

ACID HYDROLYSIS OF CELLULOSE

IN MUNICIPAL REFUSE

A Division of Research and Development
Open-File Report (RC-02-68-11)

written by

Richard A. Chapman, Sanitary Engineer

U.S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
Public Health Service

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P u b l i c H e a l t h S e r v i c e
Environmental Health Service
Bureau of Solid Waste Management
1970

ABSTRACT

Purpose

Efforts of this research project are being directed toward developing reaction rates for the formation and decomposition of glucose from the cellulose in refuse in an acid hydrolysis process at various temperatures and acid concentrations. The rate at which new products such as 5-methylhydroxyfurfural; levulinic acid and formic acid are formed is also being investigated. The hydrolysis reaction is being studied at temperature conditions not previously studied, up to 230°C. The hydrolysis process economics will be estimated to determine if it is competitive with other methods producing the same materials.

Methods

A high-pressure, continuously stirred reactor is being used for the determination of reaction rates. An injection system is being used to introduce reactants once the desired temperature is reached. The reaction rates for the formation of glucose, 5-methylhydroxyfurfural, levulinic acid and formic acid are being determined at acid concentrations of 0.2, 0.4, and 0.8 percent and at temperatures of 190°C, 210°C, and 230°C.

Results

Preliminary results indicate that in the temperature range of 190°C to 230°C, glucose decomposes at the rate predicted by extrapolation of low temperature (170°C to 190°C reaction rates data. Also, quantitative saccharifications of refuse indicate that the cellulose content of municipal refuse delivered to the Center Hill, Cincinnati incinerator is between 40 and 45 percent.

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I. ACKNOWLEDGEMENTS

This project is one of many supported by the Bureau of Solid Waste Management directed at the utilization of solid wastes. A study conducted by Ionics, Inc. under Contract No. PH-86-67-204 (*Conversion of Organic Solid Wastes into Yeast, An Economic Evaluation*), provided some useful information related to this project.

I would like to thank Mr. Robert Fagan of Dartmouth College working under Research Grant No. EC-00279-02, *Kinetics of Porteous Refuse Hydrolysis Process*, for his helpful suggestions. Also, the assistance of Robert Thurnau, William Kaylor, and Raymond Loebker of the Bureau of Solid Waste Management, is greatly appreciated.

II. INTRODUCTION

Municipal solid waste contains between 40 and 60 percent paper which is currently processed and disposed of by incineration, sanitary landfilling, or other suitable methods. With the increased use of disposable paper goods such as limited-wear clothing, hospital apparel, bedding, and packaging materials, the amount of paper in refuse will certainly increase^{1,2}. The development of a suitable and economic process for the utilization of waste paper will considerably reduce the amount of waste that must be disposed of and will reduce the wastage of a natural resource. One such process under investigation and being reported here incorporates a weak acid hydrolysis reaction in which cellulose present in municipal refuse is converted to glucose, 5-methylhydroxyfurfural, levulinic acid and formic acid.

In the acid hydrolysis process the B-glucosidic linkages of alpha cellulose are broken and glucose is formed at high temperatures (above 170°C) and in the presence of a catalyst (sulfuric acid). As the reaction continues, the glucose is converted to 5-methylhydroxyfurfural which in turn breaks down to form levulinic acid and formic acid.

Kinetic data for the hydrolysis of wood cellulose was developed by Saeman³ for relatively low temperatures (170°C-190°C) and for sulfuric acid concentrations between 0.4 and 1.6 percent by weight. He determined that under these conditions up to about 25 percent by weight of the wood can be converted to glucose.

The Madison Wood Sugar Process and various modifications of the basic process have been developed^{4,5,6,7} using Saeman's kinetic data. By means of extensive recycling (up to 18 cycles) and detention times of 7 to 8 hours, about 50% of the cellulose in the wood is converted to fermentable sugars in the modified Madison process. Approximately, 33% sugar yields have been obtained from the 66% cellulose fraction of wood fibers. Past efforts have yielded about 50 gallons of alcohol per ton of wood by fermentation.

Recently, Porteous⁸ designed a process for the hydrolysis of cellulose in municipal refuse. His process is designed to operate at 230°C and with 0.4 percent sulfuric acid. By extrapolating Saeman's kinetic data, he predicted that about 55 percent of the cellulose in refuse can be converted to glucose. Refuse contains from 50 to 60 percent paper whose cellulose content is about 75 percent, therefore, refuse contains about 40 percent cellulose. If 55 percent of the cellulose in refuse is converted to glucose, as indicated by Porteous, then about 22 percent of the refuse weight can be converted to glucose. Since 33 percent of wood can be converted to fermentable sugar and 22 percent of refuse can also be converted to fermentable sugar, it can be postulated that one and one half tons of refuse can produce as much fermentable sugar as one ton of wood. Furthermore, since one ton of wood produces 50 gallons of alcohol then one ton of refuse should produce about 33 gallons of alcohol.

In the Porteous plant design, the detention time is about one minute. This short retention is operable because at high temperatures the reaction proceeds at a much more rapid rate and only one cycle is needed as opposed to eighteen cycles in the modified Madison Wood Sugar Process. Therefore, it appears that the Porteous design will permit smaller and hopefully less expensive process components for a comparable volume throughput with a comparable production of desired materials.

The Porteous process appears to be profitable and has the potential to reduce the amount of solid waste requiring disposal. However, kinetic data needs to be developed and verified for the hydrolysis of cellulose present in paper only and in mixed municipal refuse at high temperatures, up to 230°C, before practical process design can begin.

III. METHODS

High Temperature, High Pressure Equipment

A two liter MagneDrive Packless Autoclave* is being used for the hydrolysis kinetic studies. Initial runs determined that a method was required to introduce the sulfuric acid into the autoclave once the operating temperature was achieved to establish valid kinetic data under isothermal conditions. An injection system and a rinse system were designed and installed whereby the acid and rinse water were nitrogen injected. The high pressure reactor was barricaded with sandbags and the controls remotely located to reduce the possibility of injury to the researcher.

Subsequent reactor runs indicated that the sulfuric acid was reacting with the type 316 stainless steel in the reactor and Cr^{+3} ions were being formed. The Cr^{+3} ions were in turn interfering with either the hydrolysis reaction or with the method for glucose determination, because very low yields of glucose were found. To overcome this problem the following action was taken:

- A glass liner was placed inside the autoclave
- A glass sampling tube was installed
- The cooling coil was removed
- The thermowell and stirrer shaft were teflon coated
- A teflon impeller was fabricated and installed.

*Mention of Commercial Products does not imply endorsement by the
U.S. Public Health Service

Further reactor runs indicated that Cr^{+3} ions were still present for 10 minutes after the acid was injected and then disappeared. To eliminate this problem, the acid injection reservoir was lined with nylon tubing which corrected the Cr^{+3} ion associated difficulty. Figures 1 and 2 show the reactor before and after modification, respectively.

Analytical Methods for Product Determination

A quantitative saccharification procedure whereby all of the cellulose is converted to glucose was used to determine the amount of cellulose present in paper⁹. Glucose was determined by the orthotoluidine colorimetric method which exclusive for aldohexoses¹⁰.

5-hydroxymethylfurfural was determined by a colormetric method involving a reaction with aniline acetate¹¹. Organic acids are determined with a Waters Associates Automatic Organic Acid Analyzer¹². The technique utilizes silica gel chromatography to separate mixtures of metabolic acids. Indicator titration permits photometric plotting of concentration from a recording photometer. The glucose procedural details can be found in Appendix I.

Review of Saeman's Equipment and Analytical Methods

To better understand the comparison of Saeman's results and those presented here, a brief description of Saeman's methods and equipment is in order. The experiments on the hydrolysis of wood and the decomposition of sugars were carried out in sealed glass bombs heated by direct steam in a rotating digester. Soft glass culture tubes (16 x 150M

FIGURE 1
REACTOR BEFORE
MODIFICATIONS

STIRRER

COVER
(316 SS)

SUPPORT

SHAFT
(316 SS)

COOLING
COIL
(316 SS)

SAMPLING
TUBE
(316 SS)

HEATING
JACKET

13" INSIDE DEPTH

THERMOWELL
(316 SS)

IMPELLER
(316 SS)

BODY
(316 SS)

3½" I.D.

5"

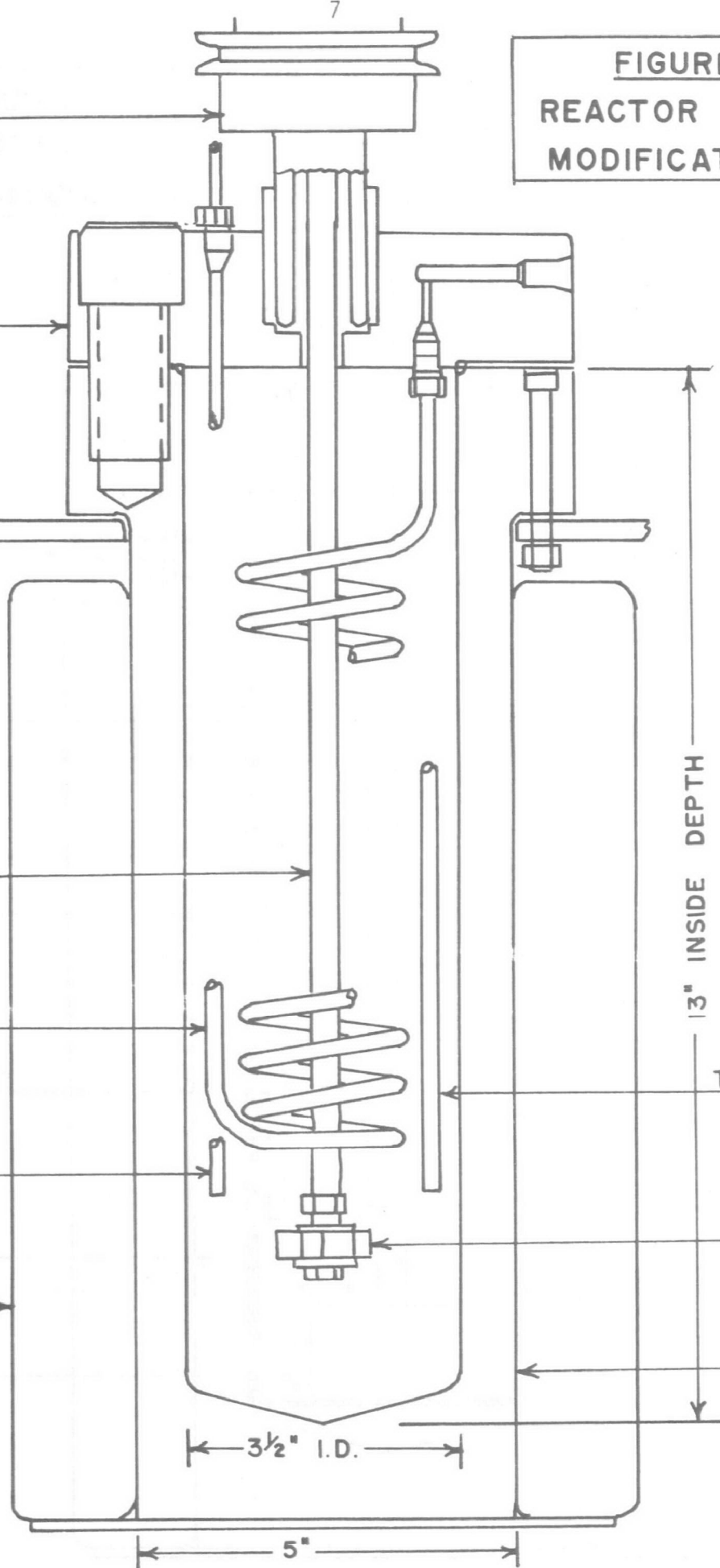
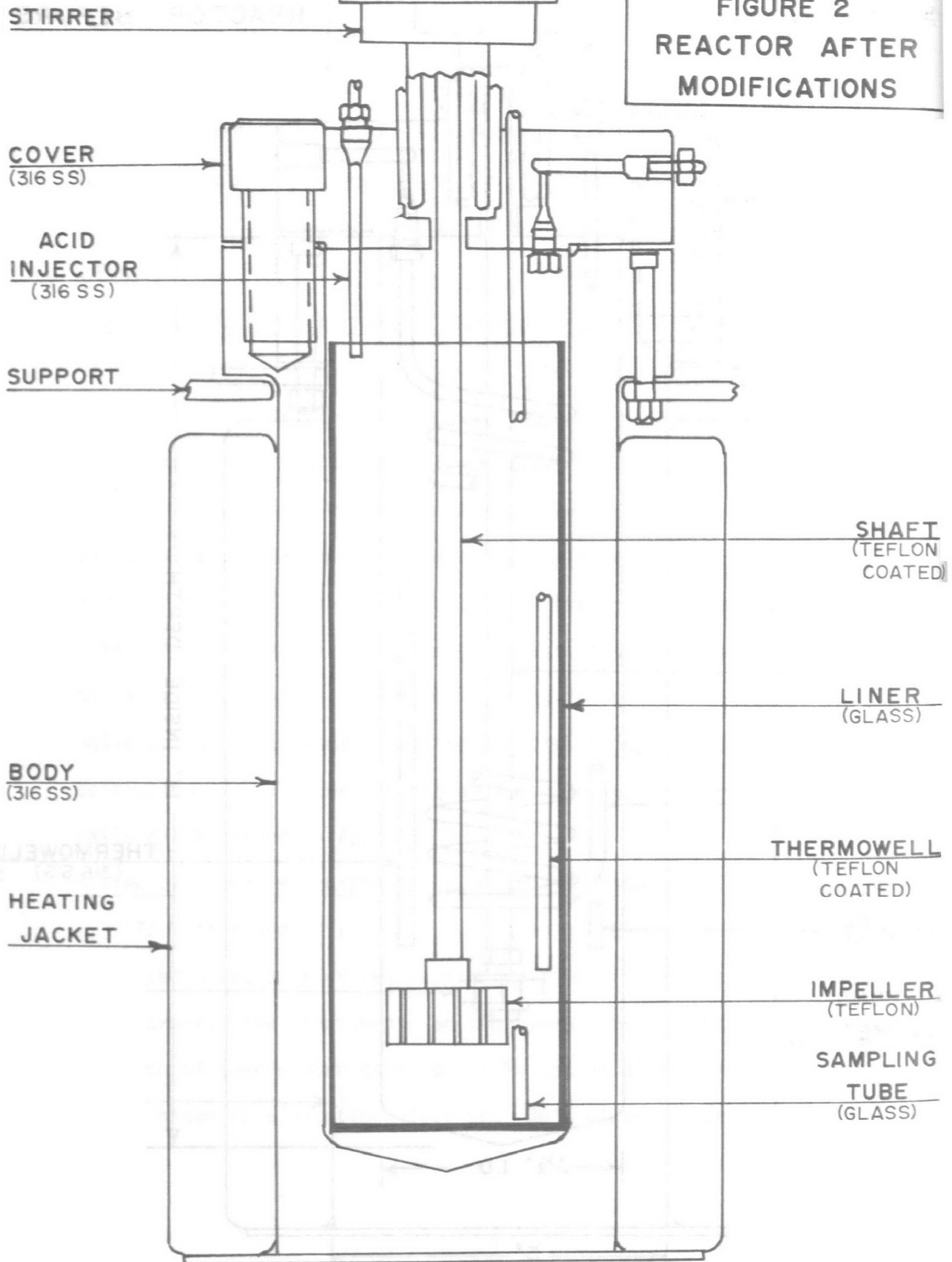


FIGURE 2
REACTOR AFTER
MODIFICATIONS



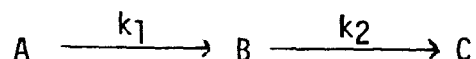
were filled with the reactants, sealed and placed in the digester.

About 1.5 minutes were required to reach the desired steam pressure/temperature in the digester and an equal time was required to drop it to atmospheric pressure.

Sugar analyses were made by the Shaffer and Somogyi method¹³ using their developed reagent and a 30 minute boiling time. Unhydrolyzed carbohydrate material was determined by subjecting the residue to a quantitative saccharification followed by sugar analysis.

Experimental Theoretical Basis and Design

Saeman showed that the hydrolysis of cellulose is described by the following consecutive first order reactions.



where: A = Cellulose

B = Glucose

C = Glucose decomposition products

k_1 and k_2 = Reaction Rates

The amount of A, B, or C present at any time during the reaction is described by the following formulas¹⁴:

$$A = A_0 e^{-k_1 t} \quad \text{Eq. 1}$$

$$B = \frac{A_0 k_1}{k_2 - k_1} (e^{-k_1 t} - e^{-k_2 t}) \quad \text{Eq. 2}$$

$$C = A_0 \left[1 + \frac{1}{k_1 - k_2} (k_2 e^{-k_1 t} - k_1 e^{-k_2 t}) \right] \quad \text{Eq. 3}$$

where: A_0 = the initial concentration of cellulose

t = time in minutes after the reaction begins

The time at which net glucose production reaches a maximum is given by:

$$t = \frac{\ln k_2 - \ln k_1}{k_2 - k_1} \quad \text{Eq. 4}$$

The maximum net glucose yield is given by the formula:

$$B_{\text{max.}} = A_0 \frac{\left[\frac{k_2}{k_1} \right] \frac{k_2}{k_1 - k_2}}{(k_1)} \quad \text{Eq. 5}$$

Temperatures of 190°C, 210°C, and 230°C with acid concentrations of 0.2, 0.4, and 0.8 percent by weight were chosen as the conditions at which the hydrolysis reaction would be studied. The lower temperature and acid conditions were chosen because previous research on the hydrolysis of wood cellulose¹⁵ indicated that hydrolysis temperatures less than 190°C with acid concentrations less than 0.2 percent did not produce significant glucose yields. The upper temperature and acid concentrations were chosen because extrapolation of low temperature reaction rates indicated that with hydrolysis conditions more severe than 230°C and 0.8 percent acid, the time to maximum net glucose yield was less than one minute which would not allow for adequate process control.

Previous research efforts^{16,17} have shown that sulfuric acid,

hydrochloric acid or phosphoric acid can be used as a catalyst in the hydrolyses process. Sulfuric acid was chosen as the catalyst because it stimulates greater net glucose yields than phosphoric acid and although comparable net glucose yields can be obtained using either sulfuric acid or hydrochloric acid, sulfuric acid is less expensive and less corrosive.

The initial experimental design involved the solution of equation 2:

$$B = \frac{A_0 k_1}{k_2 - k_1} (e^{-k_1 t} - e^{-k_2 t})$$

Kraft paper and Whatman No. 2 filter paper that had been ground in a Wiley Mill to a particle size less than 0.5 mm were chosen as the cellulosic materials to be initially hydrolyzed. A quantitative saccharification was performed on the samples to determine the amount of cellulose present. The samples were then hydrolyzed at different temperatures and acid concentrations. At various times (t) during the reaction, the amount of glucose (B) was determined. The initial concentration of cellulose (A_0) was known from the quantitative saccharification. The reaction rates k_1 and k_2 can then be found by fitting the least squares curve for B through the two points. As Atkinson and Hunter¹⁸ proved, this is a very efficient method of determining k_1 and k_2 . However, sampling times and glucose content must be determined very accurately for optimum determination of k_1 and k_2 . During the initial trial runs some difficulties were experienced with the glucose determination due

to the presence of Cr^{+3} ions in the hydrolysate. The Cr^{+3} ions in the hydrolysate came from the type 316 SS acid injection system which was subsequently lined with nylon tubing to overcome the problem.

After correcting the Cr^{+3} ion difficulty, the experimental design was changed to permit close monitoring and better understanding of the reaction and more confidence in the results. The first portion of the revised experimental design involved the study of the rate at which glucose is converted to 5-methylhydroxyfurfural, k_2 in Equation 2.

The hydrolysis of glucose is described by the formula:

$$B = B_0 e^{-kt} \quad \text{Eq. 6}$$

where: B = the amount of glucose present at time t

B_0 = the initial amount of glucose

t = time, minutes

k = reaction rate.

To determine the value of k at each temperature and acid concentration, glucose was injected into the reactor and samples were taken at various times and analyzed for glucose content. A plot of the logarithm of the remaining glucose versus time is a straight line whose slope is the reaction rate k_2 .

The second portion of the revised experimental design will involve the study of the hydrolysis of the filter paper. At each temperature and acid concentration, the filter paper is to be hydrolyzed and samples taken at various times and analyzed for glucose content. Equation 2 can then be solved for k_1 since A_0 , initial cellulose

content, is known from the quantitative saccharification procedure and k_2 is known from the hydrolysis of glucose. The amount of 5-methylhydroxyfurfural, levulinic acid and formic acid produced by the hydrolysis reactions will be monitored to aid in the determination of the rate at which they are formed.

The next phase of the research work will determine the effect of paper concentration and particle size on the production of glucose and other compounds. Once this has been found, samples of refuse will be hydrolyzed to determine if the reaction rates vary from those associated with filter paper hydrolysis.

To determine the amount of potential glucose contained in refuse, samples are periodically taken whenever the Center Hill Laboratory hammermill is operated. These samples are then ground in the Wiley mill and exposed to a quantitative saccharification procedure whereby all the cellulose is converted to glucose. From this information, a good estimate is obtained of hydrolyzable cellulose in municipal refuse.

RESULTS AND DISCUSSION

Initial Experimental Design to Elaborate for Simple Solution of Reaction Rates

Table 1 and figures 3 through 7 show the glucose yields versus time obtained by the hydrolysis of filter and Kraft paper at various temperatures and in the presence of 0.2 percent by weight sulfuric acid. Also shown are the glucose yields from the extrapolation of Saeman's reaction rates.

In each case, the experimentally determined glucose yield was less than that predicted by the Saeman reaction rate extrapolation. Also, in each experimental determination, the time to maximum glucose yield was less than expected from the extrapolation of Saeman's data. There were two reasons for these discrepancies. One was that Cr^{+3} ions were injected into the reactor with the sulfuric acid and interfered with the glucose determination. This resulted in a deceptively low indication of glucose present. The second reason for the discrepancies was that the cellulosic material was placed in the reactor and heated for as long as three hours before the operating temperature was obtained. During this time the cellulosic material was being thermally degraded. Therefore, less cellulose was available when the acid was injected and the hydrolysis reaction began. The heating also made the remaining cellulose more susceptible to the hydrolyses reaction and resulted in higher than expected initial yields of glucose and a shorter time to maximum yield.

TABLE 1 - GLUCOSE YIELDS FROM KRAFT PAPER AND WHATMAN No. 2 FILTER PAPER

DATE	PAPER TYPE	PAPER CONC. (g/l)	TEMP. (°C)	ACID CONC. (%by wt)	TIME (min.)	GLUCOSE YIELD (%)	SAEMAN'S GLUCOSE YIELD (%)
3/12/69	Kraft	1	190	0.2	10	21.4	9.5
					56	27.4	32.0
					90	19.0	33.8
					107	14.9	32.5
					120	11.6	31.0
3/13/69	Kraft	1	210	0.2	2	17.4	14.0
					7	31.2	34.0
					9	32.2	39.0
					12	32.0	41.5
					15	28.4	42.4
					20	20.4	40.4
3/18/69	Whatman No. 2 Filter paper	10	190	0.2	10	17.5	9.2
					56	31.5	32.2
					90	27.9	34.0
					107	25.5	32.8
					120	23.4	31.1
3/19/69	Whatman No. 2 Filter Paper	10	210	0.2	2	15.5	14.5
					7	24.6	33.7
					9	26.3	38.0
					12	27.8	41.2
					15	27.8	42.0
					20	25.0	40.0
3/27/69	Whatman No. 2 Filter Paper	10	230	0.2	2	19.1	47.0
					3	18.5	50.5
					4	16.1	48.7
					6	10.5	39.1
					10	3.6	18.8
					15	1.6	6.6
					20	1.0	2.2

FIGURE 3

HYDROLYSIS OF KRAFT PAPER

190°C, 1 g/l PAPER, 0.2% wT/wT. H_2SO_4

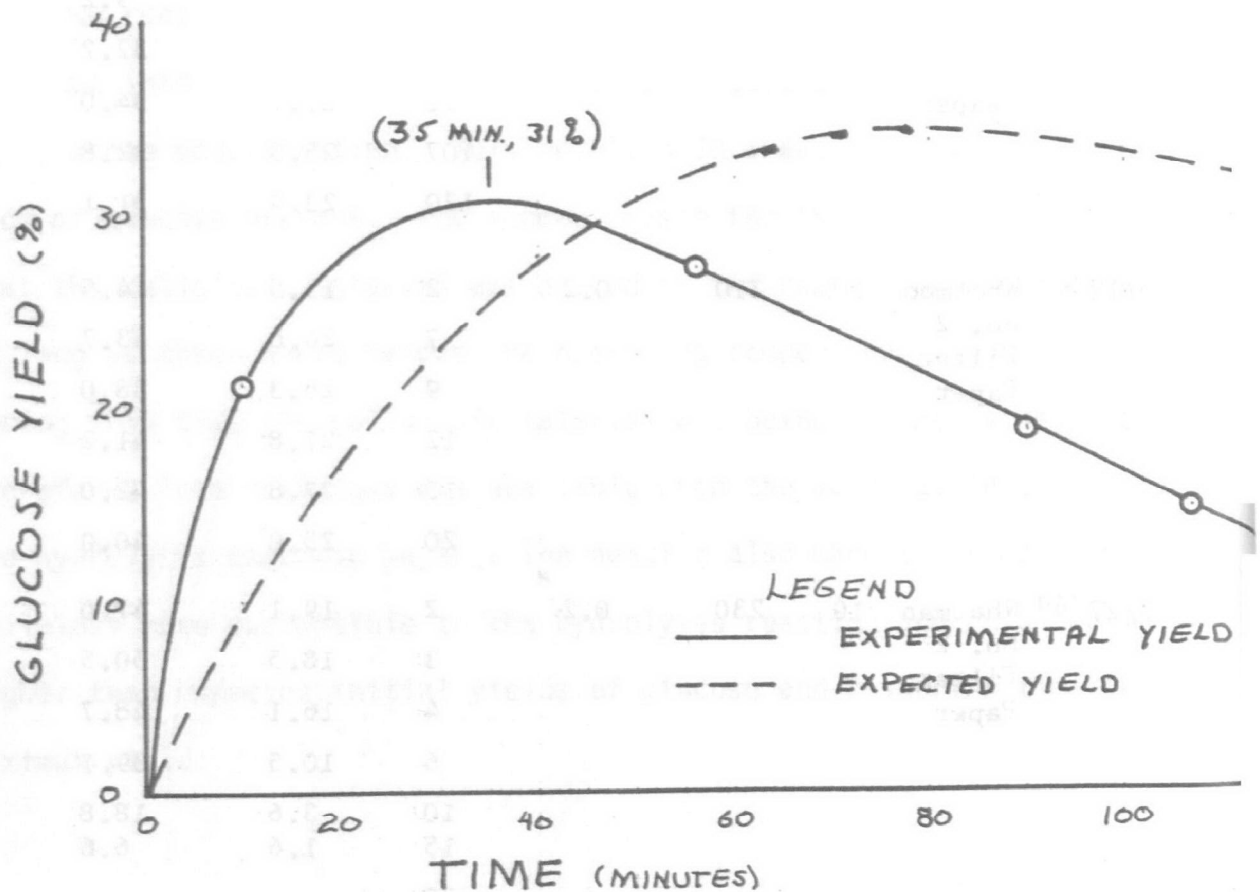


FIGURE 4

HYDROLYSIS OF KRAFT PAPER

210°C , 18/L PAPER , 0.2 % WT/WT. H_2SO_4

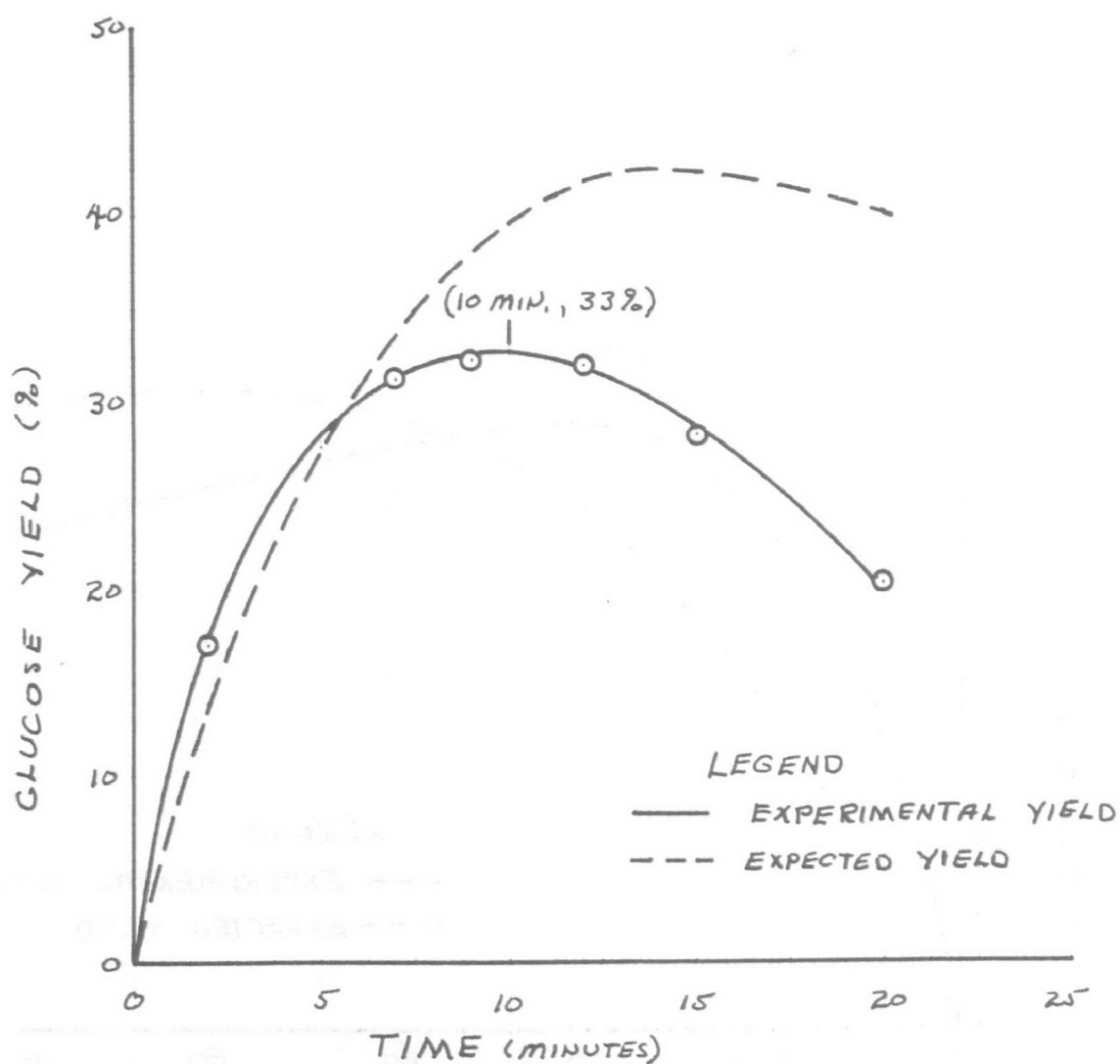


FIGURE 5

HYDROLYSIS OF FILTER PAPER

190°C, 10 g/l PAPER, 0.28 wt/wt. H_2SO_4

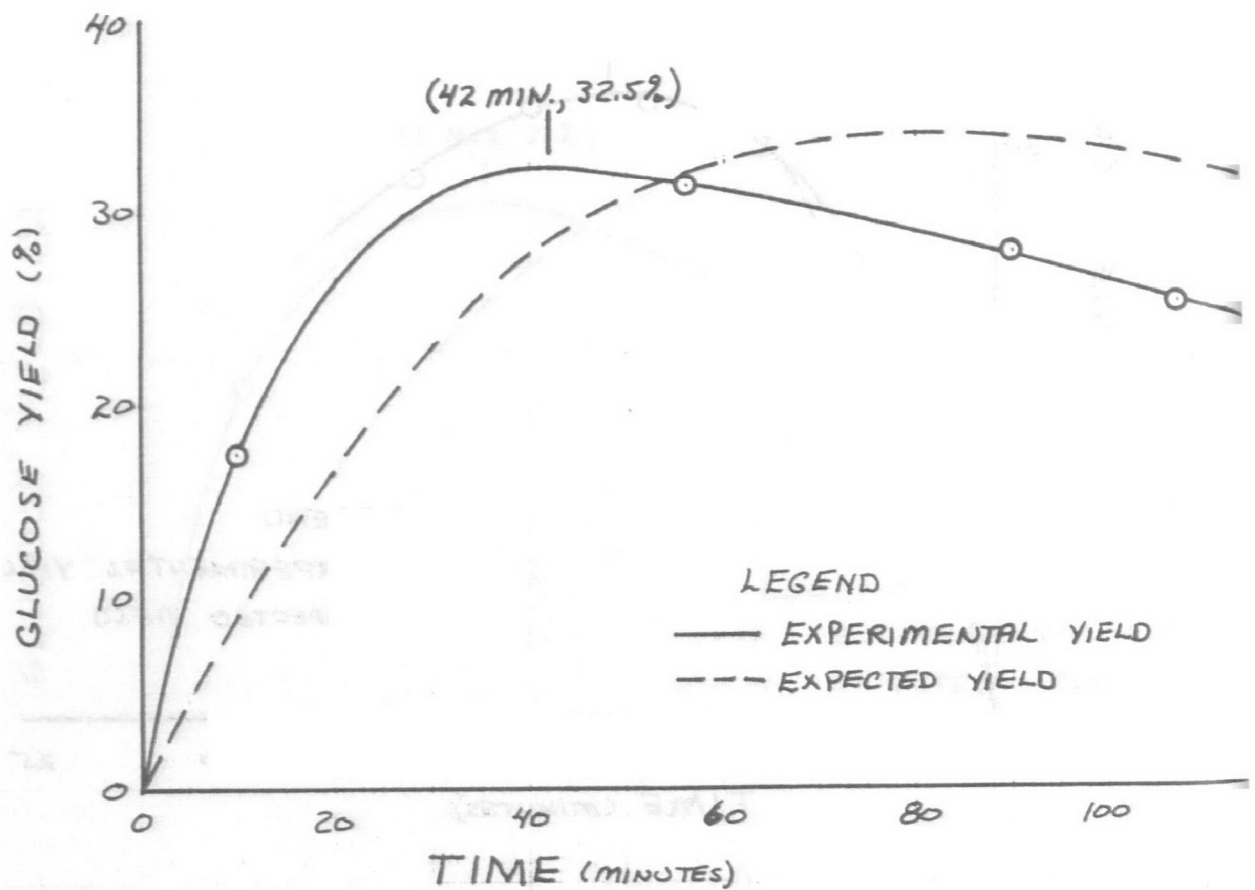


FIGURE 6

HYDROLYSIS OF FILTER PAPER

210°C, 10 g/l PAPER, 0.2% wT/wT H_2SO_4

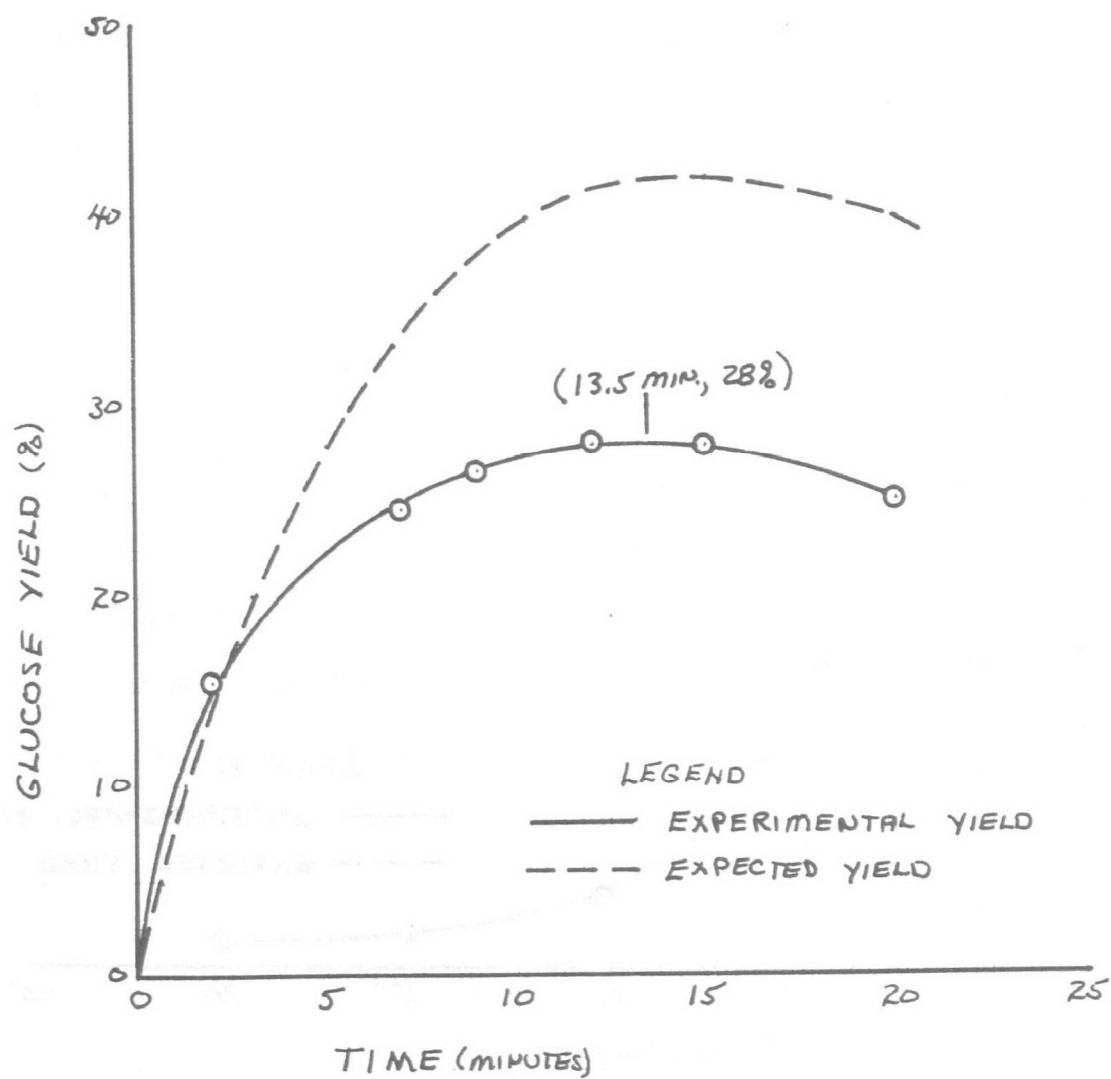
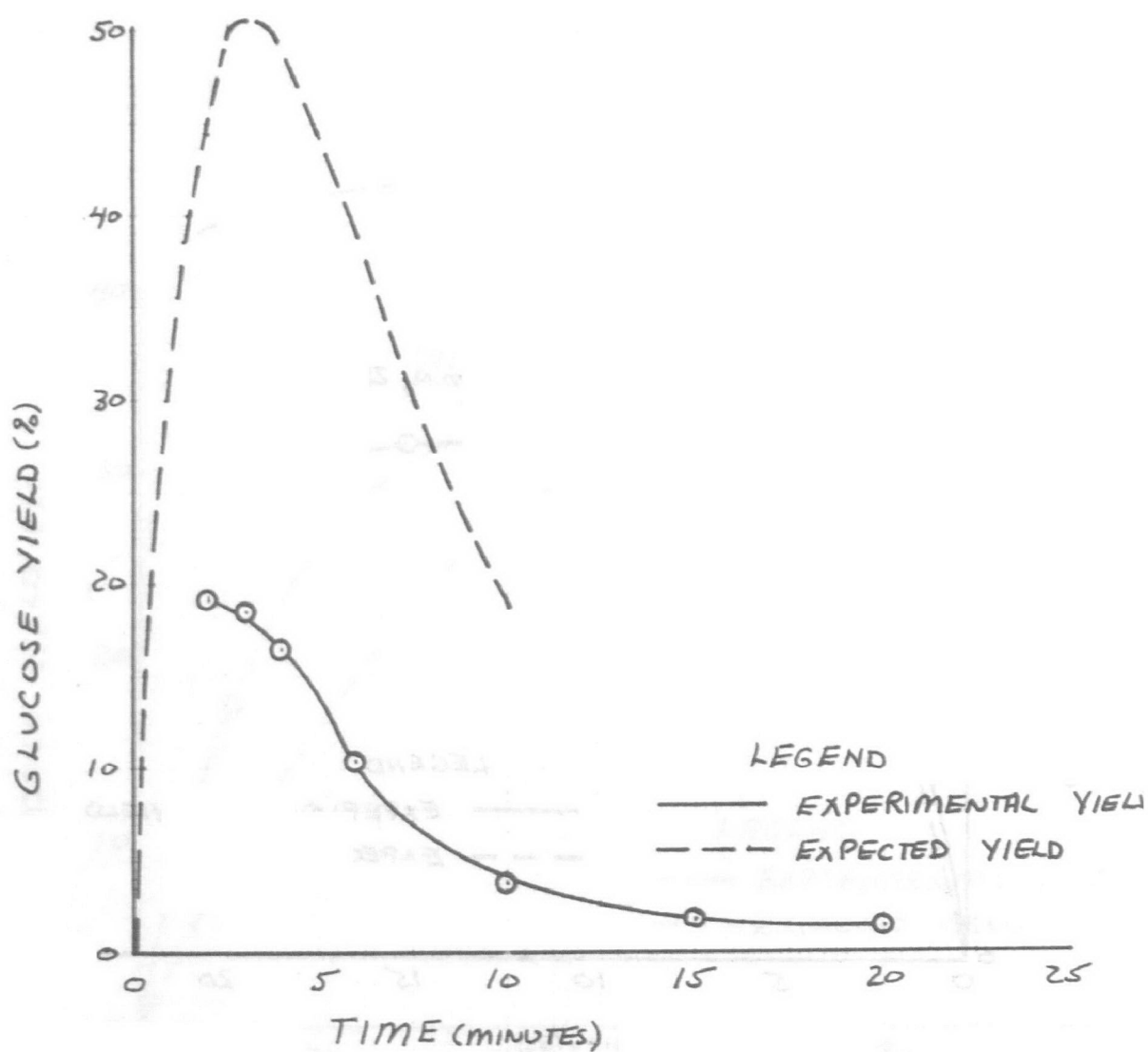


FIGURE 7

HYDROLYSIS OF FILTER PAPER

230°C, 10 g/L PAPER, 0.2% w/wt H_2SO_4



Revised Experimental Design Facilitates Determination of Reaction Rates

To provide a more complete understanding of the hydrolysis reaction and more confidence in the results, the experimental design was changed to study the hydrolysis of cellulose and glucose separately. During the first portion of the study, the rate at which glucose hydrolyzed under various conditions of temperature and acid concentration was studied. The second phase of the revised experimental design, the hydrolysis of cellulose, is just beginning and the results will be presented in a future report.

Figures 8 through 16 show the various conditions and rates of glucose decomposition. A summary of the experimentally determined rate constants is given in table 2. Also shown are rate constants calculated from equation 7, the formula derived by Saeman to describe the hydrolysis of fermentable sugars at temperatures in the 170°C to 190°C range.

$$k = 2.39 \times 10^{14} C_s^{1.02} e^{-\frac{32,870}{RT}} \quad \text{Eq. 7}$$

Where C_s = concentration of sulfuric acid, %

R = gas constant, 1.9865

T - absolute temperature, °K

Figure 17 is a plot of the logarithm of the reaction rates calculated from equation 7 as a function of the reciprocal of the absolute temperature for each of the three acid concentrations. Also shown are the experimentally determined reaction rates in the 190°C to 230°C range.

FIGURE 8

7/23/69

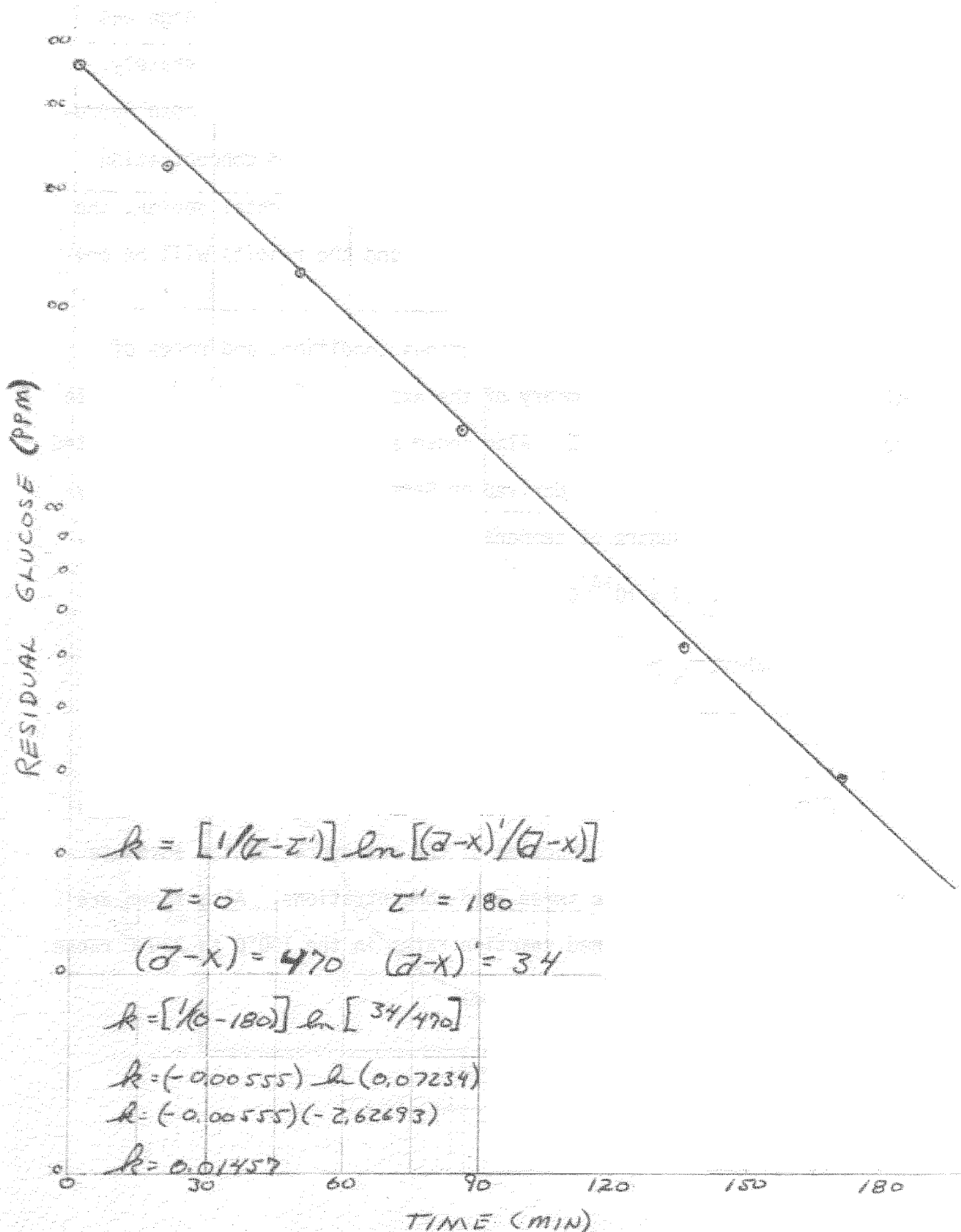
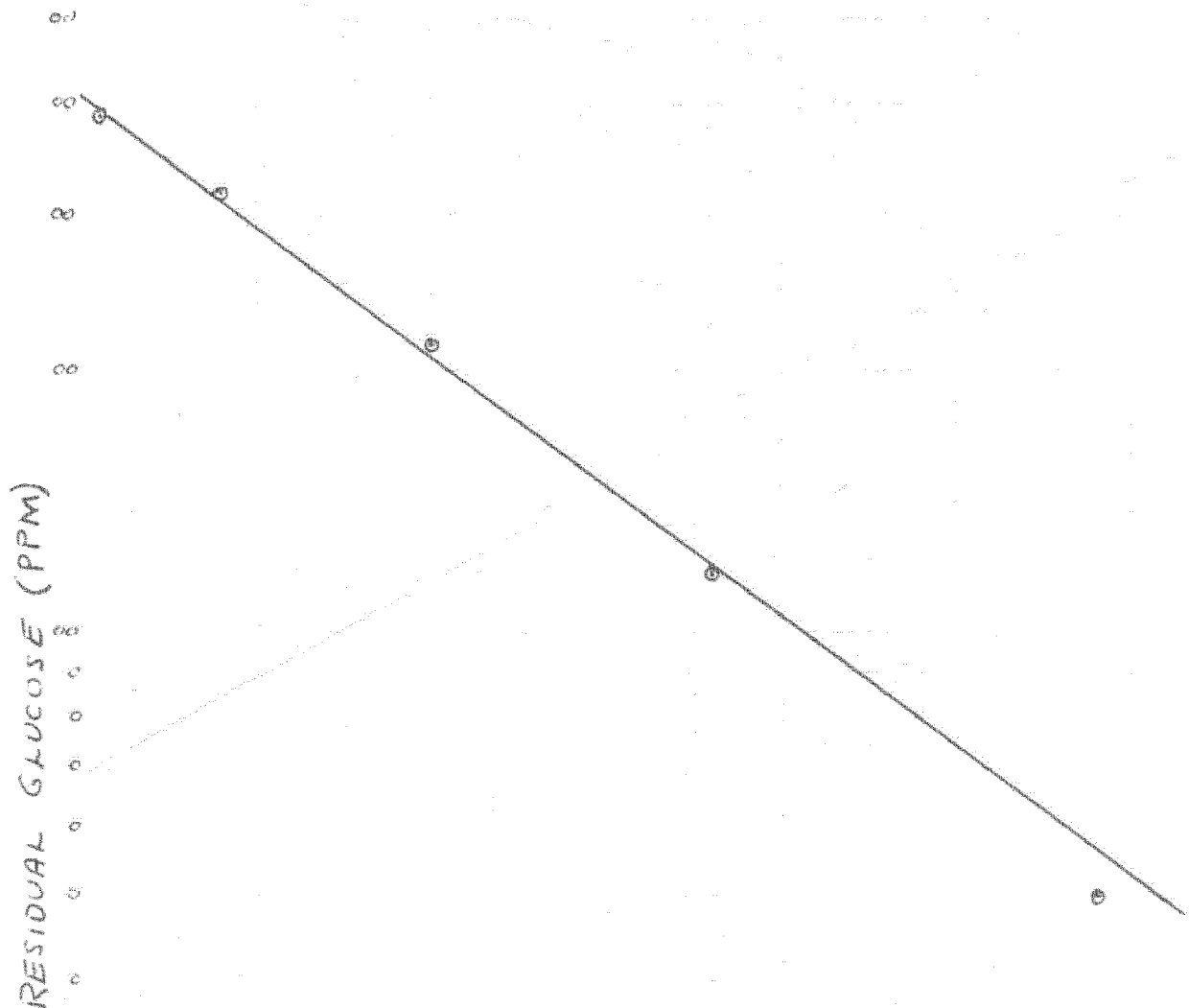
DECOMPOSITION OF
GLUCOSE190°C, 0.2% H₂SO₄

FIGURE 9

7/25/69

DECOMPOSITION OF
GLUCOSE210°C, 0.2% H₂SO₄

$$k = \left[\frac{1}{(t-t')} \right] \ln \left[\frac{(a-x')}{(a-x)} \right]$$

$$t = 0$$

$$t' = 30$$

$$(a-x) = 410$$

$$(a-x') = 53$$

$$k = \left[\frac{1}{(0-30)} \right] \ln \left[\frac{53}{410} \right]$$

$$k = (-0.03333) \ln (0.1293)$$

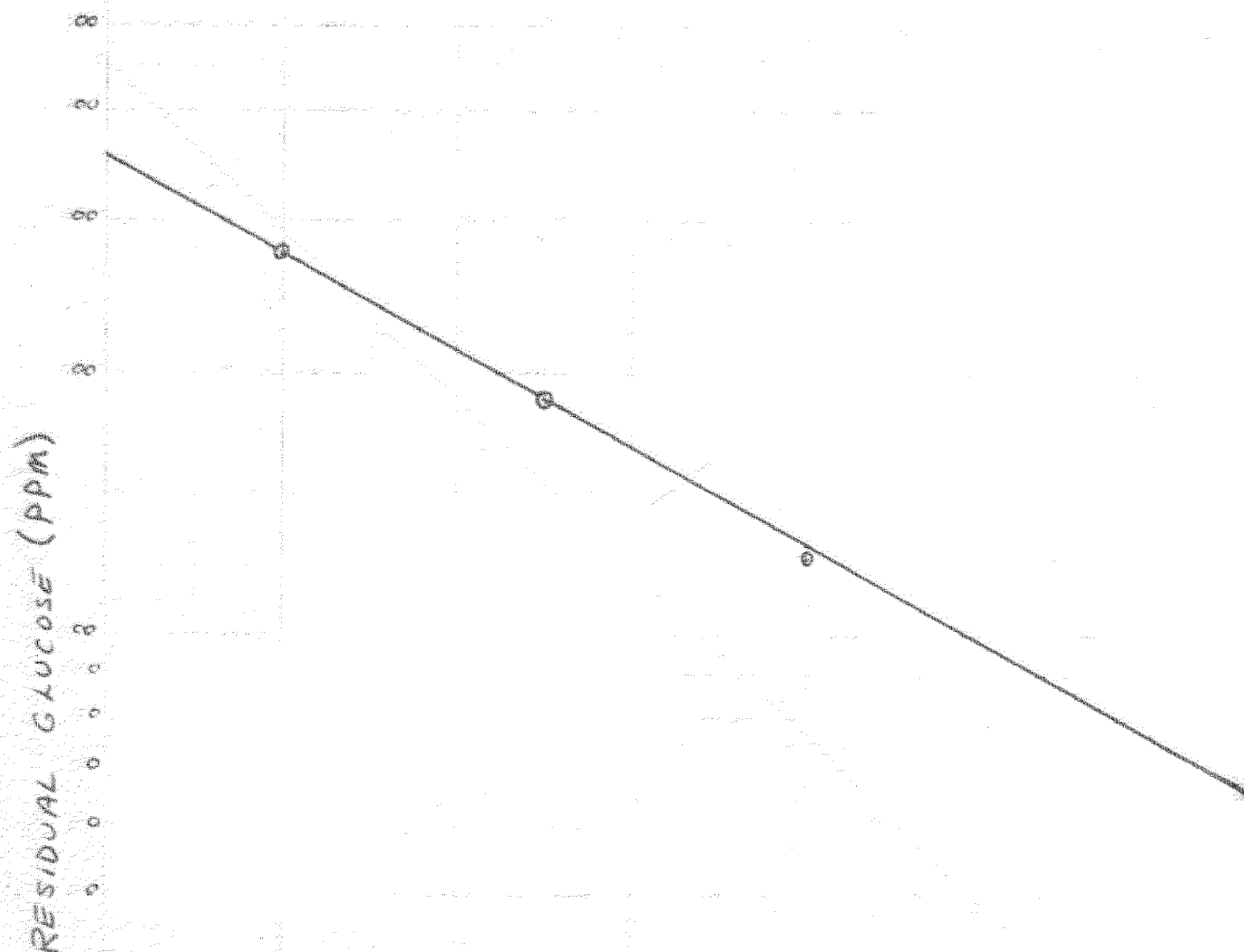
$$k = (-0.03333) (-2.04562)$$

$$k = 0.06818$$

TIME (MIN.)

FIGURE 10

7/28/69

DECOMPOSITION OF
GLUCOSE230°C 0.2% H_2SO_4 

$$k = \left[\frac{1}{t - t'} \right] \ln \left[\frac{(a - x')}{(a - x)} \right]$$

$$t = 0$$

$$t' = 7$$

$$(a - x) = 355$$

$$(a - x') = 59$$

$$k = \left[\frac{1}{0 - 7} \right] \ln \left[\frac{59}{355} \right]$$

$$k = (-0.14285) \ln (0.1662)$$

$$k = (-0.14285)(-1.79456)$$

$$k = 0.2564$$

TIME (MIN)

FIGURE 11

7/29/69

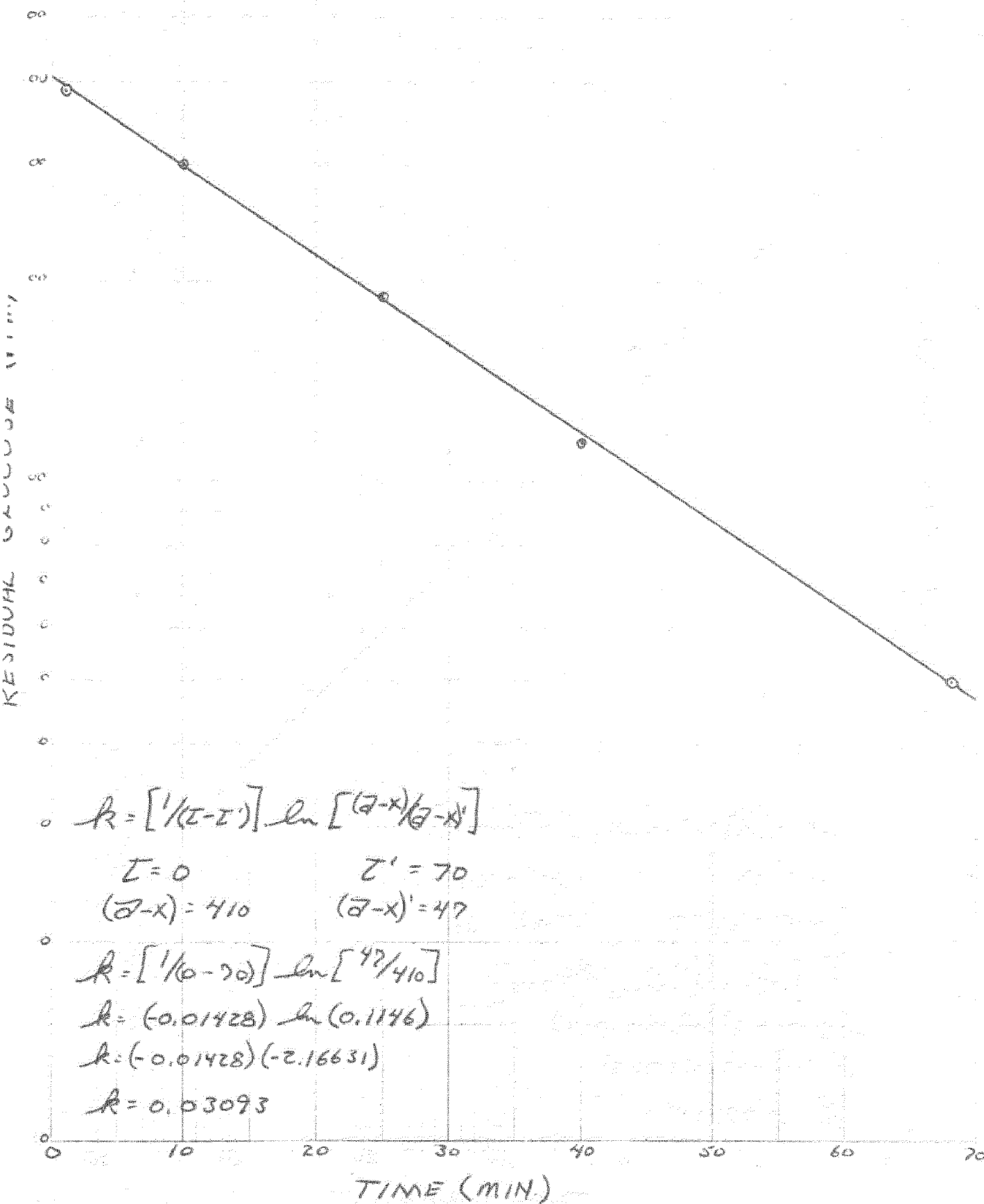
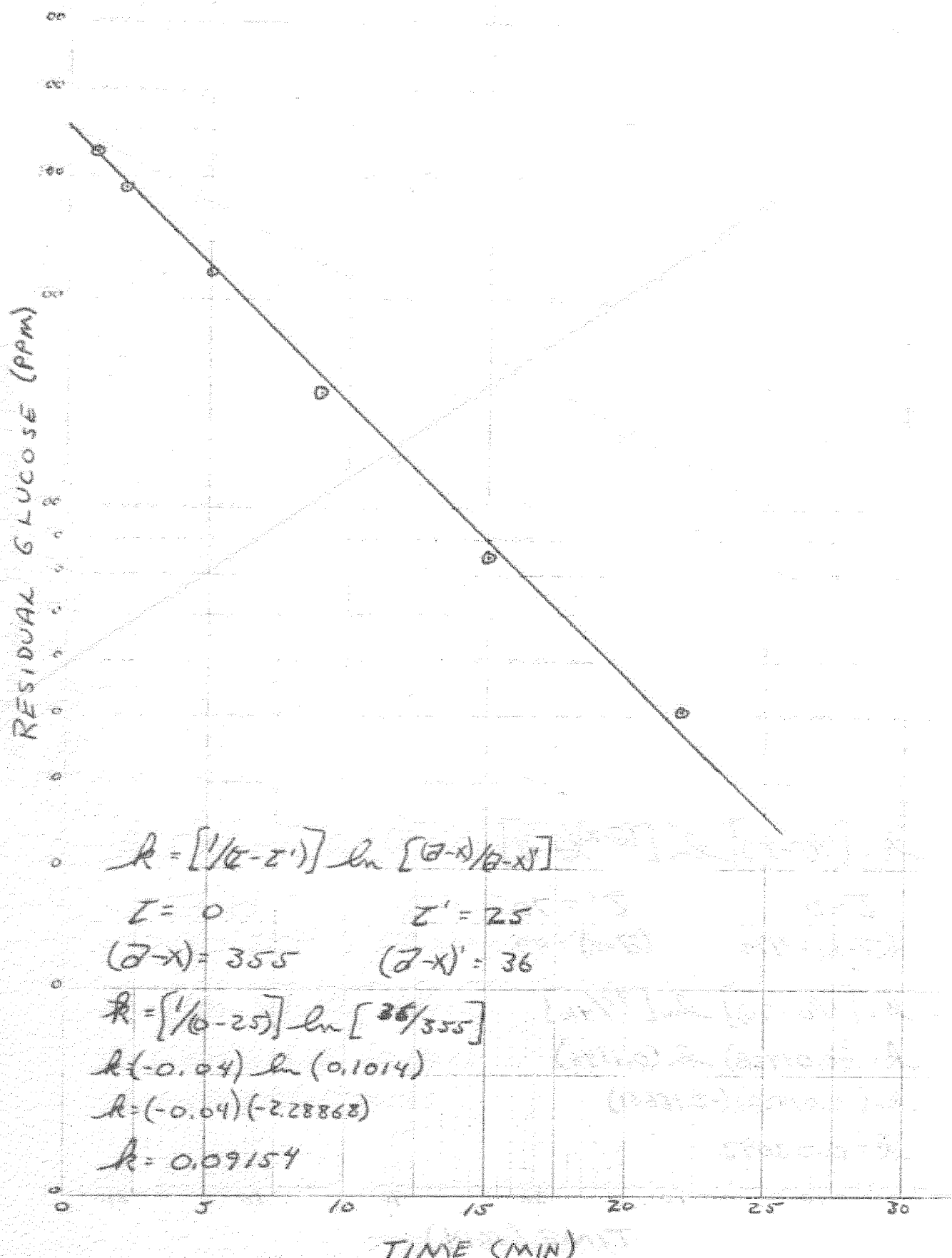
DECOMPOSITION OF
GLUCOSE190°C, 0.4% H₂SO₄

FIGURE 12

7/30/69

DECOMPOSITION OF
GLUCOSE206°C, 0.4% H₂SO₄

$$R = \left[\frac{1}{(Z - Z')} \right] \ln \left[\frac{(Z - X)}{(Z - X')} \right]$$

$$Z = 0$$

$$Z' = 25$$

$$(Z - X) = 355$$

$$(Z - X') = 36$$

$$R = \left[\frac{1}{(0 - 25)} \right] \ln \left[\frac{355}{36} \right]$$

$$R = (-0.04) \ln (0.1014)$$

$$R = (-0.04) (-2.28868)$$

$$R = 0.09154$$

FIGURE 13

7/31/69

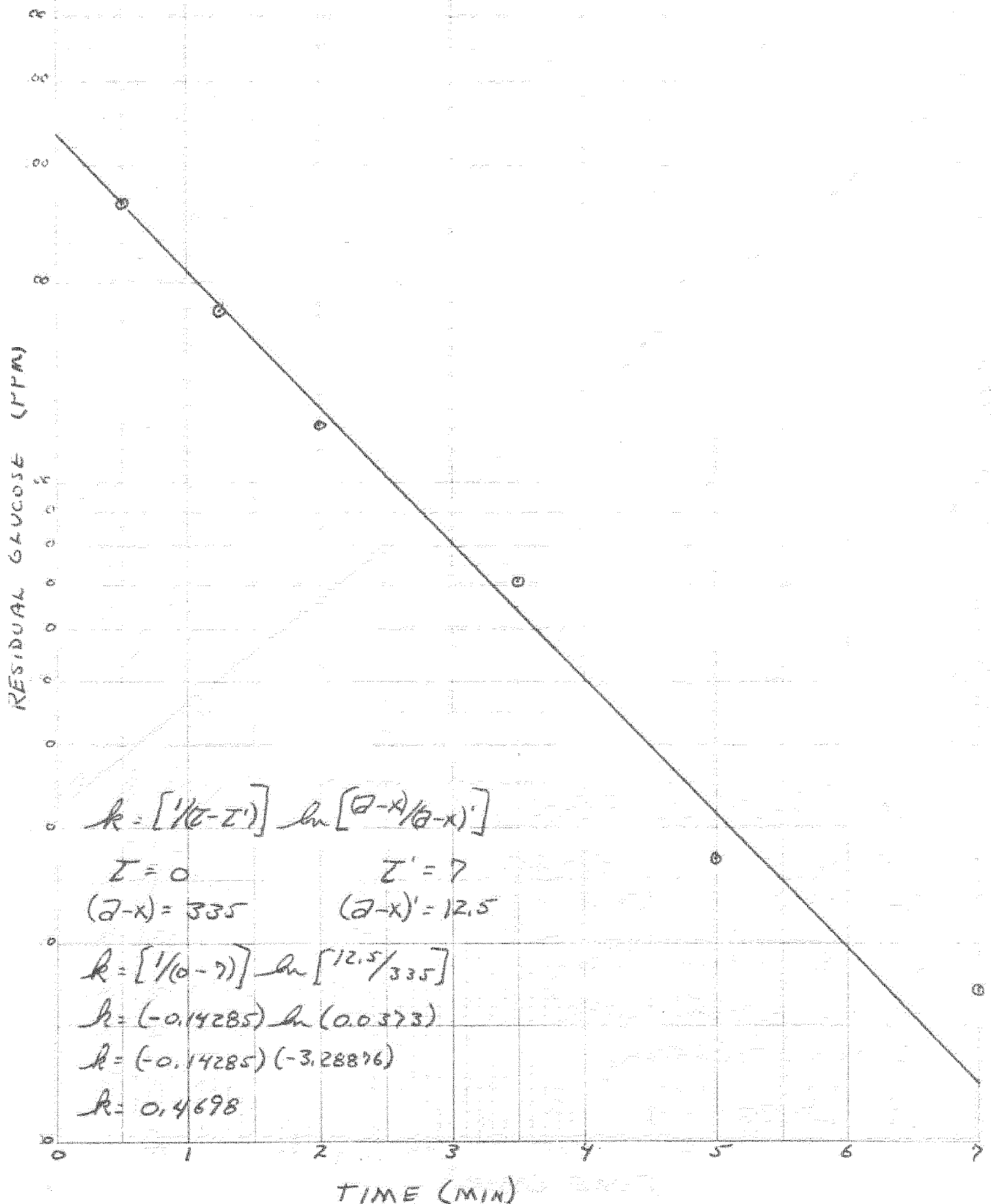
DECOMPOSITION OF
GLUCOSE230°C, 0.4% H₂SO₄

FIGURE 14.

8/1/69

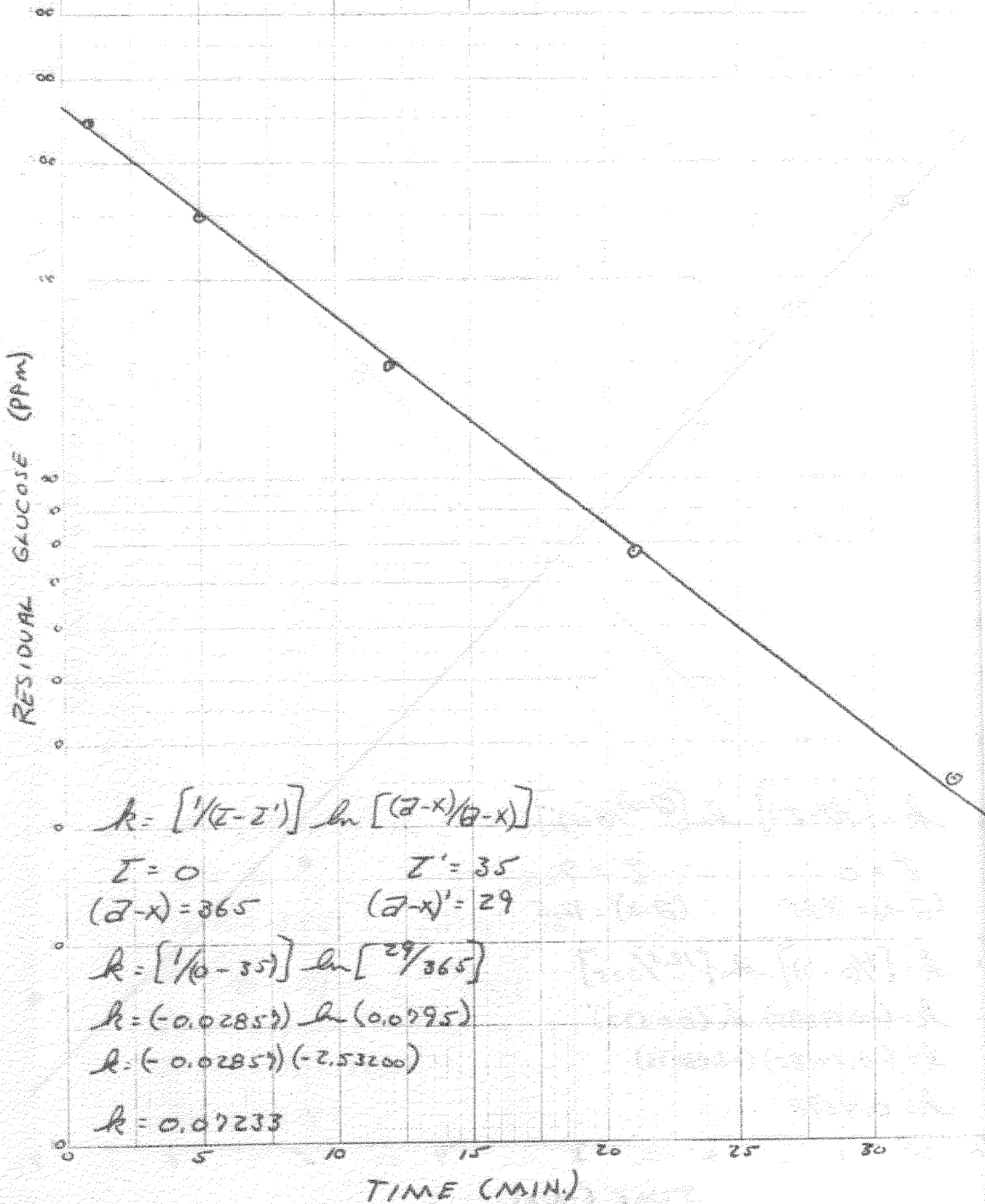
DECOMPOSITION OF
GLUCOSE195°C, 0.82 H₂SO₄

FIGURE 15

8/4/69

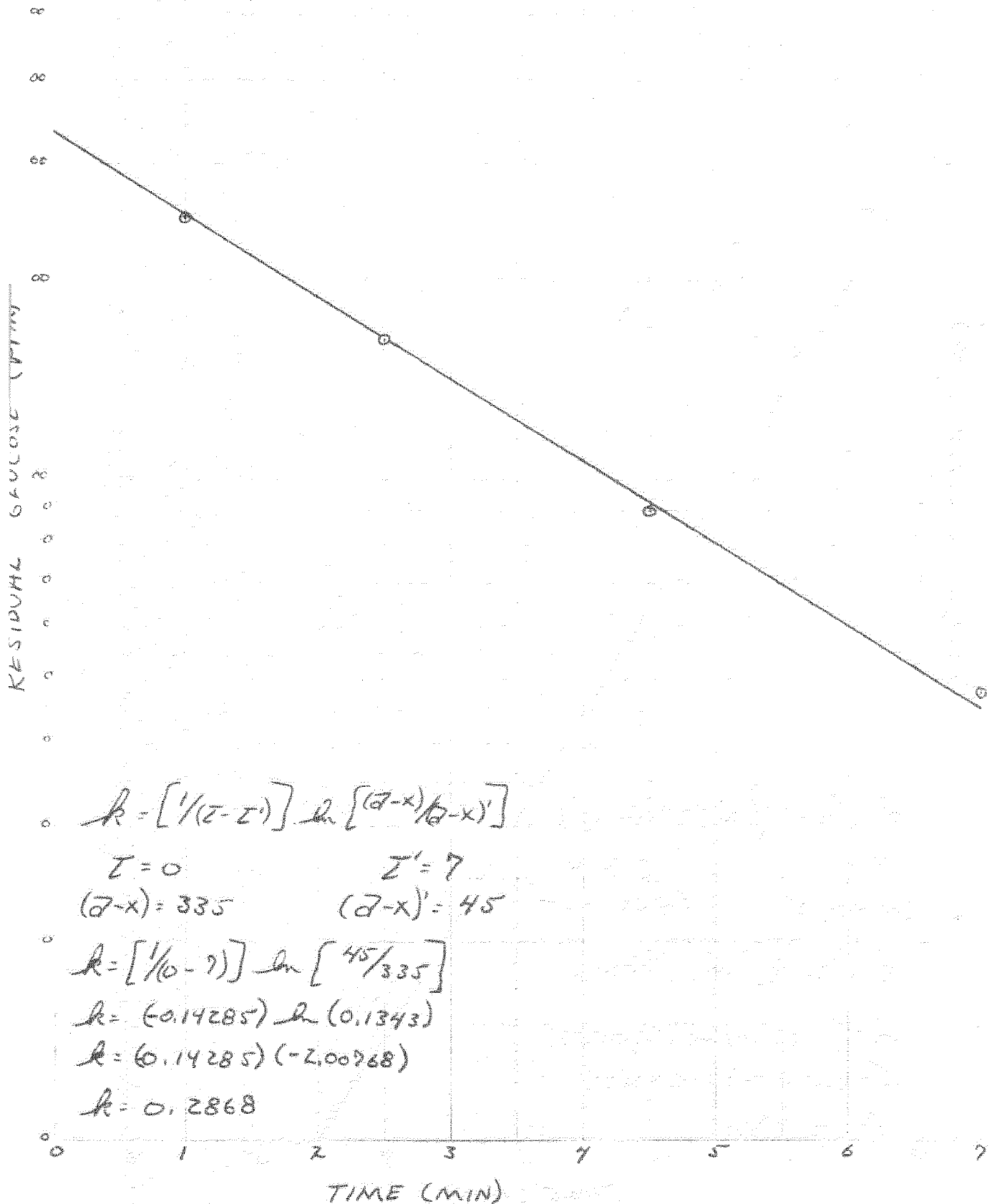
DECOMPOSITION OF
GLUCOSE212°C, 0.88 H₂SO₄

FIGURE 16

8/5/69

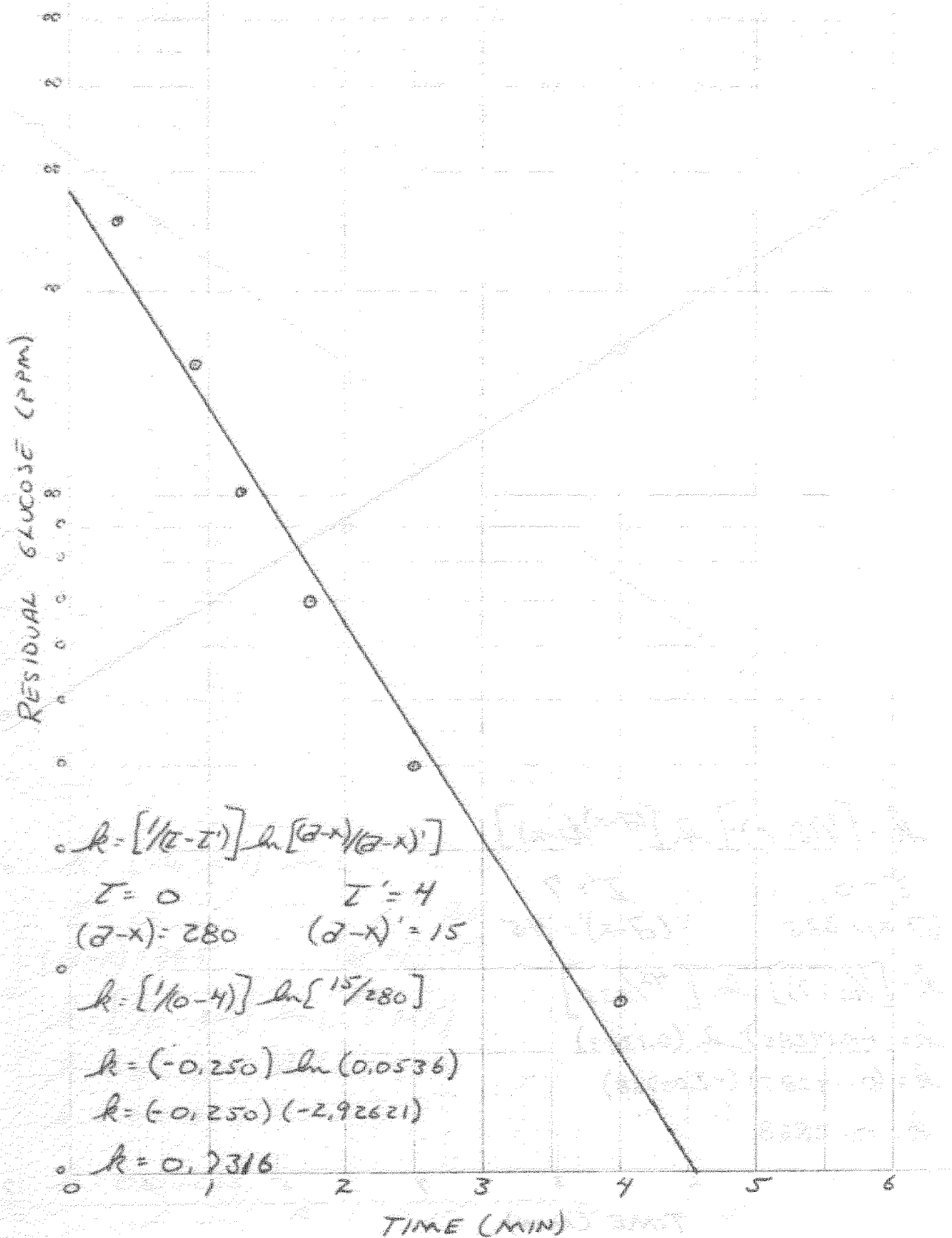
DECOMPOSITION OF
GLUCOSE226°C, 0.88 H₂SO₄

TABLE II - DECOMPOSITION OF GLUCOSE IN 0.2%, 0.4% and 0.8% SULFURIC ACID AT VARIOUS TEMPERATURES

H_2SO_4	(°C) Temperature	k_{exp1} (min^{-1})	k_{Saeman} (min^{-1})
0.2	190	0.0146	0.0142
	210	0.0682	0.0621
	230	0.256	0.242
0.4	190	0.0309	0.0287
	206	0.0915	0.0946
	230	0.470	0.491
0.8	195	0.0723	0.0852
	212	0.287	0.294
	226	0.732	0.765

TEMPERATURE $^{\circ}\text{C}$

32

230 220 210 200 190 180 170

FIGURE 17

RELATION OF FIRST ORDER REACTION
CONSTANT k TO TEMPERATURE IN
DECOMPOSITION OF GLUCOSE WITH
 H_2SO_4 AT VARIOUS STRENGTHS
EXTRAPOLATED FROM SAEMAN'S DATA
AT $170^{\circ}\text{C} - 190^{\circ}\text{C}$

○ EXPERIMENTALLY OBTAINED
REACTION CONSTANTS AT
 $190^{\circ}\text{C} - 230^{\circ}\text{C}$

FIRST ORDER REACTION CONSTANT (k , MIN.^{-1})

1.0
0.50
0.20
0.10
0.050
0.020
0.010
0.005
0.002

0.8% H_2SO_4
0.4% H_2SO_4
0.2% H_2SO_4

EXTRAPOLATION OF
SAEMAN'S DATA

SAEMAN'S
EXPERIMENTAL
RANGE

200 205 210 215 220 225

RECIPROCAL OF THE ABSOLUTE TEMPERATURE
($1/\text{K}^{\circ} \times 10^5$)

It appears that there is no significant difference between the experimentally determined reaction rates and the reaction rates calculated from equation 7.

A rigorous statistical comparison of the results will be conducted to determine the necessity of further experimental efforts related to the decomposition of glucose.

As indicated earlier, P_orteous⁸ recently designed a hydrolysis process for the production of glucose from cellulose in municipal refuse. The operating conditions of his process were 230°C with 0.4 percent sulfuric acid concentration. The kinetic data used by P_orteous was extrapolated from the work done by S_aeman in the 170°C to 190°C range. It appears that the extrapolation of S_aeman's reaction coefficients for the decomposition of glucose gives valid values at higher temperatures. Therefore, it seems reasonable to accept the reaction coefficients used by P_orteous for glucose decomposition.

The reaction rates used by P_orteous for the formation of glucose are also extrapolated from the work S_aeman did on the hydrolysis of wood chips. It is quite possible that refuse associated cellulose hydrolyzes at a faster rate than is predicted by the extrapolation to 230°C of the wood hydrolysis work at 170-190°C. Therefore, reaction coefficients at temperatures up to 230°C will have to be determined experimentally for final process design.

The production of 5-methylhydroxyfurfural was monitored as the glucose hydrolyzed at various conditions. Figures 18 and 19 give an indication of the effect of temperature and acid concentration on the

FIGURE 18

EFFECT OF TEMPERATURE ON
YIELD OF 5-METHYLHYDROXYFURFURAL

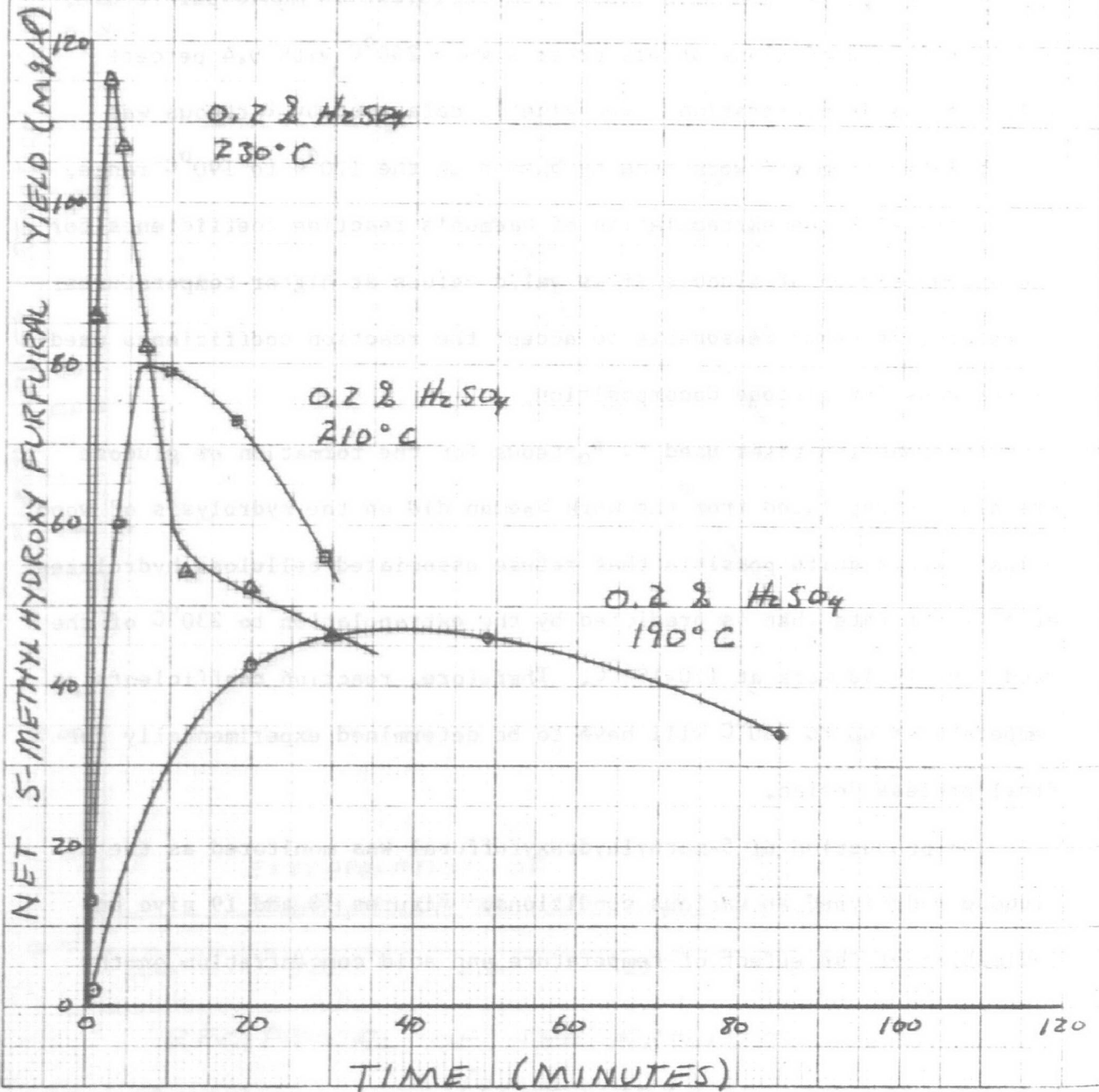
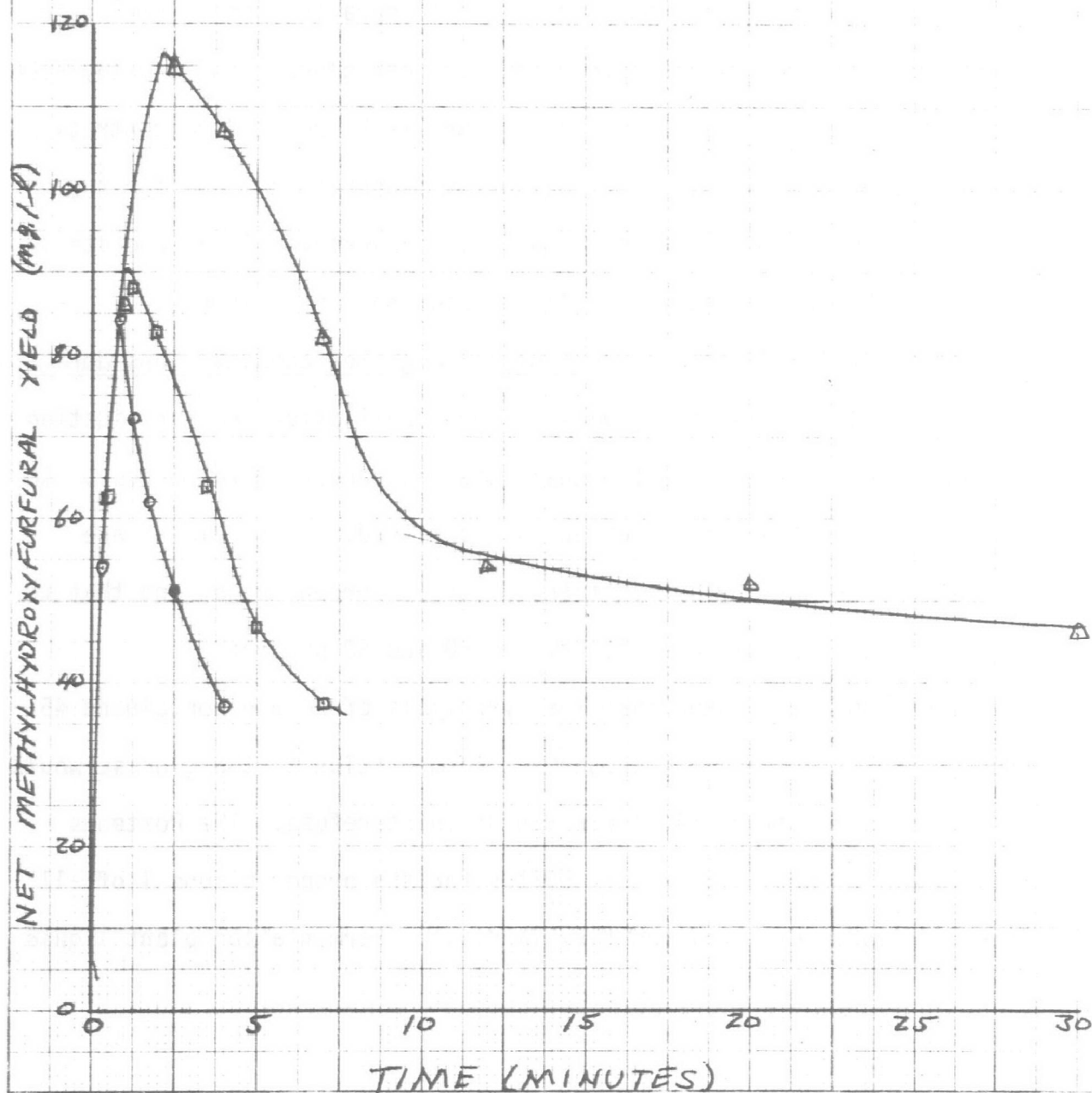


FIGURE 19

EFFECT OF ACID CONCENTRATION
ON YIELD OF 5-METHYLHYDROXYFURFURAL



5-methylhydroxyfurfural yield. The reaction rates governing its production and decomposition have not yet been fully determined. However, in figures 18 and 19, it appears that the 5-methylhydroxyfurfural is present in the hydrolysate for an adequate time to facilitate its removal. As indicated in figures 18 and 19, the greatest 5-methylhydroxyfurfural yields were obtained at 230°C with a 0.2 percent sulfuric acid concentration. Therefore, it would appear that operating conditions could exist for the near maximum production of both glucose and 5-methylhydroxyfurfural at a relatively high temperature with low acid concentrations. Also it should be possible to choose the proper conditions for the production of maximum amounts of both 5-methylhydroxyfurfural and its decomposition products, namely, levulinic acid and formic acid.

Refuse Potential Glucose Content High Enough For Economic Consideration

Table III shows the results of the quantitative saccharification of ground refuse whereby all the cellulose was converted to glucose. An average yield of 40 to 45 percent was obtained. These yields are reasonable in that refuse contains 50 to 60 percent paper and that the cellulose content of paper is between 60 and 80 percent.

Porteous calculated that the hydrolysis of refuse containing 45 percent cellulose and the subsequent fermentation of the glucose would yield a net profit of \$4.21 per ton of input refuse. The Porteous estimated net profit allows \$4.50/ton for the proper disposal of all nonhydrolyzed refuse by sanitary landfill. Fermentation plant liquid

TABLE III - POTENTIAL GLUCOSE CONTENT OF REFUSE

Sample Number	Date Ground	Number of Determi- nations	Approximate Sample Size (g.)	Mean Glucose Yield (%)	Standard Deviation
19 D	10/10/68	5	0.5	38.1	2.36
26 E	10/19/68	5	0.5	45.5	3.24
11 D	10/30/68	5	0.5	43.7	1.95
11 D	10/30/68	5	3.8	39.3	1.61

effluent treatment has been considered by Porteous with allowance of 3¢/pound for BOD load reduction. Based on our preliminary work and Porteous financial estimates, it seems possible that the hydrolysis process would be economical in locales where the cellulose content of refuse is similar to that delivered to the Cincinnati Center Hill incinerator. The process economics could be more favorable if the hydrolysis process is designed for the production of 5-methylhydroxy-furfural or levulinic acid and formic acid as well as glucose.

V. PRELIMINARY PROCESS ECONOMIC EVALUATION

Glucose Price and Market Potential

Porteous⁸ showed that glucose produced by the hydrolysis of refuse is competitive with other raw materials in the production of ethanol by fermentation. Unfortunately, only about 17 million gallons (about 5 percent of total) of ethanol are produced annually by fermentation¹⁹. Using the Porteous design this is equivalent to the ethanol production from about 5 hydrolysis - fermentation plants processing 250 tons/day of refuse. Therefore, it appears that other uses for the glucose produced from the hydrolysis of the cellulosic portion of refuse must be found.

Recently Fogan²⁰ determined that the acid hydrolyses of refuse will produce glucose at 2-3 cents per pound which is competitive with blackstrap molasses provided the plant processes at least 350 tons/day of refuse containing 50 percent paper. Understandably, larger plants processing refuse with higher paper contents could produce glucose at an even more competitive price.

In 1967 approximately 300 million gallons of blackstrap molasses were used in the industrial production of drugs, citric acid, vinegar and ethanol²⁰. This indicates that about 1 million tons of such sugars were consumed in processes that could equally as well use the product of a hydrolyses plant²¹. This is equivalent to the glucose output of about 30 hydrolysis plants processing 500 tons/day each of refuse with a 50 percent paper content which is equal to approximately 3 percent of

the United States daily production of 500,000 tons¹ of municipal refuse.

Methylhydroxyfurfural Price and Market Potential

Methylhydroxyfurfural is formed by the hydrolysis of glucose and is present in the hydrolysate at the time of maximum glucose yield. Further hydrolysis results in an increase in the methylhydroxyfurfural yield.

Methylhydroxyfurfural is polyfunctional and can be used to synthesize a wide variety of compounds. It behaves like a normal primary alcohol and, in some instances, as an aromatic aldehyde. Ring reactions include addition, ring cleavage and ring cleavage followed by closure to give 6-membered hetrocyclic rings. Little attention has been given to exploiting this interesting compound, probably because of the difficulty of obtaining sizable quantities of high-quality material²¹.

As stated earlier, about 22 percent by weight of refuse can be converted to glucose. Figures 18 and 19 show that at 230°C and 0.2 percent acid concentration, that about 120 mg of methylhydroxyfurfural is formed from 500 mg of glucose. This is equivalent to about a 24 percent conversion. Therefore, if 22 percent by weight of refuse can be converted to glucose, and 24 percent of the resulting glucose can be converted to methylhydroxyfurfural, then it follows that about 5 percent of the refuse weight can be converted to methylhydroxyfurfural.

But, little attention has been given to exploiting methylhydroxyfurfural because of the difficulty in producing sizeable quantities of high-quality material. If sizeable quantities can be produced by the hydrolysis of the cellulosic portion of refuse then it is possible

that many uses for it might be found. The current consumer price for methylhydroxyfurfural is \$14.75 for 5 grams²² which is equivalent to \$83 per ounce. Undoubtedly, large quantities cost less per gram and if sizeable quantities become available the price will drop. However, it appears that the production of methylhydroxyfurfural from refuse would be profitable.

Levulinic Acid and Formic Acid Price and Market Potential

Levulinic acid and formic acid are produced by the hydrolysis of glucose with methylhydroxyfurfural as an intermediate product. About 40 percent yields are obtained from glucose using sulfuric acid as the catalyst.²¹ Therefore, if 22 percent by weight of refuse can be converted to glucose and 40 percent of glucose converted to levulinic acid and formic acid then about 9 percent of refuse by weight can be converted to these acids. This is only a rough approximation and is true only if the glucose is recovered at the time of maximum yield and then hydrolyzed to levulinic acid and formic acid. The actual yield would be higher than the 9 percent indicated because there is levulinic and formic acid present in the hydrolysate at the time of maximum glucose yield and would therefore add to the 9 percent yield previously mentioned.

The 1967 production of formic acid was 18 million pounds and sold at about 15 cents per pound²³. Formic acid has many industrial applications including its use in electroplating, dying and processing of textiles, and in the production of formates and esters including cellulose esters²⁴.

Despite the low cost of the raw material (glucose) that can be used to produce levulinic acid, it has not been marketed as an inexpensive chemical intermediate. The controlling economic factor appears to be the high cost of recovery from dilute impure solutions²¹. Levulinic acid is produced in small quantities and is available from major chemical suppliers at about \$3.50 per pound²².

Once the problem of product recovery is solved, and levulinic acid is available at a lower cost, many uses for it should materialize, for levulinic acid reacts to form many interesting heterocyclic compounds²¹. Projected uses for levulinic acid that appear to have merit include the production of sebacic acid and nylon type polymers²¹. There is one use to which levulinic acid can immediately be put. It has been found that its sodium salt has ideal properties as an anti-freeze agent. It has definite advantages over ethylene glycol for this purpose. It is a water soluble solid and is therefore more easily marketed than the liquid glycol. It is less corrosive to the iron parts of internal combustion engines than is tap water itself and has no detrimental effect on the rubber connections used in engines²⁵.

VI. SUMMARY AND CONCLUSIONS

The preliminary results are as follows:

1. At temperatures between 190°C and 230°C and in the presence of 0.2 to 0.8 percent sulfuric acid, glucose decomposes at the rate predicted by the extrapolation of reaction rates determined at temperatures between 170°C and 190°C and in the presence of similar acid concentrations.
2. Refuse delivered to the Cincinnati Center Hill Incinerator contains about 40 to 50 percent cellulose that can be converted to glucose.
3. The process designed by Porteous for the production of glucose from the cellulosic portion of refuse and its subsequent fermentation to ethanol is realistic.
4. Glucose can be produced at a price competitive with blackstrap molasses by hydrolyzing refuse associated cellulose.
5. About 3% of the nations 180 million tons per year of municipal refuse can be hydrolyzed to produce a quantity of glucose equivalent to the annual consumption of blackstrap molasses.
6. Methylhydroxyfurfural, levulinic acid and formic acid formed by the hydrolysis of cellulose in municipal refuse are of economic value and if sufficient quantities are produced the price will probably become low enough to promote their extensive use in the chemical industry.

VII. FUTURE RESEARCH EFFORTS

The following tasks are planned for the completion of this research effort:

1. The determination of reaction rates governing the formation of glucose from cellulosic materials by the acid hydrolysis process at temperatures between 190°C and 230°C and in the presence of 0.2 to 0.8 percent sulfuric acid. This task should be completed by the end of the third quarter of Fiscal Year 1970.

2. The confirmation of preliminary results indicating that between 190°C and 230°C Glucose decomposes at a rate predicted by the extrapolation of reaction rates in the 170°C to 190°C temperature range. This task should also be completed by the end of the third quarter of Fiscal Year 1970.

3. The determination of reaction rates for the formation of glucose by the hydrolysis of the cellulosic portion of municipal refuse. This phase of the project should be completed by the end of Fiscal Year 1970.

4. The determination of reaction rates governing the formation of hydroxymethylfurfural, levulinic acid and formic acid from the cellulosic portion of refuse by the acid hydrolysis process. The projected completion date for this task is by the end of Fiscal year 1970.

5. The study of different pretreatment methods of municipal refuse and its effect on the production of glucose, hydroxymethylfurfural, levulinic acid and formic acid. The completion date for this task is predicted to be by mid Fiscal Year 1971.

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APPENDIX I

GLUCOSE, o-toluidine

1. Pipette, with a rubber bulb, 6.0 ml. of o-toluidine into a test tube.
2. Add 1 ml. sample, mix well.
3. Place in boiling water bath for 10 minutes, cool to room temperature in cold water.
4. Read in a spectrophotometer against reagent blank, at 630 m μ , in %T. Obtain value from calibration curve.
5. If value is too high to read, dilute volumetrically with glacial acetic acid, read, correct by appropriate dilution factor.

Reagent:

Mix 60 ml. o-toluidine with 1.5 gms thiourea in 1 L volumetric flask. Dilute to volume with glacial acetic acid, mix well. Transfer to brown glass bottle, Keeps at least 2 months at room temperature but must be well stoppered. It should be clear and colorless.

Note:

1. The reaction occurs only with aldohexoses, and will therefore react with galactose. The color follows Beers Law in concentrations up to 1000 mg. percent.
2. Solutions must be at room temperature when read. Warm solutions give falsely high values. Color is stable for 20-30 minutes.
3. o-toluidine will vary from batch to batch, and a new calibration curve must therefore be made when new stock toluidine is used.

Most commercial o-toluidines are not pure enough, Eastman Kodak is at present the best available. Thiourea is added to stabilize the reagent and to prevent turbidity.

References: the present method is a modification of several in the literature.

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