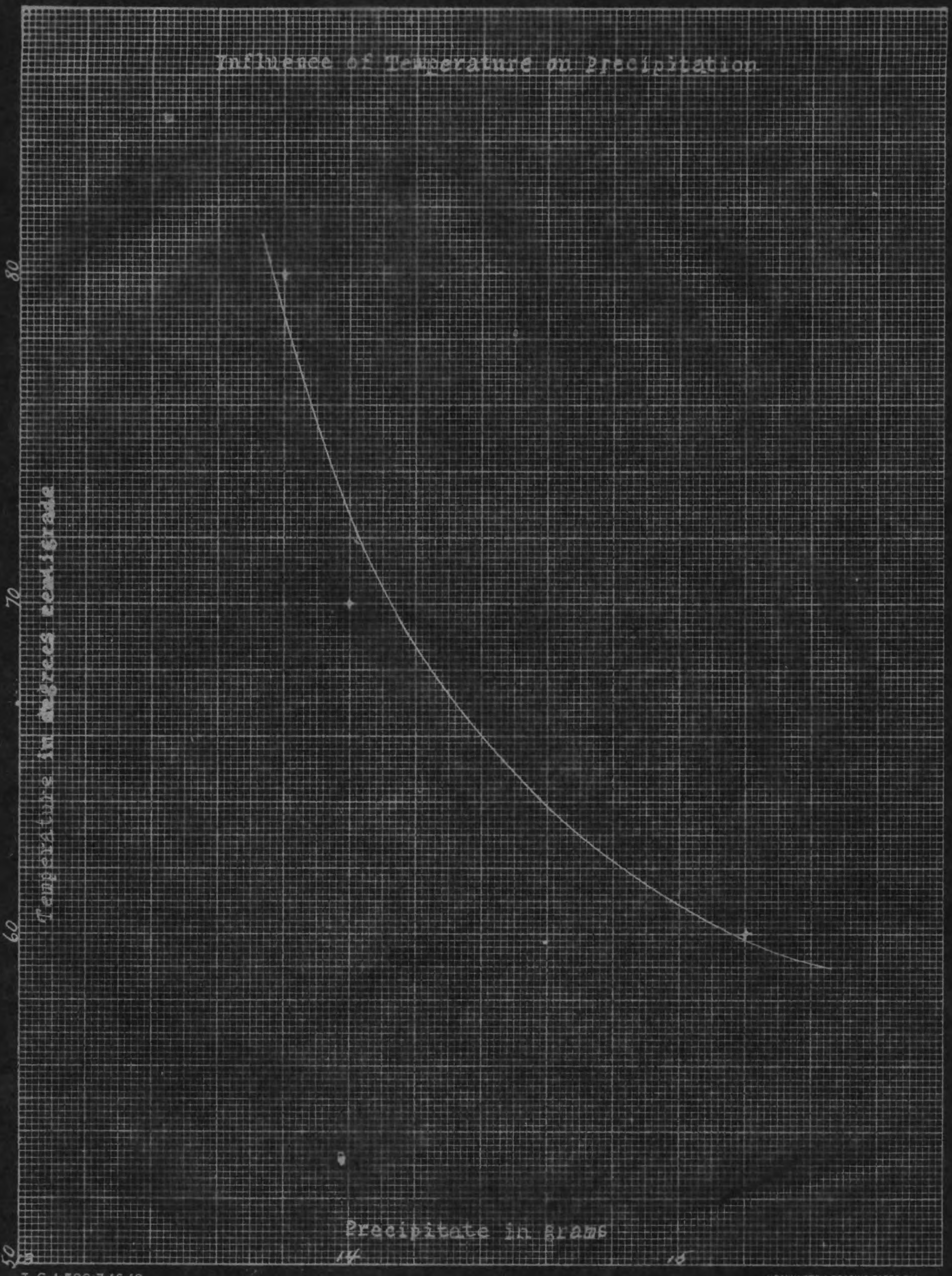
T. C. 1-500-7-16-19.

"BANKNOTE" TRACING PAPER 208
K & E CO., N.Y.

III. Effect of Temperature and Pressure

Sulphuric Acid in Gr.	Time in hours	Pressure in #/□	Temp.in °C	Volatile acid in Gr. Equiv. of NaOH	Sugar in Grams.
2.5	4	47.5-48.5	139-141	.153	.480
2.5	4	90	165-170	.142	.193
2.5	6	47.5-48.5	139-141	.131	.322
2.5	6	90	165-170	.142	.415
2.5	8	47.5-48.5	139-141	.142	.444
2.5	8	90	165-170	.131	.706?

This table indicates that the temperature and pressure ranges described in the table have little effect in the yield of volatile acids. Undoubtedly, this was because the temperatures maintained were below those which would give the best hydrolyses.



Influence of Temperature on Precipitation

T. C. 1-500-7-16-19.

"BANKNOTE" TRACING PAPER 200
K & E CO., N.Y.

PRECIPITATION BY CARBONIC ACID

General

Rinham made a careful study of this subject. The organic matter is present in the black liquor as the sodium salt of the weak acids, which may be precipitated by carbon dioxide at 75°C in the presence of sodium chloride at the proper concentration. It contains one-third of the resinous matter soluble in alcohol. If heated to 180° C in presence of alkali it forms a colloid which can be used as sizing.

He used Kiln gas which contains 25% carbon dioxide for precipitation. The concentration of the solution was adjusted to 90 g. V1920, and 40 g. NaCl per liter before precipitation. After the precipitation the alkali was recovered as bicarbonate, formic and acetic acids were separated and the other acids are precipitated as calcium salts and destructively distilled.

Experimental

Experiments have shown that 70°C is the best temperature to carry out the precipitation. For higher temperature, the free organic acid is partly soluble while at low temperature, it is very hard to filter due to the colloidal nature of the precipitate.

The experiments performed are listed below. All precipitates are air dried.

Effect of temperature on Precipitation.

Black Liquor	125 gr.
Dilution	to 250 cc.
Passing CO_2	2 hours.
NaCl added	10 g.

Temperature °C	Precipitate Grams.
8°	13.8
7°	14.0
6°	15.2

Undoubtedly, this shows the decrease in solubility with decrease in temperature

The more concentrated the solution is, the higher the yield in the precipitate due also to the solubility effect.

Experimental results are as follows:

Black Liquor	125 g.
Passing CO2	2 hours.
Temperature	70 °C.

Dilution	Yield.
No dilution	32.8 g.
to 150 cc.	18.7 g.
to 200 cc.	16.2 g.
to 250 cc.	13.3 g.

The presence of salt increases materially the weight of the precipitate as following data show:

Black Liquor	*125 g.*
No dilution	
Temperature	70°
Passing CO_2	2.5 hours.

Salt	Yield
No salt	48 g.
6.5 g.	60 g.

There is practically no salt present in the precipitate when salt is added to this liquor.

As there is no material difference in all the precipitates, they are combined, digested with concentrated sulphuric acid and distilled. The results appear to indicate that 20% of the weight of the liquor used can be recovered as volatile acids, probably a mixture of formic and acetic acid.

Conclusion if any:

The experiments performed are more in the nature of a progress report on the problems. Certainly the acid treatment is more promising of results than the lime treatment from the standpoint of the amount and value of the decomposition products.

The time at my disposal is too short to make any detailed study of a particular phase of the subject but it is hoped that this thesis will offer attractive openings for further research.

APPENDIX

Patents in Connection with By-Product from Soda Liquor

Wood Alcohol from the product of Soda Cellulose Manufacture. J. & O. V. Bergstrom.
Swedish 42374- April 18, 1917.

Treating Sponaceus Product. O. B. Carlson.
Swedish 41758 - Dec. 1916.
Swedish 41295 - "

Recovery of Alkali and Other Substances in Cellulose Product. O. G. Stage.
Canadian 187136 - November 1918.

Sodium Carbonate and Aldehyde from Black Liquor.
U. S. 1196290 - August 1916.

Removel by dialysis.
D. R. P.

Treating the Liquid by Electrolysis.
N. A. Laught.
British 20489, Sept. 1909.
D. R. P.224411, July 1909.

Introduction of Sodium Carbonate to Precipitate The Organic Substances. E. L. Rinmen.
Canadian 133463.

Extract Evaporated Product from Concentrated lye.
Swedish 41295 - Sept. 1916.

Acetic Acid from waste Soda Liquor.
V. Drewsen.
M. S. 1298478.

Acetone, alcohols, and other volatile substances from Waste Soda Liquor. V. Drewsen.
M. S. 1298479.
M. S. 1298480.

Sodium Acetate from Waste Soda Liquor.
V. Drewsen.
M. S. 1298481.