ACID HYDROLYSIS OF REFUSE

U.S. ENVIRONMENTAL PROTECTION AGENCY

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ABSTRACT

To recover some of the value of municipal solid waste, a new dis-
posal process was studied which uses the cellulose portion of refuse,
mainly paper, as a raw material for the production of sugar by acid
hydrolysis. Experiments to predict the sugar yield were performed,
and the resulting information was used in the design of a proposed
hydrolysis plant to establish the economics of the system.

A sugar yield of 51% is predicted with 1% acid at 230°C. With
this yield it is concluded that sugars from the hydrolysis plant can
be produced at costs competitive with molasses sugars. This conclusion
is valid for municipalities with populations greater than 200,000,
producing refuse containing 50% paper, or populations of 100,000 pro-
ducing refuse containing 60% paper. It is also shown that such sugars
could be used to produce ethanol at a price comparable to the existing
market price. Refuse disposal by acid hydrolysis under these conditions
might save $600,000 a year for a community of 200,000 people which was
previously disposing of its waste at $3/ton.

INTRODUCTION

The lowest predicted disposal cost for modern incineration is $3/ton.[1] At this rate, solid waste disposal would cost a city of approximately 200,000 people $600,000 per year. Andrew Porteous, a 1967 graduate of Thayer School of Engineering, Dartmouth College, proposed a disposal process which would utilize refuse as a raw material. Porteous' process consisted of hydrolyzing the available cellulose content of refuse, mainly paper, to sugar. The sugar in turn could be used to produce the saleable product of ethanol by fermentation. His economic study showed that in some cases such a process would not only eliminate the disposal cost but make a profit as well.

Because of the great economic potential of the process, a research program was established to study the process in greater depth. Porteous' economic analysis was based on the assumptions that (1) paper cellulose would hydrolyze like wood cellulose, and (2) the kinetic model experimentally determined for wood cellulose at temperatures below 200°C could be used to predict higher yields at 230°C. In order to test these assumptions it was necessary to establish new hydrolysis techniques and perfect quantitative analysis procedures for sugar and cellulose. The information gained from laboratory work and process analysis was used to modify Porteous' original process design and reevaluate the economics of the system.

1. SOLID WASTE AND ITS DISPOSAL

1.1 Current Disposal Methods

There are currently just two acceptable means of solid waste disposal—incineration and sanitary landfill; the former requires a large capital investment, and the latter, large areas of available land. The cost of disposal varies with the area, and ranges from $1 to $12 per ton with an average value of approximately $4.50 per ton.

1.2 Refuse Composition

A knowledge of the composition of solid waste is necessary, if any technological advancement is to be made in the field of solid waste disposal. The classification of solid waste by weight and composition is hampered by its heterogeneous composition and its offensive nature. Table 1-1 is a breakdown of solid waste by composition derived from a study done by Bell[2] in 1963. Table 1-2 is a compilation of municipal solid waste composition obtained through the Public Health Service.

The actual composition of municipal refuse varies with the location sampled and the season of the year. Thus it is difficult to arrive at a set average composition for the country. Generally, it is possible to say that paper is the main component of refuse, 40 to 60% by weight, followed by food waste, and then metal and glass products. It is believed that there will be an increasing amount of paper and synthetic materials produced each year. A large part of this waste is derived from packaging material. Table 1-3[3] shows the increasing trend of solid waste produced from packaging material consumption alone. An

Table 1-1

COMPOSITION AND ANALYSIS OF AN AVERAGE
MUNICIPAL REFUSE, ref. (2)

	Percent of Total Refuse	Approximate Analysis "as received" basis, moisture	Weight percent Volatile Matter
Rubbish, 64%			
Paper, mixed	42.0	10.24	75.94
Wood and bark	2.4	20.00	67.89
Grass	4.0	65.00	--
Brush	1.5	40.00	--
Greens	1.5	62.00	26.74
Leaves, rips	5.0	50.00	--
Leather	0.3	10.00	68.46
Rubber	0.6	1.20	83.98
Plastics	0.7	2.00	--
Oils, Paints	0.8	0.00	--
Linoleum	0.1	2.10	64.50
Rags	0.6	10.00	84.34
Sweepings, street	3.0	20.00	54.00
Dirt, household	1.0	3.20	20.54
Unclassified	0.5	4.00	--
Food wastes, 12%			
Garbage	10.0	72.00	20.26
Fats	2.0	0.00	--
Noncombustibles, 24%			
Metallics	8.0	3.00	0.5
Glass and Ceramics	6.0	2.00	0.4
Ashes	10.0	10.00	2.68

Organic Analysis of Composite

	Percent
Moisture	20.73
Cellulose, Sugar, Starch	46.63
Lipids (fats,oils,waxes)	4.50
Protein, 6.25N	2.06
Other organic (plastics)	1.15
Ash,metal,glass, etc.	24.95
	100.00

Analysis of Composite Refuse, As Received Basis

Moisture	20.73	Sulfur	0.16
Carbon	28.00	Non Com.	24.93
Total Hydrogen	3.50	Ratio C:(H)	39.4
Available Hydrogen	0.71	Btu/Lb.	4,917
Oxygen	22.35	Btu, dry	6,203
Nitrogen	0.33	Btu, M and AF	9,048

Table 1-2

MUNICIPAL SOLID WASTES COMPOSITION
PERCENT OF TOTAL WEIGHT, AS RECEIVED

A	B	C	D	E	F	G	H	I	J	K
Source/Date	Metal Products	Glass Products	Paper Products	Food Wastes	Plastic Rubber Leather	Yard Wastes	Cloth Synthetics	Wood	Dirt, Rock Bricks Rubble	Remarks
(1)	10	8	43	22	<1	<1	-	2	-	-
(2)	8	6	57	-	-	-	-	-	-	Arithmetic Avgs.
(3)	7	2	54	15	2	-	-	2	-	Arithmetic Avgs.
(4)	9	6	-	11	-	-	-	-	-	-
(5)	8	-	40	10	3*	-	-	7	-	)*Combination of F and H
(5)	11	-	53	17	4*	-	-	1	-	)Arithmetic Avgs.
(6)	7	14	38	31	-	-	4	-	-	-
(7)	9	8	42	28	3*	3	-	3	-	*Combination of F and H
(8)	11	11	46	26	3	2	<1	<1	<1	-
(9)	8	5	61	9	3	4	2	2	6	-
(10)	8	7	56	8	3	9	3	2	2	-

SOURCE/DATE

1) Municipal Refuse Disposal, (APWA), Chandler, Arizona   1953   Table 13, p. 52
2) Municipal Refuse Disposal, (APWA), Chicago, Illinois   1956-1958   Table 9, p. 47
3) Aero Jet General Corp., Waste Management Study, California   1956   Table 11-15, p. II-27
4) Solid Wastes Program, Work in progress; unpublished data   1966   Univ. of Louisville, Ky.
5) Kaiser, E.R., New York University   1966
6) Solid Wastes Program, Work in progress; unpublished data   1967   Quad City, New Jersey
7) Solid Wastes Program, Work in progress; unpublished data   1966   Cincinnati, Ohio, T.S. Study
8) Solid Wastes Program, Work in progress; unpublished data   1967   Johnson City, Tenn., T.S. Study
9) Solid Wastes Program, Work in progress; unpublished data   1968   Ogden, Utah, Tech.Services Study
10) Solid Wastes Program, Work in progress; unpublished data   1968   Alexandria, Va., T.S. Study

Table 1-3

PACKAGING MATERIALS CONSUMPTION
(Ref. (3))

MATERIAL	MILLIONS OF TONS	
	1966	1976
Paper & Paperboard	25.2	36.9
Glass	8.2	11.9
Metals	7.1	8.4
Wood	4.1	4.4
Plastics	1.0	2.5
	45.6	64.1

accurate study of waste composition is necessary before a municipality

can make a reliable decision on what method of disposal would be most

economic for its community.

1.3 Utilization of Municipal Refuse

Since paper is the main component of waste, it is desirable to

devise recycling processes using paper as the raw material. Porteous[5]

suggested a process which would convert the cellulose portion of paper,

approximately 75%, to glucose by means of sulfuric acid hydrolysis.

The basis for the hydrolysis is that cellulose is a polymer composed

of individual glucose units. The glucose can be used as a raw material

for fermentation to ethyl alcohol. In this manner, the bulk of the

refuse is converted to a utilizable raw material, which can be sold to

cover the disposal cost of the residual waste. Since the residual

waste is inert, it can be disposed of at a lower cost than can the raw

refuse. Porteous' preliminary study showed the process has an economic

advantage over all other existing means of disposal, thus warranting

further study.

1.4 Summary of Alternatives

Table 1-4 summarizes the available disposal methods and their re-

lated disposal cost. Incineration and sanitary landfill are the only

disposal alternatives open to most cities. Since land is becoming more

scarce, the cost of sanitary landfill will continue to increase for

many municipalities. Although heat recovery systems and other techno-

logical improvements in incineration will help cut cost, there will

always be some associated disposal cost. With this as a basis, it is

Table 1-4

ALTERNATIVE DISPOSAL METHODS

Method	Comments	Cost $/Ton
Open Burning	No longer legal	-
Sanitary Landfill	Requires large land areas	1 - 12
Incineration	Must contain antiair pollution devices	3 - 7
Composting	Little available market. Depends on dumping fee	2 - 7

seen that refuse will have to help pay for its own disposal cost. Using

refuse as a raw material for the production of sugar by acid hydrolysis

is one such attempt at accomplishing this goal.

2. THE HYDROLYSIS OF CELLULOSE

The concept of hydrolyzing cellulose containing materials to sugar is not a new one. Meiler and Scholler[6] in 1923 studied the acid hydrolysis of cellulose dextrine and the first plant to convert wood to sugar with subsequent fermentation was built in Germany just prior to World War II. This plant was built to offset the ethanol shortage which existed during that period. The principal research conducted in the U.S. was by Saeman[7] who was contracted by the War Production Board during World War II to develop a practical process for producing ethanol from wood waste. Saeman's work established the kinetic model which describes the hydrolysis of cellulose in dilute acid solutions.

2.1 The Chemistry of Cellulose

Cellulose is a fibrous tissue found in the cell walls of plants and trees. It is a polysaccharide composed of long chains of glucose units, a six carbon carbohydrate, connected at hydroxyl groups, glycosidic bonds.
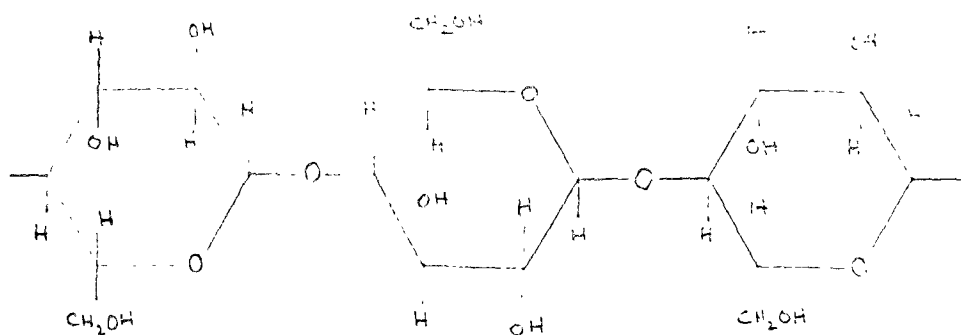
The other polysaccharides which are found in the cells of plants are called hemicelluloses. They are unrelated to cellulose and consist of pentose units, a five-carbon carbohydrate.

Cellulose is the main component of paper and the amount of cellulose in the paper varies with the grade of paper produced. The pulp used for making paper is prepared from wood by chemical or mechanical treatment. This treatment breaks down the wood fibers, eliminating the lignin and most of the easily destroyed hemicellulose. The main methods of pulping, with their resulting cellulose contents are: Sulfite 86%, Kraft 80%, and mechanical 50%. The exact amount of cellulose in any given type of paper depends on which pulp or pulps are used and the amount of filler which is added to the paper. The amount of cellulose in paper ranges from approximately 95% in rag paper to 50% in newspaper.

Cellulose and hemicellulose undergo the following hydrolysis reactions with acid acting as a catalysis:

Cellulose $\xrightarrow{\text{ACID}}$ Hexose $\longrightarrow$ decomposition products acids

Hemicellulose $\xrightarrow{\text{ACID}}$ Pentose $\longrightarrow$ decomposition products furfural

The hydrolysis reactions can be either homogeneous or heterogeneous, depending upon the acid concentration of the solution. Hemicellulose is an easily hydrolyzable material which will yield mainly the pentose, xylose, which upon further reaction produces furfural. The more stable of the two, cellulose, upon hydrolysis yields glucose, which subsequently decomposes to hydroxymethylfurfural and finally levulinic and formic acid.

In its natural state, cellulose is not only linked by glycosidic bonds but by hydrogen bonding in a crystalline lattice. Cellulose is soluble in concentrated solutions of 72% sulfuric, 85% phosphoric, and 45% hydrochloric acid. In such solutions the hydrolysis reaction is first order homogeneous and due to the low reaction temperatures proceeds with very little decomposition of the sugars. A process based upon high acid concentration would give high yields of sugar, but the high cost associated with using large amounts of acid places the process in an undesirable economic state. Dilute acids, less than 2%, can be used if the reaction temperature is increased. This reaction is heterogeneous, since the crystalline state of the cellulose remains intact. The exact kinetic mechanism of the reaction is not known but the results have been modeled with a standard $A \xrightarrow{K_1} B \xrightarrow{K_2} C$ irreversible reaction rate model. Sulfuric and hydrochloric acid with their high ionization coefficients are the best catalysis for the reaction since they give the highest ratio of rate of formation to rate of decomposition of sugar. Sulfuric acid is usually preferred for use since it is easier to handle and less costly than hydrochloric acid.

2.2 Dilute Acid Hydrolysis of Wood Cellulose

Porteous' original process[5] for waste disposal by cellulose hydrolysis was based on a kinetic study performed by Saeman[7] on wood. Saeman attempted to show that the hydrolysis of wood cellulose in dilute sulfuric acid could be described by an $A \xrightarrow{K_1} B \xrightarrow{K_2} C$ consecutive reaction with cellulose $\xrightarrow{K_1}$

reducing sugars $\xrightarrow{K_2}$ sugar decomposition products. Saeman performed his experiments in sealed glass bombs heated by direct steam in a rotating digester.

The rate constant for the decomposition of the sugars, K_2, was determined by reacting sugar solutions in the glass bombs at temperatures from 170° to 190°C with acid concentrations from 0.4 to 1.6%. The decomposition of both hexose and pentose sugars was studied and it was found that glucose, the main component of cellulose, was the most stable. Plots of the logarithm of the residual sugar concentrations versus reaction time gave straight lines. Since the integrated equation of a first order reaction is, $B = B_o e^{-K_2 T}$, the logarithm of the concentration, $\log B = \log B_o - K_2 T$, will give a straight line with the slope equal to K_2. Saeman's results, therefore, showed that the reaction was first order. The results of this experimentation are summarized in the following empirical equations taken from Saeman's work.

Rate Constants for Sugar Decomposition

$$K_2 = 1.86 \times 10^{14}\, c^{1.02}\, e^{-\frac{32700}{RT}} \tag{1}$$

$$K_2 = 2.39 \times 10^{14}\, c^{1.02}\, e^{-\frac{32870}{RT}} \tag{2}$$

with C = concentration of acid

R = 1.98 cal/g mole deg. K

T = Temp. deg. Kelvin

Equation (1) was derived by measuring the residual reducing sugar content of the solution and equation (2), by measuring the residual fermentable sugar content. Since sugars act as a reducing agent, a simple analysis for sugar is a test of the

reducing power of the solution. Although valid when degraded sugars are not present, it gives false values when degraded sugars are present. This is explained by the additional reducing power of the first oxidation state of glucose. The only reliable measure is based on equation (2) which is calculated with a test specific for glucose. This equation was derived using a pure homogeneous glucose solution and is only a means of approximating the reaction rate for the actual decomposition of sugars in the presence of wood cellulose.

The rate constant for the formation of sugar from cellulose, K_1, was determined by reacting ground samples of Douglas fir wood with a dilute acid solution in the heated glass bombs. After a measured period of time the vessels were quenched and analyzed for the unreacted wood cellulose content. Since wood is not entirely cellulose and no direct measure of cellulose content is possible, an indirect method of quantitative saccharification was employed to measure the cellulose content. The unreacted wood cellulose, referred to as the residual cellulose, was washed free of the dilute acid-sugar solution and reacted under conditions which gave quantitative yields of sugar without sugar decomposition. Consequently the quantitative saccharification procedure described in Appendix I uniquely measured the residual cellulose of the sample. Obviously when the quantitative saccharification is applied to an unreacted sample of wood, it determines the original cellulose content of the wood, which is referred to as the potential sugar yield of the sample. When the quantitative saccharification is applied to a reacted sample of wood (residual), it gives the remaining cellulose content which is referred to as the residual potential sugar yield.

The rate constant, K_1, was then determined by plotting the logarithm of the residual potential sugar (unreacted cellulose) as a function of reaction time. Again straight lines occurred, indicating the first order kinetics of this reaction.

The Douglas fir wood samples were hydrolyzed under the same temperature and acid conditions used for determining the decomposition of glucose. The effect of particle size was studied by hydrolyzing particles from 1/200 to 1/20 of an inch. It was found that with particle sizes greater than 1/20 of an inch, there was a mass transfer effect which slowed down the hydrolysis reaction. Subsequent experiments were performed with 1/30 of an inch particles. Liquid to solid ratios, wt/wt basis, of 5 to 1, 10 to 1, and 20 to 1 were tested. The results of these tests indicated that the rate of reaction increased as the liquid to solid ratio increased, but that the effect was minor when compared to the effect of acid concentration and temperature on the reaction. Saeman derived the following empirical equation for K_1 from this experimentation.

$$K_1 = 1.73 \times 10^{19} \, c^{1.34} \, e^{-42900/RT} \tag{3}$$

Saeman indicated that this reaction rate constant was only valid for the crystalline or resistant portion of the cellulose in the wood. Amorphous or easily hydrolyzable cellulose in the wood decomposed before the reaction temperature was reached and this reaction, since essentially instantaneous, was not included in the analysis for K_1. He proved this assumption by hydrolyzing amorphous free cellulose and showing that the obtained sugar yields could be described by equations (2) and (3) and the $A \longrightarrow B \longrightarrow C$ reaction model.

The high activation energy of rate constant K_1 indicates that although it was derived for a heterogeneous solid-liquid reaction, the reaction is not mass transfer controlled. The higher the activation energy, the more temperature dependent the reaction is. Since diffusion is not so temperature dependent, it is concluded that the reaction is not diffusion controlled.

With the $A \xrightarrow{K_1} B \xrightarrow{K_2} C$ irreversible reaction, as the reaction proceeds, the cellulose concentration, A, decreases, the decomposed products concentration, C, increases, and the glucose yield, B, goes through a maximum. This yield of interest is that of glucose, the maximum value of which is given by

$$B_{max} = \frac{K_1}{K_2} \uparrow \left(\frac{K_2}{K_2-K_1}\right) \text{ at } \theta^* = \frac{\ln K_2/K_2}{K_2-K_1} \tag{4}$$

This equation is derived from the integrated equations for the reaction in section 3.1. Since the empirical equations (2) and (3) for K_1 and K_2 show that K_1 will increase faster than K_2 with an increase in acid concentration or temperature, the maximum yield of glucose, equation (4), should also increase with these conditions. This was shown by Saeman in his original work[7] to be true over the range of 170 to 190°C. On this basis Porteous extrapolated Saeman's data to 230°C with a 0.4% acid concentration, and predicted a yield of 55%. Figure 2-1 taken from a more recent publication of Saeman's work[8] shows that a yield of approximately 47% was obtained under these conditions. There was no explanation of the discrepancy between the predicted and experimentally obtained results.

Figure 2-1

SUGAR YIELD versus RESIDUAL POTENTIAL SUGAR
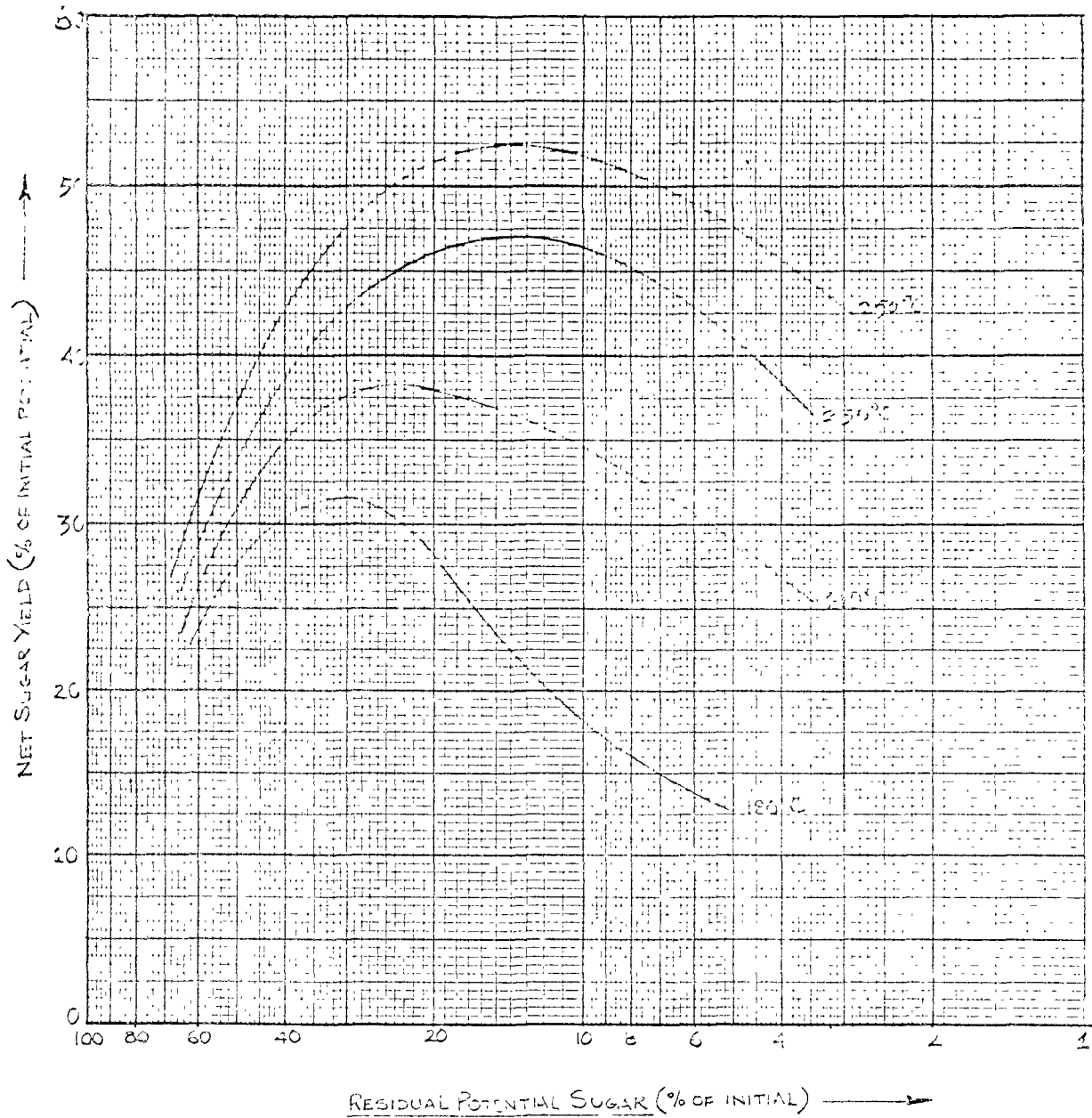
Saeman's empirically derived results only hold for the crystalline portion of cellulose and most cellulosic material contains both amorphous and crystalline cellulose. Saeman also found that cotton cellulose decomposed at a rate different from that of wood cellulose. The rate of hydrolysis of paper cellulose, especially at higher temperatures, therefore, cannot be strictly inferred from Saeman's work since its crystalline structure may be modified both by the paper making process and any pretreatment performed in the hydrolysis process. The kinetics and yields associated with paper cellulose hydrolysis had to be found experimentally before a hydrolysis process for refuse paper could be designed.

3. EXPERIMENTAL APPARATUS AND PROCEDURE

An experimental program was established to determine the ultimate potential of refuse hydrolysis as a solid waste disposal process. Since Porteous based his preliminary economic study on an extrapolation of Saeman's kinetics for wood cellulose, it was necessary to determine whether such an assumption was valid. If it were found that paper hydrolyzed at a different rate than wood cellulose, then a model for paper hydrolysis would have to be determined. Although it was not necessary to determine exactly what reaction was occurring, a model for predicting the yield under various conditions of hydrolysis had to be found. Such a model was necessary for the design of the hydrolysis plant and the determination of the most economical operating conditions for the plant. Once this information was obtained, the total economics of the system could be determined.

The laboratory apparatus had to contend with the high temperature (>220°C), high pressure (>400 psi), and the corrosive atmosphere anticipated for the process. Moreover, the fact that the yield of glucose reached a maximum in a short time made the design of a reliable laboratory procedure very difficult.

A quantitative saccharification procedure which would completely hydrolyze cellulose to glucose without decomposition products is found in Reference 9 and summarized in Appendix I. This experimental analysis is based on initial high acid concentration, 72% H_2SO_4, to dissolve the cellulose at room

temperature, followed by treatment with diluted 4% H_2SO_4 at an elevated temperature. This procedure determines the potential glucose in any cellulosic material such as refuse, and is essential in any kinetic study since the original amount of cellulose must be known before the kinetic parameters can be interpreted. The glucose analyses were performed with an O-toluidine colorimetric test described in Reference 9 and modified by Dr. Sanka, Mary Hitchcock Memorial Hospital, Hanover, N.H., for work in blood and urine sugar analysis. This test is outlined in Appendix II. It is a micro test based on the specific reaction of aldohexoses with O-toluidine in accordance with Beers Law.

3.1 Kinetic Model

Saeman[7] showed that the hydrolysis of the resistant wood cellulose is described by an $A \xrightarrow{K_1} B \xrightarrow{K_2} C$ reaction governed by the following equations. (A = cellulose, B = glucose, C = decomposed sugar).

$$\frac{\partial C_A}{\partial t} = K_1 C_A \tag{5}$$

$$\frac{\partial C_B}{\partial t} = -K_2 C_B + K_1 C_A \tag{6}$$

Integration of (5) and (6) gives

$$\frac{C_A}{C_{A_O}} = e^{-K_1 \theta} \tag{7}$$

$$\frac{C_B}{C_{A_O}} = \frac{K_1}{(K_2 - K_1)} (e^{-K_1 \theta} - e^{-K_2 \theta}) \tag{8}$$

$$\frac{C_{B(MAX)}}{C_{A_O}} = \left(\frac{K_1}{K_2}\right)^{\left(\frac{K_2}{K_2 - K_1}\right)} \tag{9}$$

$$\theta^* = \frac{\ln K_2 - \ln K_1}{K_2 - K_1} \qquad (10)$$

where C_A = concentration of A

C_{A_O} = initial concentration of A

θ = time

θ^* = time to max yield of B

K_1 = reaction rate constant for A to B reaction

K_2 = reaction rate constant for B to C reaction

The classical experimental approach for determining rate constants was used by Saeman. He assumed isothermal conditions for the reaction and that the heat up and cool down time for his glass vessels would be negligible when compared with the raction time for temperatures below 190°C. The amount of original and subsequent cellulose was determined by a quantitative saccharification. Thus, by reacting the cellulose for various lengths of time, the log of the cellulose concentration versus time could be plotted and the first order rate constant K_1 determined. The same procedure was used to determine the first order reaction rate constant K_2 with the cellulose replaced with a known concentration of glucose.

Saeman's experimental equipment limited his reaction temperature to a maximum value of 190°C, but extrapolation of Saeman's results indicated that a higher yield could be expected at higher temperatures.

3.2 Isothermal Kinetic Study

The first experimental procedure was designed to determine if Saeman's data could be extrapolated to temperatures above 190°. It was thought that a simple approach to this problem would be to assume that Saeman's empirically derived equation (2)

for the decomposition rate of glucose would hold for higher temperatures. Therefore, knowing the original concentration of cellulose from a quantitative saccharification K_2 from equation (2) and the yield of glucose versus time from experimentation, it would be possible to determine K_1 by a trial and error solution involving equation (8). If the determined values of K_1 were the same as those predicted by Saeman's empirical equation (3), it would be concluded that the hydrolysis of paper cellulose is the same as the hydrolysis of wood cellulose and Saeman's empirical equations would be valid for such work.

Initial kinetic studies were performed in 1" x 4" stainless steel (316) nipples capped and sealed with Teflon tape. The reaction temperature was obtained by placing the reaction vessels into a high temperature oil bath. A temperature-time history was recorded by sealing a chromel-alumel thermocouple in one of the vessels. A number of preliminary tests gave inconsistent results with very low yields. Since it was thought that the acid was reacting with the vessels and causing lower than expected yields, a 25 x 100 mm glass culture tube was placed in the stainless steel vessels. This alleviated the corrosion problem and increased the measured yield by 300%. A new temperature-time curve was recorded and all remaining tests were made using the glass liner. 0.2 gr brown paper bag samples were prepared by cutting up the bag into approximately 1/10" squares. The samples were placed in glass culture tubes and 5 ml of 0.5 percent sulfuric acid solution was added. The glass tubes were then sealed in the stainless steel vessels

and placed in the constant temperature bath for a measured
period of time. At the end of this time the vessels were
quenched in ice water, and analyzed for glucose content. The
heat of reaction for cellulose decomposition is approximately
10 K cal/g-mole. Therefore the adiabatic temperature rise was
calculated to be 2°C under the experimental conditions used
in this study. However, the conditions are far from adiabatic;
hence the error in neglecting heat effects of the reaction was
certainly less than 2°C. An experimental temperature-time
trace indicated isothermal conditions after an initial heat-up
period, the reactor temperature being a constant 4°C below the
indicated bath temperature.

A corrected isothermal reaction time was determined as
follows

$$t_1 = t_2 - t_3 - 1/2\, t_4$$

where:

t_1 = reaction time used in kinetic calculations

t_2 = time that sample resides in bath

t_3 = time to heat sample from room temperature
to 170°C in the bath, as determined from
a heat-up curve

t_4 = time to heat from 170°C to final bath
temperature

The main cause of error in kinetic calculations was the
time to heat the sample from 170°C where the reaction rate
first becomes significant, to the final temperature. This
heat-up time was found to be between 2 and 3 minutes; thus
for temperatures above 210°C and reaction times approaching
3 minutes, the error due to heat-up was very large.

3.3 Acid Injection Bomb

The isothermal kinetic analysis based on the results of
the experimental procedure outlined in Section 3.2 was in error
due to the time necessary for the bombs to reach isothermal
conditions. It was believed that this error could be elimi-
nated by building an acid injection bomb system. Such a system
was constructed using a 2" x 4" SS-316 pipe with a glass liner
as the reactor. The reactor, charged with 150 ml of water and
0.5 grams of paper, was heated in a high temperature bath until
it reached the desired temperature. The hydrolysis was ini-
tiated by injecting 1 ml of acid through a three way ball
valve by nitrogen pressure. After a measured period of time
a sample was drawn off and flashed to room temperature. It
was found that the reactor required more than two hours to
reach isothermal conditions and that during this time the
paper had undergone thermal degradation.

The initial paper-water charge volume was kept large
compared to the injected acid volume to prevent the lower
temperature acid from cooling down the reactor. Using less
than 1 ml of acid solution would result in large error in the
final desired acid concentration, due to transfer losses in
the valve and tubing. Although a smaller reactor volume would
have a shorter heat up time, the required high volume ratio
and lower limit on the injected acid volume prevented the use
of such a system. An attempt to circumvent the thermal de-
gradation was made by injecting a fine paper slurry into the
reactor. The reactor was charged with 150 ml of 0.5% acid
solution and brought to the desired temperature. 5 ml of

water with 0.1 gram of powdered paper was then injected into the reactor. It was found that the paper failed to pass freely through the valves and tubing into the reactor. The modifications necessary to allow such operation precluded its use for such experimentation.

3.4 Nonisothermal Kinetic Study

Due to the difficulties of obtaining an isothermal system, a new approach to the problem was attempted. It was believed that a non-isothermal kinetic analysis could be performed by means of a modified curve fitting routine. It was assumed that the proposed $A \xrightarrow{K_1} B \xrightarrow{K_2} C$ kinetic model was valid and that the rate constants followed Arrhenius' equation, $K = Ce^{-\Delta H/RT}$. There are then at a given acid concentration four parameters, the two pre-exponential constants (C's) and two activation energies (ΔH's), which had to be calculated to determine the overall kinetic model. The following method was used to determine these parameters.

A sample of paper or refuse which had been run through a Wiley ball mill to produce 2 mm particles was placed in a glass culture tube with a specified amount of acid solution. This vessel was placed in a 1" x 4" stainless steel nipple and sealed. The cap of the nipple was taped with a 1/4" N.P.T. such that a Swagelock thermocouple well connector could be screwed into the cap. The thermocouple well consisted of a 1/4" stainless steel tube coated with Teflon tape. A chromel-alumel thermocouple was placed in the well, which had been previously filled with oil, to measure the liquid temperature within the vessel. This vessel was placed in a constant temperature bath which had been set at 260°C. A constant record

of the temperature-time history was kept by use of a thermo-coupld chart recorder. Samples were removed from the bath at various intervals of temperature, quenched in ice water, and analyzed for sugar content. Six to eleven samples were used for each acid concentration run, and at the start of each acid run a sample quenched when the temperature reached 180°C was analyzed for both sugar and residual potential sugar (cellulose) content. The data obtained from such a procedure consisted of 1) quantitative potential sugar (cellulose content) at 180°C, 2) sugar yield at intervals of temperature, and 3) temperature-time history. The differential equations which describe such a system are:

$$\frac{\partial A}{\partial t} = K_1 A(t) \tag{11}$$

$$\frac{\partial B}{\partial t} = K_1 A(t) - K_2 B(t) \tag{12}$$

where A = concentration of cellulose

$\qquad$ B = concentration of sugar

$\qquad$ $K_1 = C_1 e^{-\Delta H_1/RT}$ = rate constant 1

$\qquad$ $K_2 = C_2 e^{-\Delta H_2/RT}$ = rate constant 2

$\qquad$ R = 1.98 cal/g deg. K

$\qquad$ T = deg. Kelvin

$\qquad$ t = time

With calculated initial conditions on A and B at 180°C, a temperature-time function derived from a 4th order polynomial curve fit for the data, and values for C_1, ΔH_1, C_2, ΔH_2, equations (11) and (12) could be numerically integrated for the sugar yield as a function of time. It was necessary to search for the values of C_1, ΔH_1, C_2, and ΔH_2 which resulted in yields

of sugar which best agreed with those obtained experimentally.
Once such parameters were determined from the non-isothermal
analysis, the kinetic model could be used to predict the yield
for an isothermal reaction.

A Hooke-Jeeves pattern search[10] and a Runge-Kutta numer-
ical analysis were used to determine the rate constant para-
meters which minimized the sum of the square errors between
the predicted and the experimental sugar yields. Insurance of
convergence was determined by generating hypothetical experi-
mental yields with four given parameters, and using these
yields to repredict the parameters with the previously des-
cribed computer program. The final sum square error from
this analysis was 1×10^{-6} and convergence was obtained in
120 seconds on a G.E. 630 time-sharing system.

4. EXPERIMENTAL RESULTS AND ANALYSIS

The apparatus and procedures described in Chapter 3 were used to determine the yields and kinetics of paper hydrolysis. It was found that an accurate kinetic analysis based on isothermal conditions would not be possible. Reaction half lives of less than one minute were expected at temperatures >220°C, and under such fast reaction conditions it was not possible to build an apparatus with a heat-up time small enough to be ignored. A non-isothermal kinetic analysis was therefore used in determining the kinetics of the reaction.

4.1 Isothermal Analysis Results

A preliminary study of acid hydrolysis was performed with temperature conditions which were to be isothermal. Runs were made at bath temperatures of 200°C, 210°C, and 220°C. The yields of sugar on a weight sugar/weight paper basis are shown in Figure 4-1. A kinetic study was performed on this data as indicated in Section 3.1, but it was hampered by an inaccurate quantitative saccharification procedure and the actual non-isothermal state of the system.

An accurate quantitative saccharification is essential since a knowledge of the amount of cellulose in the paper is needed to correct yields to a weight sugar per weight potential sugar (cellulose) basis. This change of base is necessary since the kinetic model is for the hydrolysis of cellulose, and paper is not 100% cellulose. The main difficulties in the quantitative saccharification were caused by lack of a suitable low

Figure 4-1

SUGAR YIELD versus REACTION TIME
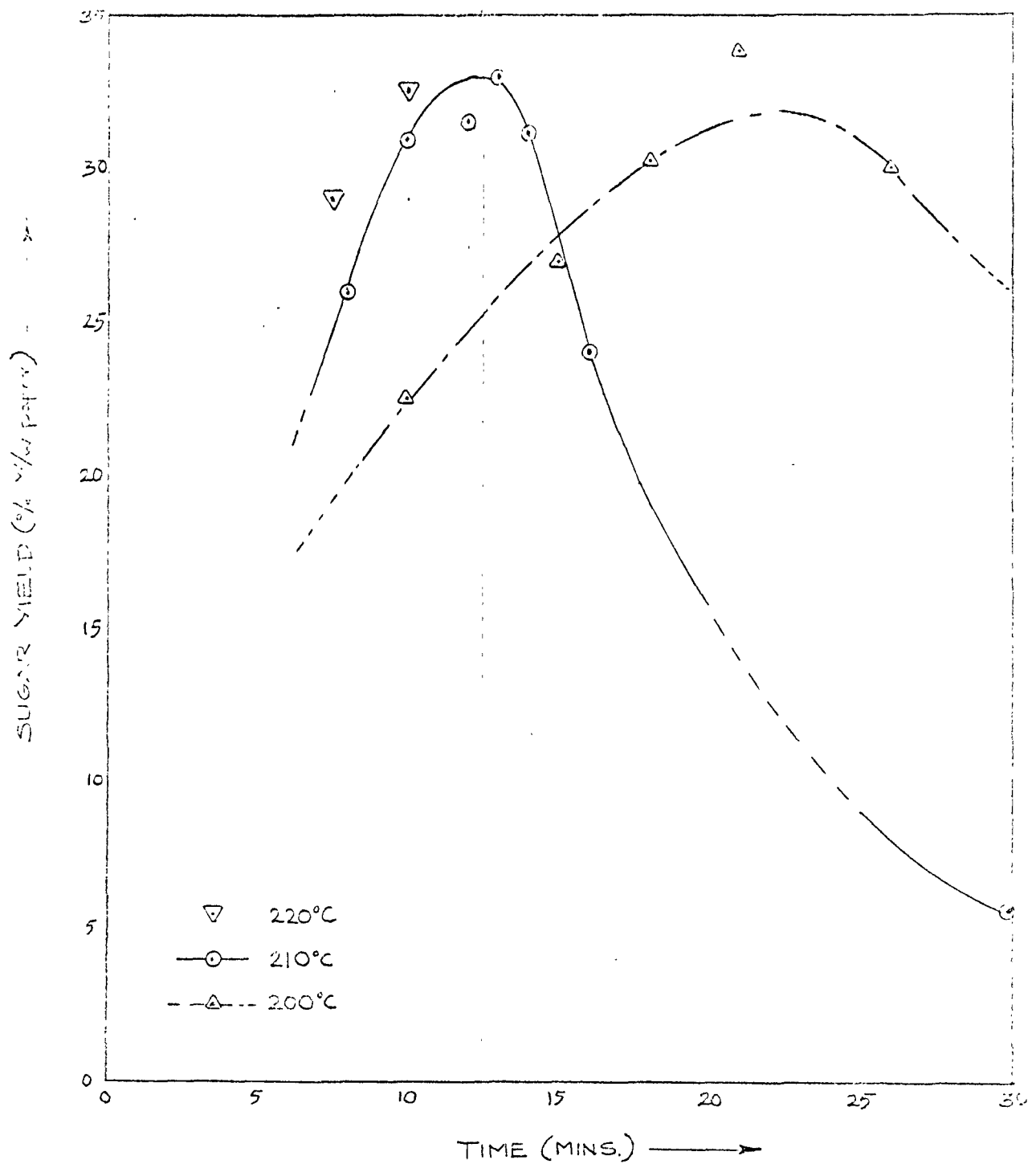
temperature bath for the first step of the analysis and by
using too large a particle size in the procedure. The time
necessary to reach isothermal conditions also caused error
which could not be neglected in a kinetic analysis.

In spite of these difficulties the data obtained showed
that paper could be hydrolyzed to sugars and that the yield of
sugar passed through a maximum as would be expected if the
proposed reaction sequence held. Further evidence of such a
series reaction is that the time to maximum yield decreases as
the bath temperature increases. The yields, although lower
than expected, did indicate that further experimentation was
justified. Moreover, at the end of this series of experimen-
tation, a better understanding of the hydrolysis reaction and
related chemical analysis was obtained, so that more effort
could be given to the determination of the reaction model
itself.

4.2 Non-Isothermal Analysis Results

The cellulosic materials used for the acid hydrolysis ex-
periments were tested quantitatively for their potential sugar
yields which is an indication of their cellulose content.
Table 4-1 contains the results of this quantitative sacchari-
fication. These yields represent the total experimental poten-
tial aldohexose content of the sample. The fermentable aldo-
hexose sugars are glucose, galactose, and mannose. Table 4-2,
taken from Reference (8), shows the expected percent composi-
tion of these sugars in Kraft paper. The main contribution to
the quantitative sugar yield will come from glucose. Glucose
can be formed from both amorphous and crystalline cellulose.
Mannose and gelactose are mainly derived from non-crystalline

Table 4-1

QUANTITATIVE SACCHARIFICATIONS

SAMPLE	YIELD Weight Sugar/Weight Paper %
Ground Kraft Paper	86
Ground Kraft Paper	84
Slurried Kraft Paper	84.8
Slurried Kraft Paper	80.5
Ground Refuse #1	38.0
Ground Refuse #1	38.4
Ground Refuse #2	52.6
Ground Refuse #2	52.6

Table 4-2

CARBOHYDRATE COMPOSITION OF KRAFT PAPER PULP[8]

Component	Percent
Glucose Galactose	82.4
Mannose, Arabinose	7.0
Xylose	9.2
Uronic Anahydride	1.4

polysaccharides. Although the main portion of cellulose in paper is believed to be in the crystalline form, the exact amounts of amorphous and crystalline forms are not knc wn.

Samples of milled Kraft paper, approximate particle size 2mm, were hydrolyzed with 20 ml of 0.2%, 0.5%, and 1% by weight sulfuric acid solutions. The yields and temperature time histories are shown in Appendix II. Selected samples, quenched when the temperature reached 180°C, were filtered and reanalyzed for their potential sugar yield. In this manner a hydrolysis sugar yield and residual potential sugar yield were known at 180°C. These yields were then used as the initial conditions for the 4-dimensional search outlined in Section 3.3. Arrhenius' equation was used to relate the rate constant to the reaction temperature. The computer program found in Appendix IV was used to perform the search which determined the pre-exponential factors and activation energies that would best fit the data for the 0.5% acid runs. It was then assumed that these activation energies could be used for the 0.2% and 1% acid experiments, thus only requiring a search on the two pre-exponential parameters for this data. The Arrhenius equations for the calculated values are:

0.2% $\quad K_1 = 1.661 \times 10^{19} * e^{-\Delta H_1/RT}$

$\quad\quad\quad K_2 = 2.21 \times 10^{14} * e^{-\Delta H_2/RT}$

0.5% $\quad K_1 = 7.59 \times 10^{19} * e^{-\Delta H_1/RT}$

$\quad\quad\quad K_2 = 2.67 \times 10^{14} * e^{-\Delta H_2/RT}$

1% $\quad\quad K_1 = 2.95 \times 10^{20} * e^{-\Delta H_1/RT}$

$\quad\quad\quad K_2 = 5.57 \times 10^{14} * e^{-\Delta H_2/RT}$

with

ΔH_1 = 45127 cals/g mole

ΔH_2 = 32800 cals/g mole

In an acid catalyzed reaction the overall reaction rate is usually proportional to the acid concentration as well as the reactant concentration. Although this would normally result in second order kinetics, the fact the acid concentration is constant allows the rate constant to be expressed as,

$$K_i = K_0 C^m \qquad C = \text{acid concentration Wt. \%}$$

where K_i is the overall constant K_1, K_2 shown above.

Since the reaction activation energies are the same for low acid concentrations, the acid effect will be contained in the pre-exponential factors of Arrhenius equations for K_1 and K_2, $P_i = P_0 C^m$ where P_i is the pre-exponential of K_i in $K_i = P_k e^{-\Delta Hi/RT}$. A plot of the log of the pre-exponential factors versus the log of the acid concentration should give straight lines within the slope of the line. Figure 4-2 shows that this relationship held for K_1 but not K_2. This result can be explained, since the actual hydrolysis reaction, K_1, is known to be due to cleavage of the cellulose bonds by the hydronium ion whereas the decomposition of glucose, K_2, is a series of sugar oxidations which are not simple hydrolysis bond cleavage.

These results also showed that at zero acid concentration and high temperatures, 230°C, thermal hydrolysis would occur, but low yields would result since the ration $K_1/K_2 \approx 0.25$ is very small. This explains why thermal degradation or hydrolysis occurred in the acid injection system described in Section 3.3.

The accuracy of these fitted values was determined by performing replicate experiments at approximately 230°C. The sum square error of these replicates was 5.362×10^{-4} with 2 degrees of freedom. The largest determined curve fit error

Figure 4-2
LOG (PRE-EXPONENTIAL FACTORS) versus LOG (ACID CONC.)
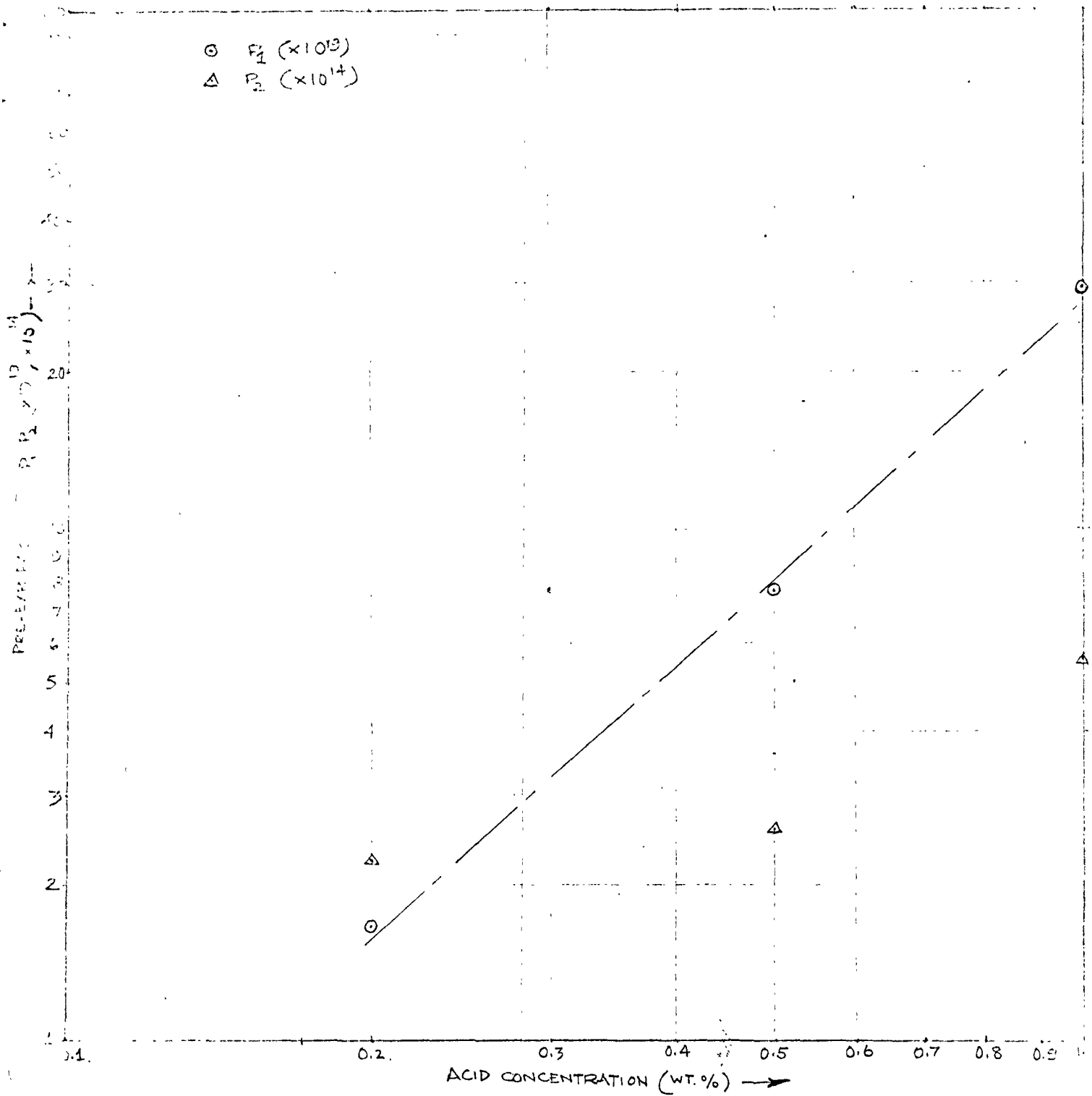
was 3.3×10^{-3} with 4 degrees of freedom. The statistical "F" ratio is therefore 6.15 which is well within the 19.25 "F" ratio at the 95% confidence interval. This test shows that there is not a significant difference between the fit and the experimental error. The actual experimental data points and the predicted curves are shown in Figure 4-3. Another question concerning the accuracy of the experimental data arises from the ice water quench time. It was found that approximately 20 seconds are required to lower the reactor temperature from 230°C to 170°C. This time would appear to contribute a great deal of error at high temperatures and acid concentration. Although this assumption would be true if the reaction continued at the 230°C rate, it is not true when it is considered that the temperature is continually dropping, as is the reaction rate. Using the reaction rates calculated for a 1% acid solution, a numerical integration was performed for a linear drop in temperature from 230 to 170°C with an initial sugar concentration of 11%. This calculation revealed that approximately a 1% loss in yield could be expected due to the quench. Since the condition used for this test is the most severe encountered, the error due to quench time was ignored.

The reliability of the predicted rate constant parameters can further be demonstrated by their ability to predict yields with temperature time curves other than those used for determining them. Initial runs with the high temperature bath produced widely different temperature time curves; this was found to be due to convection currents established by the

Figure 4-3
SUGAR YIELD versus NONISOTHERMAL TEMPERATURE (TIME)
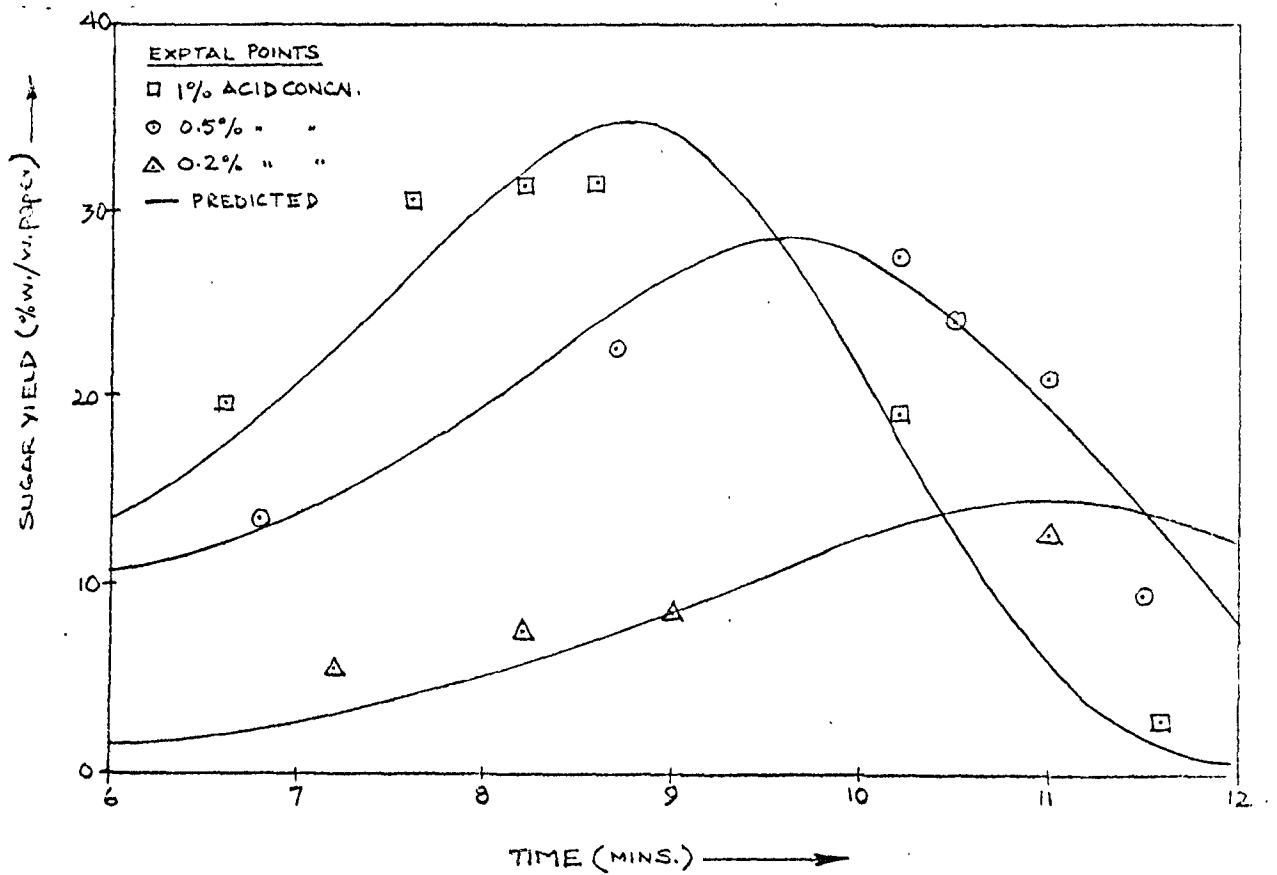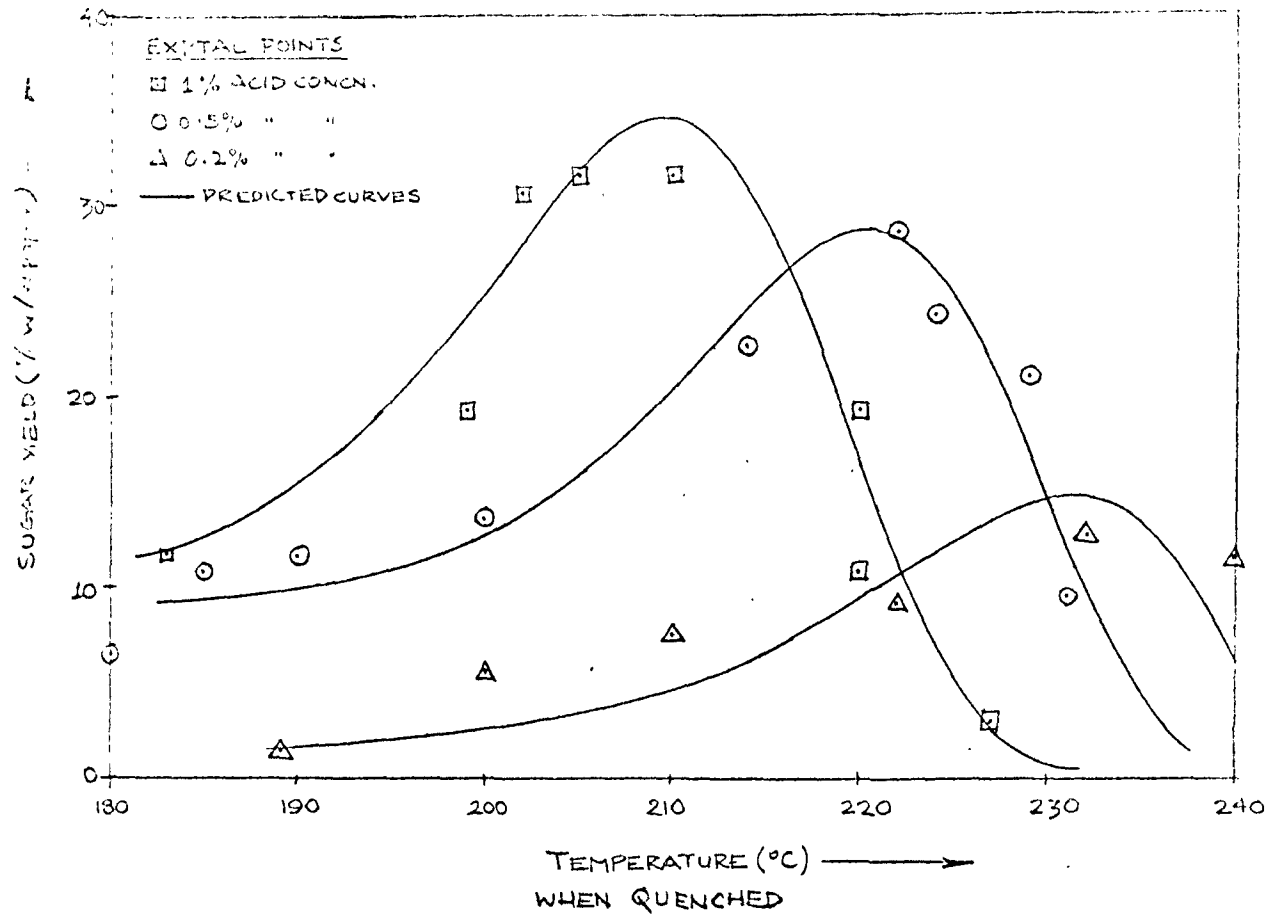
bath circulation pump. This problem was remedied by placing a metal beaker filled with oil in the bath, thus acting as a buffer between the actual bath convection currents and the test reactor. Three of these variable temperature time curves were used in conjunction with the calculated rate constants to predict the associated sugar yield curve. The following yields were obtained in this manner.

| | | 0.5% Acid | |
Curve	Quench Time	Experimental Yield	Predicted Yield
I	8.6 min.	0.30	0.30
II	5.6 min.	0.24	0.21
III	6.1 min.	0.325	0.315

It is seen from these results that the agreement between predicted and experimental yields is very good.

Since the proposed hydrolysis plant will operate with a paper slurry, it was necessary to determine whether a significant change in rate constants would occur if fibrous material were used in place of ground particles. A sample of Kraft paper was pulped with water in a standard Waring blender. This sample was then dried and 0.5 gram samples were prepared from the fibrous sheet. These samples were mixed with 20 ml of 0.5% acid producing a fibrous slurry which was then hydrolyzed. The agreement between predicted and experimental results, Figure 4-4, indicates that the determined relationship holds for fibrous samples as well as ground samples. It is therefore possible to predict isothermal yields for plant operations using a pulped paper slurry.

Figure 4-4

SUGAR YIELD (KRAFT FIBERS) versus NONISOTHERMAL TEMPERATURE
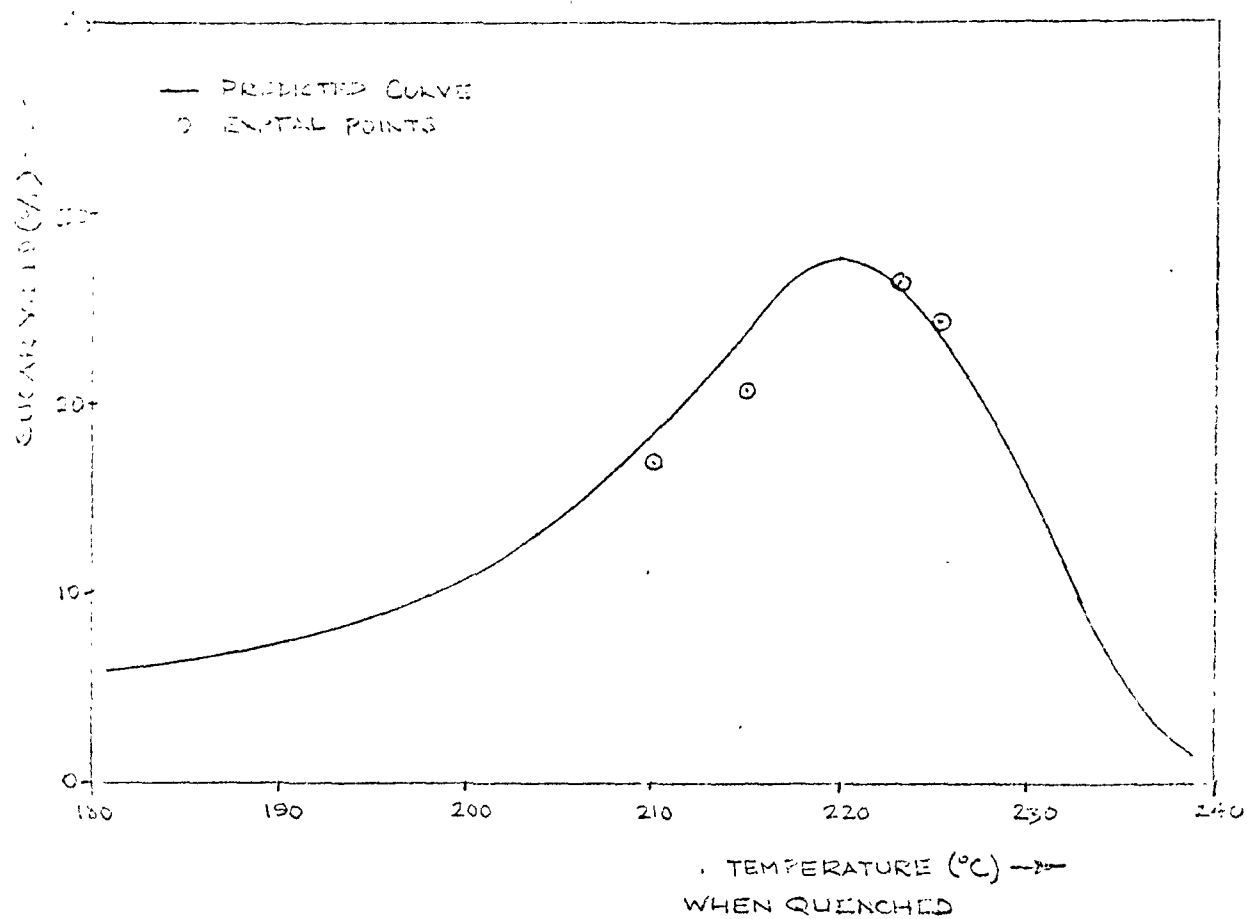
Referring again to Figure 4-3, it is noticed that approximately 6 to 11% sugar yields were obtained at lower temperatures between 170°C and 180°C. Saeman's rate constants for crystalline cellulose indicates that yields of this magnitude, at low temperatures and short heat up, should not be obtained. It is believed that the discrepancy can be explained by the different regions of cellulose hydrolyzed. Saeman's original kinetic data applied to what was called the resistant portion of cellulose. He discovered that when working with untreated ground wood, all plots of residual potential sugar versus time, extrapolated back to zero time, gave a value for the potential sugar yield below that obtained experimentally by quantitative saccharification. It was believed that the difference between the original 66.6% potential sugar and the extrapolated 44% at zero time was due to easily hydrolyzable amorphous cellulose. His calculated rate constants, therefore, held only for the resistant portion of cellulose. It is believed, from the hydrolysis of paper results, that it also contains a portion of easily hydrolyzable cellulose.

This kinetic study shows that the easily hydrolyzable portion of cellulose accounts for the sugar yields at low temperature values and that the kinetic parameters estimated here are for the residual cellulose. It is not valid to assume that these kinetics only apply to residual crystalline cellulose. Browning[11] explains that during hydrolysis, cleavage in the amorphous regions can cause rearrangement and crystallization of the amorphous cellulose. The calculated rate constants for paper hydrolysis may therefore be a combination of rate constants

for the amorphous-crystalline cellulose. The important point
is that the model was shown to predict the correct yield under
various hydrolysis conditions. It is of no great importance
for the engineering plant design to determine exactly what
reaction is occurring; it is important to be able to predict
the yield under various conditions of hydrolysis.

The predicted isothermal yields of sugar from paper cellu-
lose are shown in Figure 4-5. For these calculations it was
assumed that 10% of the original potential sugar yield would
hydrolyze instantaneously. This value is based on the experi-
mentally determined sugar yields of 6 to 11% from the easily
hydrolyzed portion at low temperatures. This curve gives the
residence times necessary to obtain maximum yield at various
temperatures and acid concentration. If the original potential
sugar content of the paper refuse is known, this curve will
give the predicted isothermal yields of sugar.

The original prediction by Saeman for wood that an in-
crease in acid concentration and temperature causes an increase
in overall glucose yield is shown to hold true. 10% yield in-
crease is shown to occur by doubling the acid concentration at
230°C and a 10 degree rise in temperature results in approxi-
mately a 5% yield increase.

4.3 Experimental Analysis Conclusions

It was shown by the experimental analysis that paper
cellulose does hydrolyze to sugar and that the hydrolysis
reaction could be modeled by the $A \xrightarrow{K_1} B \xrightarrow{K_2} C$ irreversible
reaction model used by Saeman. The reaction rate constants

Figure 4-5

PREDICTED ISOTHERMAL SUGARS versus TIME
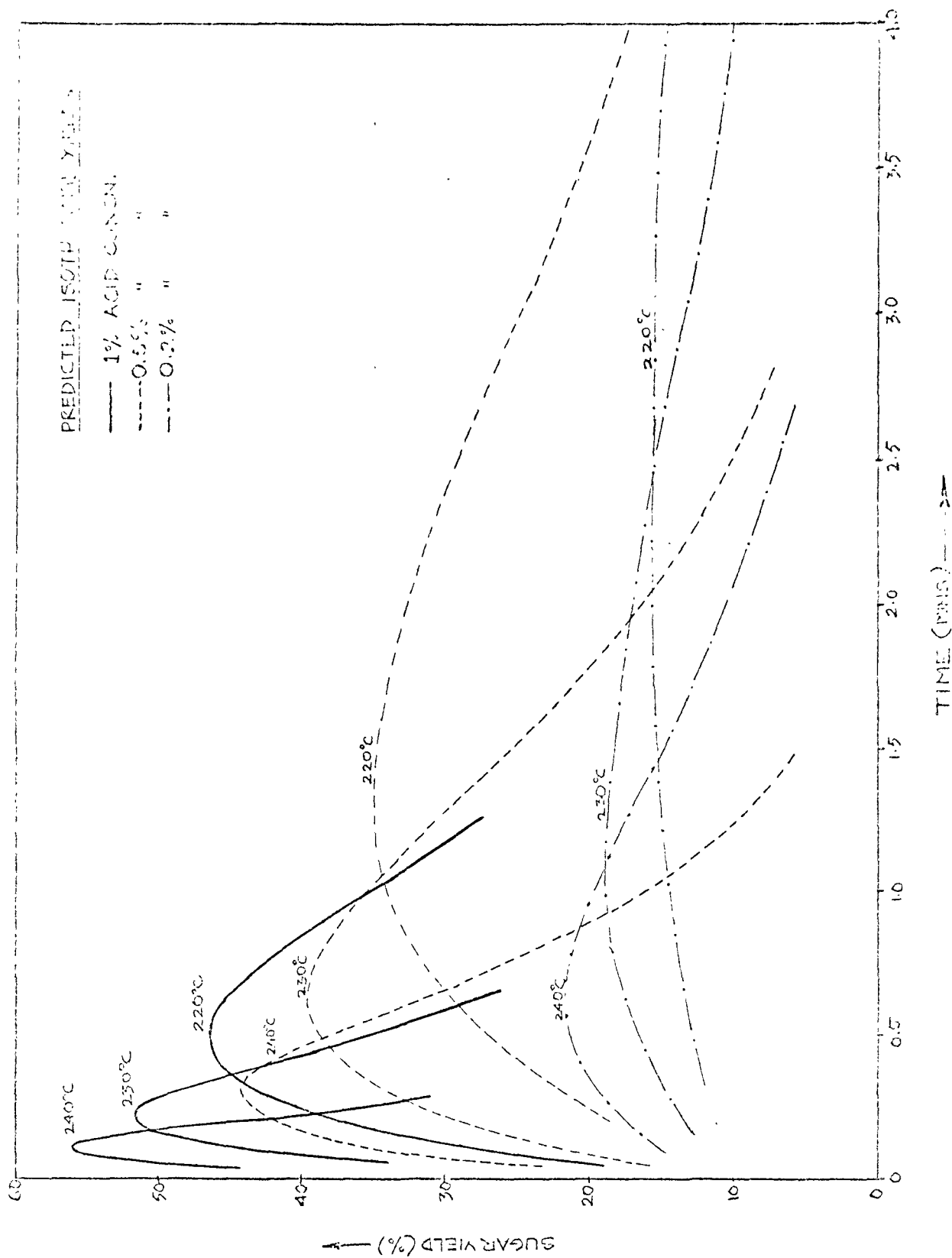
were found to be different from those calculated by Saeman, but as predicted, they both increased as temperature and acid concentration increased, with K_1 increasing faster han K_2. The increase of the ratio K_1/K_2 was not as pronounced as expected, and the yield of sugar from paper cellulose at higher temperatures was therefore lower than that predicted by Saeman. Porteous originally predicted a yield of 55% with Saeman's data at 230°C whereas the calculated kinetic model predicted a yield of 41%. This difference is reaction rates was thought to be due to the amorphous cellulose content of paper cellulose. It was also shown that the predicted reaction rates held when pulped paper fibers were hydrolyzed. It was therefore concluded that the calculated kinetics could be used in the design of a refuse hydrolysis plant under iso-thermal reaction conditions.

5. PLANT DESIGN

The information gained from the hydrolysis experimentation was used in the design of a refuse hydrolysis plant. As much of the non-cellulosic material as possible must be separated out of the raw refuse, since additional acid solution would be required for this useless material. In addition to separation, the refuse must be pretreated to produce fine particle sizes which can be hydrolyzed without mass transfer slowing down the reaction. Porteous' preliminary design pretreatment system consisted of dry pulverization followed by flotation separation and secondary shredding. Although the heavier metals would be separated out by such a system, the lighter plastics, bottles, plastic wrappings, rubber, and any pieces of cut metal entrained in the paper would be carried over to the secondary shredder. Moreover, secondary shredding produces particle sizes of approximately one inch which would result in lower sugar yields due to the lack of intimate contact of the acid with the paper fibers. A proven separation system, used in pretreating waste paper for reuse as paper pulp, was adapted in place of Porteous' system. Almost complete separation of the above materials would be obtained and the resulting paper slurry would consist of fine fibers, the size controlled by the pulper operation, which were proven to be easily hydrolyzable.

A continuous flow reactor, as recommended by Porteous, was incorporated in the design with an additional feature of a cellulose recycle stream. The experimental results indicated

that approximately 25% of the cellulose would not be hydrolyzed and the recycle stream was used to hydrolyze this residual potential sugar source. Since the experimental cid injection reactor showed that cellulose would begin to decompose at high temperatures without acid, the total heating of the slurry is obtained by direct mixing with a high temperature acid stream.

Porteous designed a multi-stage system to quench the reaction and preheat the reactor feedwater stream. Although such a system allows efficient heat recovery, it does not appreciably concentrate the product sugar solution. A flash from 230°C to 100°C evaporates approximately one-quarter of the sugar solution which would only concentrate a 2% sugar solution to 2.7%. In addition, to obtain maximum heat recovery the system was designed with four flash stages between 230° and 170°C. Since there is hold up in each flash stage, the reaction will continue, and this must be taken into consideration when attempting to maintain maximum conversion residence time. In order to overcome these difficulties, a direct flash was used to quench the reaction, and a multi-effect evaporator system was designed to concentrate the sugars to a 12% solution which is the recommended concentration for ethanol fermentation.

The proposed hydrolysis plant can be separated into three stages of operation: 1) separation and pretreatment of raw refuse, 2) hydrolysis of cellulosic material, and 3) the concentration of the sugars. The first stage eliminates the majority of non-cellulosic material while pulping the cellulosic materials. The reactor system consists of a tubular flow reactor in which the cellulosic materials are hydrolyzed to

sugar by addition of sulfuric acid and heated water. Unreacted cellulose is recycled after flash cooling and liquid separation. Following acid neutralization, the final operation of concentrating the liquors is performed in a feed forward multiple-effect evaporator system. The inputs to the hydrolysis plant are refuse, process water, sulfuric acid, and lime. The outputs from the system are scrap iron, other metals, plastic inerts, hydrolysis waste, and a concentrated glucose sugar solution. A general plant flow sheet is shown in Figure 5-1 through 5-3.

5.1 Separation and Pretreatment System

The purpose of the separation and pretreatment system is to eliminate as much of the unhydrolyzable portion of refuse as possible and convert the refuse to a pulp slurry for the hydrolysis reactor. A system which will accomplish this task is already in existence. The paper industry employs such a system to pretreat waste paper for re-use as paper pulp. This system is described in reference (12) and is the basis for the hydrolysis plant pretreatment process.

A diagram of the separation system is shown in Figure 5-1. The incoming raw refuse is stored in a silo storage hopper. A ventilation line connects the storage hopper with the direct fired heater. A continuous flow of air is drawn from the storage hopper to the heater, thus eliminating the odor given off by the raw refuse while in storage. The storage hopper feeds the refuse to a magnetic pulley conveyor which rejects the scrap iron portion of the refuse and feeds the refuse to

Fig. 5-1. Separation System

FIG. 5-2 : REACTOR SYSTEM

FIG. 5-3 : EVAPORATION AND HEAT RECOVERY
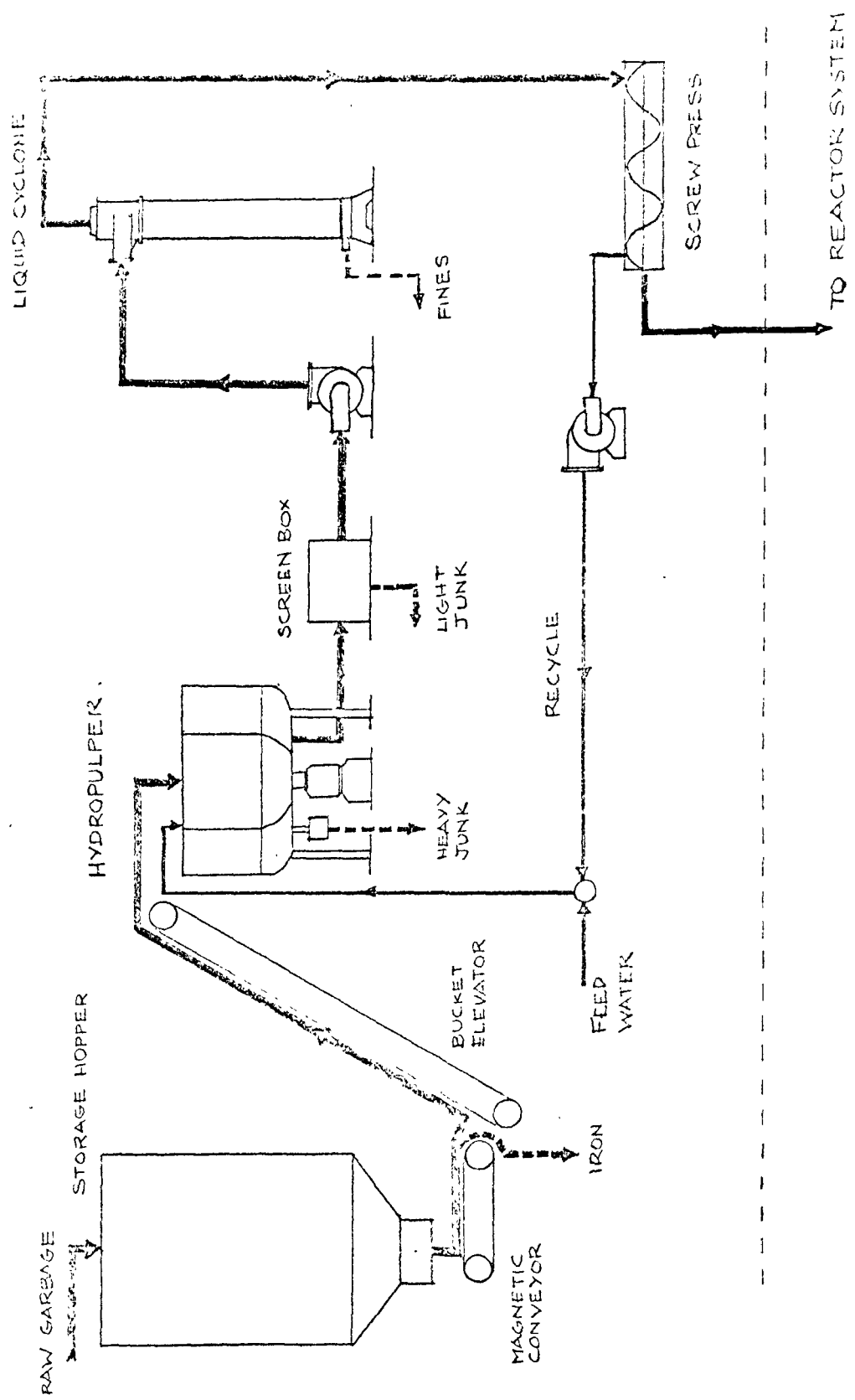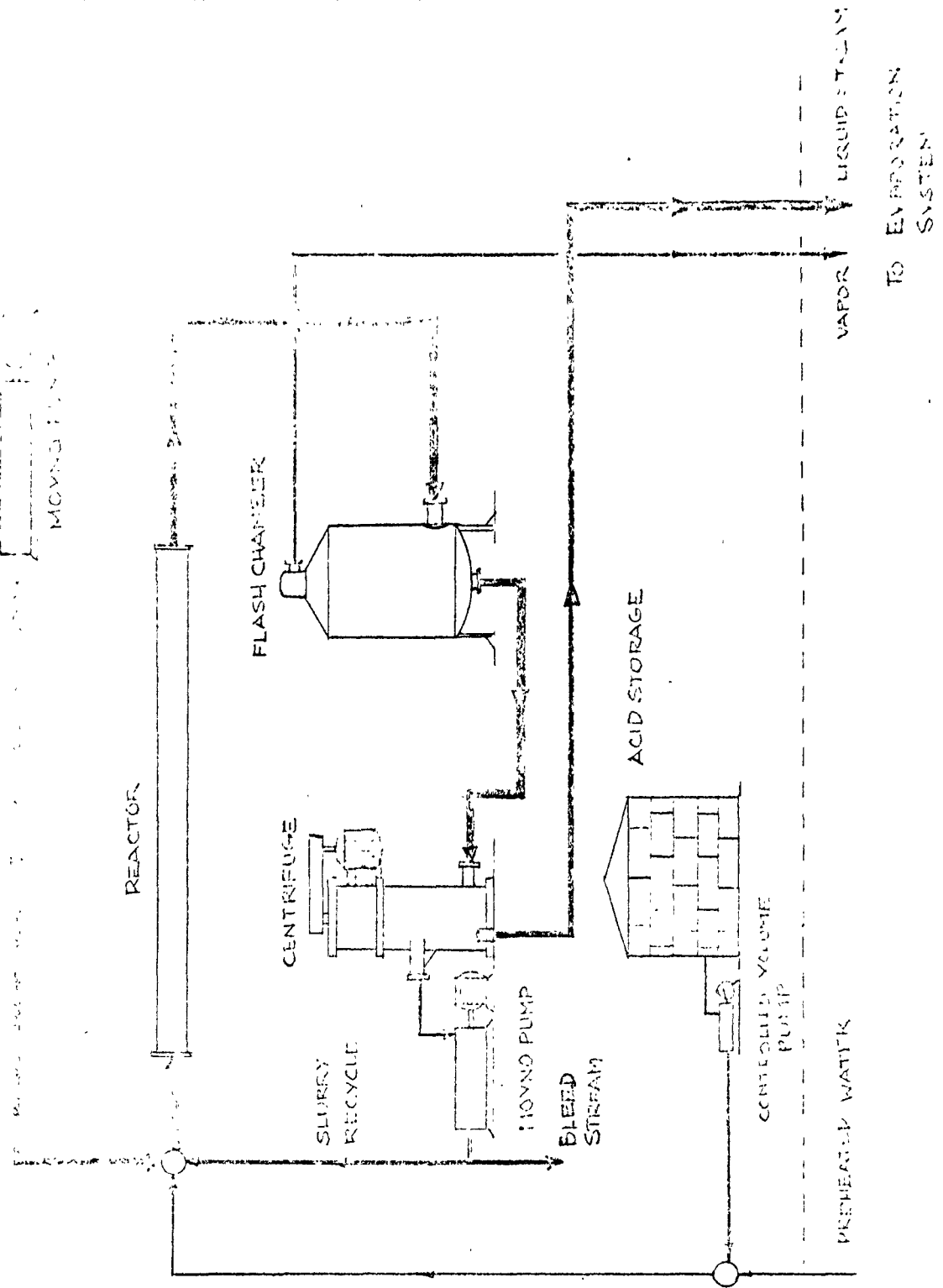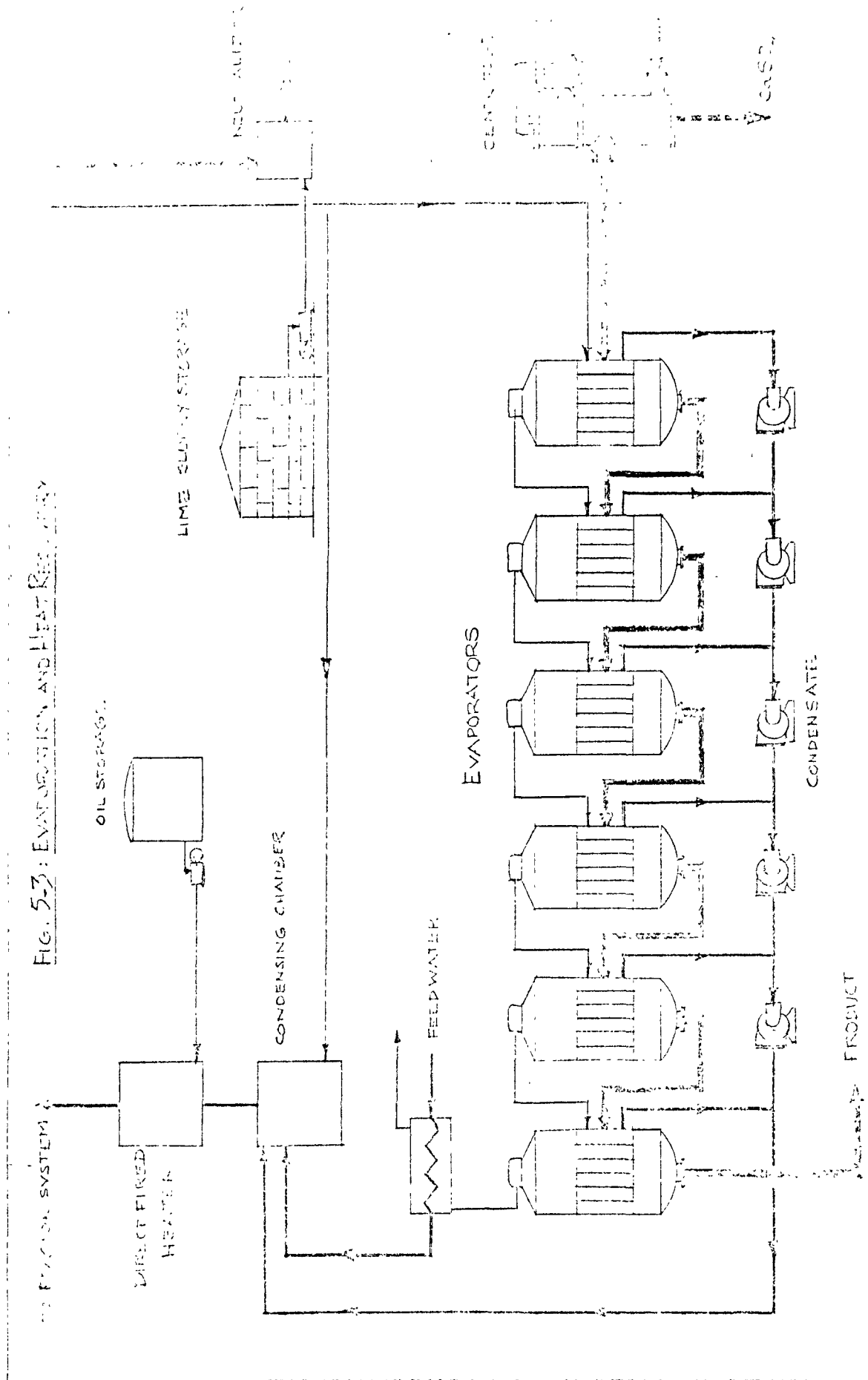
the hydropulper. The hydropulper breaks up the refuse and its "junker" carries out the larger pieces of unpulped refuse, i.e. tin cans, plastic bottles, non ferrous metals, and unbroken glass. A screen trap follows the hydropulper and eliminates the plastic films and other lighter pieces of trash. The dirt and finer pieces of glass are removed in a cyclone separator. Enough water is added to the hydropulper to produce a 2 to 3% consistency slurry which is the recommended consistency for such an operation. The pulp is dewatered in a screw press to approximately 50% by weight water. At this point the refuse is ready for the hydrolysis process.

It was assumed for calculations that the synthetics, glass, metal, and inert (rocks, etc.) portion of the refuse will be separated from the pulp. This means the pulp will consist of essentially rubbish (paper, leaves, and wood) and garbage. The pulp quality demands in the paper industry are much more stringent than for the hydrolysis process. It is therefore believed that this separation system should be adequate for the hydrolysis process.

Equipment Design Information

Storage Hopper:

Standard reinforced concrete. Design capacity based on 3 days storage at approximately 500 lb/yd^3.

Hydropulper System:

Designed and manufactured by Black Clowson, Middleton, Ohio. Capacities up to 850 tons/day. Horsepower requirements approximately 20 H.P. day/ton.

5.2 Hydrolysis Reactor System

Figure 5-2 is a flow diagram for the hydrolysis reactor system. Freshly pulped refuse is passed from the screw press into a series of Moyno pumps which bring the pulp to the desired reactor pressure. A stream junction at the inlet to the continuous flow reactor mixes the fresh pulp with recycled cellulose and enough acid solution to reach the required reaction temperature, acid concentration, and liquid to solid ratio. The acid is injected into the heated water stream prior to the mixing junction. After passing through the flow reactor, the solid-liquid slurry is flash cooled to quench the hydrolysis reaction. Vapor from the flash chamber is used as a heat source in the evaporation system. The remaining slurry is separated in a pressurized continuous flow centrifuge. The liquid continues down stream while the solid stream is partially bled of inerts and cellulose before entering a series of Moyno pumps which feed the unreacted cellulose into the mixing junction as a recycle stream.

The hydrolysis reactor was chosen from the three standard chemical reactors: batch, continuous stirred tank, and tubular flow reactor. The operations of charging, discharging, and cleaning of the batch reactor require an exorbitant amount of time and material handling which result in high cost for large scale operation. Although well suited for small amounts of costly reactants, the batch reactor would be undesirable for the large amounts of material processed in a hydrolysis plant.

The continuous stirred tank reactor is not advised for use in an $A \xrightarrow{K_1} B \xrightarrow{K_2} C$ series reaction, since the theoretical

maximum batch yield of B(glucose) is unobtainable. This can
be seen when one realizes that a CSTR is assumed to be well
mixed with outlet reactant concentration equal to the bulk
reactant concentration. An unreacted stream of A is continu-
ously added to the outlet concentration. Therefore the reac-
tion rate is not proportional to the inlet concentration, but
to the outlet concentration. Reference (13) presents a graph-
ical display of the maximum obtainable yield and required
volume of a CSTR for an $A \xrightarrow{K_1} B \xrightarrow{K_2} C$ consecutive reaction
with variable values of K_1 and K_2. It is clearly shown that
a CSTR gives a lower yield of B, and requires a greater volume
to reach its maximum yield than does a plug flow tubular reactor.

Variations and combinations of batch, semi-batch, series
CST, reactor configurations are conceivable, but the most simple
and reliable reactor for the hydrolysis reaction would be the
tubular flow reactor with a recycle stream. Such a reactor with
plug flow will give the high yield of a batch reactor and the
production capacity of a CSTR.

The design dimensions of the flow reactor will be a func-
tion of required residence time, through-put (fresh and recycle
reactants), degree of axial diffusion (divergence from plug
flow), and the desired flow velocity. The residence time is
the time to maximum yield of converted sugar. The residence
time will be determined by the reaction temperature and acid
concentration. The through-put capacity of the reactor is
governed by the total refuse handling capacity of the plant and
the amount of recycled cellulose. The size of the recycled
stream is dictated by the amount of incoming unhydrolyzable

material and unreacted cellulose. The desired recycle ratio
is ultimately determined from cost considerations. That is, as
the recycle stream is increased, the manufacturing and initial
capital cost of the plant will increase as will the product
rate of sugar. The final design recycle flow will be chosen
as that rate which minimizes the total production cost.

Divergence from plug flow of the slurry will produce a
lower expected yield and increase the required capacity of
the reactor. A study of the two phase flow of wood pulp fibers
is found in References (14, 15, 16). Such fibers exhibit three
regions of flow with increase in flow velocity. The laminar
region is characterized by a plug flow of fibers surrounded by
a thin water annulus. As the velocity increases, the fibers
begin to break up in what is termed the "transition region".
This trend continues until the fibers are completely agitated
in a region of turbulent flow. The velocity profiles associ-
ated with the flow of pulp fibers cannot be described by a
Newtonian fluid model. In Newtonian fluids an increase in
velocity results in blunter velocity profiles, whereas in the
case of pulp, an increase in fiber flow results in a sharper
profile. This tendency toward plug flow at low velocities in-
creases with an increase in fiber concentration. It was assumed
that such a fiber flow will exist in the hydrolysis reactor.
Therefore, the assumption of plug flow in the reactor will be
valid if the flow velocity is in the range of laminar fiber flow.
The transition velocity will be the limiting velocity which will
produce plug flow. Although there is no available expression
for calculating this velocity, it can be obtained empirically

from the curves in Reference (16). The transition velocity
occurs at approximately the same value for a given concen-
tration at various pipe sizes. For a five percent consistency
slurry the transition velocity is approximately 6 ft/sec. This
velocity is high enough to insure a wide range for the reactor
flow velocity. Some consideration should be given to sedimen-
tation or settling out of the solids at very low velocities,
but if desired, this effect can be reduced by a vertical flow
reactor. The optimum velocity will ultimately have to be de-
termined from a pilot plant flow reactor system.

The material of construction for the reactor must be able
to withstand the corrosive effect of the <1% sulfuric acid so-
lution at temperatures above 400°F. The selection of a material
for these conditions is hampered by the fact that most corrosion
test data are limited to the boiling point of the acid solution
at atmospheric conditions. Reference (17) indicated that the
use of nickel based, nickel containing materials, and high
chromium content stainless steel alloys might be applicable for
such conditions. Hydrolysis experiments were conducted in
cylinders of Monel, Hastalloy-B, chrome-moly, stainless 316,
and Carpenter 20 alloys. The hydrolysis in vessels of Carpenter
20 stainless steel gave the highest yield of glucose. Although
these results did not show a complete study of the corrosion
problem, they did indicate that Carpenter 20 had the best poten-
tial as a material for constructing the flow reactor. An im-
proved variety of Carpenter 20 designated as No. 20Cb-3 has
been developed. A corrosion chart for this material, taken
from a Carpenter Steel Co. technical data sheet, is found in
Figure 5-4. From this chart it can be seen that Carpenter

Figure 5-4

CORROSION RATE OF CARPENTER STEEL
No. 20Cb and No. 20Cb-3

- - - CARPENTER No. 20Cb
—— CARPENTER No. 20Cb-3

25 % H_2SO_4
20 % H_2SO_4
15 % H_2SO_4
10 % H_2SO_4
25 % H_2SO_4
10 % H_2SO_4
5 % H_2SO_4

.210

.180

.150

.120

.090

.060

.030

0

CORROSION RATE - INCHES PER YEAR (IPY)

100   110   120   130 °C
212   230   248   260 °F
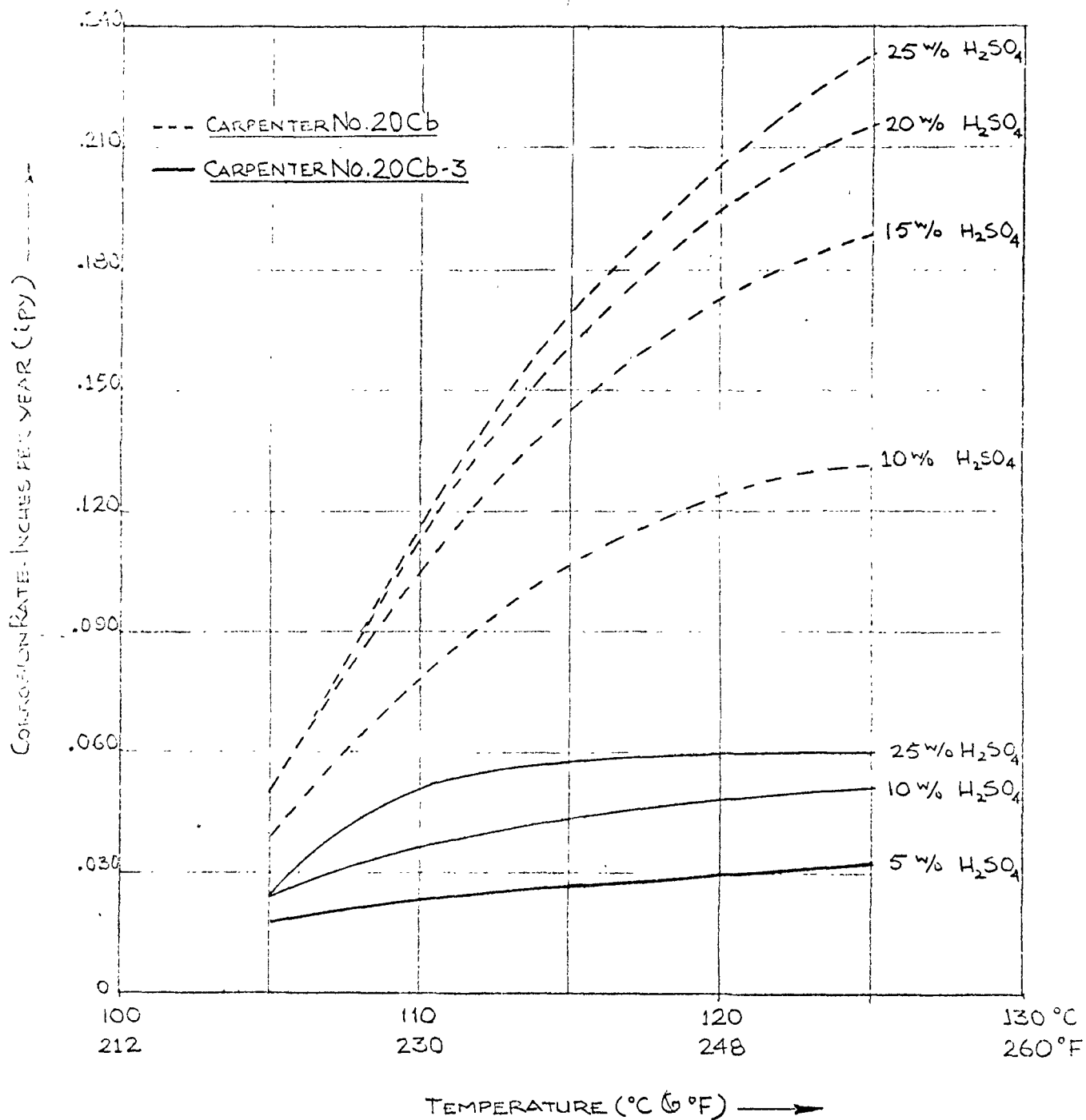
TEMPERATURE (°C & °F) ⟶

20cB-3 exhibits very good corrosion properties in dilute H_2SO_4 acid at high temperatures. For design and cost considerations it is assumed that the reactor will be made of carbon steel clad with Carpenter 20Cb-3. At a rate of 30 mpy, one inch cladding would last for twenty years.

Equipment Design Information

Reactor:

Tubular flow reactor. Design pressure 500 psi.

Carpenter 20Cb-3 cladding

Plug flow at 1 ft/sec

Flash Chamber:

Assumed residence time for adequate vapor separation of 2 minutes. Constructed of Carpenter 20 steel. Design pressure 150 psi.

Acid Storage Tank:

14 day design capacity.

Constructed of carbon steel.

Centrifuge:

Pressurized (150 psi) continuous variety.

Recommended - Sharples Super-D-Canter model with continuous screw conveyor for solid separation. Maximum design capacity limited to liquid stream of 350 gal/min.

Horsepower $\approx$ liquid flow rate. H.P. $\approx$ gal/min.

Constructed of Carpenter 20 steel.

Assumed solid moisture content at discharge of 50%.

Slurry Pumps:

Recommended Moyno positive displacement.

Maximum pressure 1000 psi.

Maximum capacity 500 gal/min.

Feed pump constructed of steel rotor and housing.

Recycle pump constructed of Carpenter 20 steel.

Water Pumps:

Standard steel motorized centrifugal pumps.

Acid Pump:

Positive displacement controlled volume feed pump.

Constructed of Carpenter 20 steel.

5.3 Concentration of Sugar Solution and Heat Recovery

Most processes which use glucose as a raw material require
at least a 6% solution (Torula yeast production) and preferably
a 12% solution (ethanol fermentation) of glucose. With a liquid
to solid ratio of 20 to 1 the glucose solution leaving the cen-
trifuge will be approximately 2% by weight glucose. The glucose
solution must therefore be concentrated after leaving the hydrol-
ysis section of the plant.

An ideal process would perform the required concentrating
while allowing the high temperature stream of water to act as
a preheat or feed for the hydrolysis reactor. Two relatively
new processes, as cited in a recent Doctorate thesis[18], which
are being tested for use in concentrating spent sulfite liquor,
perform the task to some degree. They are reverse osmosis and
electrodialysis. Reverse osmosis has proven to be effective in
concentrating liquors to 10% by weight solids. If the sugar
solution contained only glucose, this would be a feasible method
of concentration. The difficulty is that the hydrolyzed solu-
tion will contain, in addition to glucose, decomposed sugars
and other large organic molecules from the garbage portion of
the refuse. Therefore, the glucose concentration will be

initially 2%, but the total solute concentration may be greater than 4%. The upper limit of glucose concentration by reverse osmosis will be approximately 5% which is below the 12% required concentration. Although feasible for the lower limits of concentration, reverse osmosis, in its present state of development, would not be acceptable for most sugar fermentation processes. Electrodialysis has been tested experimentally but as of yet not proven economically feasible on such separation processes. Thus at its state of the art, it cannot be recommended as a means for concentrating the sugar solution.

One proven means of concentration which will allow partial use of the high temperature stream as preheat is feed forward multi-effect evaporation. The proposed evaporator scheme is shown in Figure 5-3. The recommended effects are short tube vertical evaporators. They were chosen because of their ability to be cleaned with a minimum amount of effort.

The liquid stream from the recycle centrifuge is neutralized by means of lime addition. The lime is injected in a slurry form, using an in-line mixer to insure that complete neutralization occurs. The lime, or $CaCo_3$, reacts with the sulfuric acid to produce water, $CaSO_4$, and CO_2. After neutralization the CO_2 is removed by a gas separation vessel and the $CaSO_4$ which precipitates out of solution is separated by a pressurized centrifuge. The operation of neutralization followed by separation is performed to produce a non-corrosive solution and to decrease scaling in the evaporators. Lime is used as the base because of its comparably low cost. If the glucose solution will be used for ethanol fermentation, it may

be advisable to use ammonium hydroxide as the neutralizing agent. The ammonium sulfate produced by such neutralization could then be used as a nutrient for fermentation.

The evaporator system was designed to make maximum use of the high temperature of the feed stream. The upper limit of preheat for the reactor water feed stream is set by the temperature of the flash chamber quench. This quench temperature was 177°C (350°F) since at this temperature the hydrolysis reaction will be essentially zero. The latent heat of the vapor stream from the flash chamber is used to evaporate the product stream in the first effect and to raise the temperature of the direct fired heater feed water stream. It was assumed that the vapor from the flash chamber would be free enough of impurities to be condensed directly in the heater water stream, thus eliminating a condenser and fresh feed water. This assumption was again made for the vapor formed and condensed in each effect.

The condensate from each effect (other than the last) is pumped to the condensing chamber where it is combined with the flash vapor and make up feed from the last effect's condenser. This heated stream is passed through the direct fired heater where it is brought to the required temperature for the hydrolysis reactor. A bleed off from the preheat stream could be used to prevent impurities build up if the assumption of clean vapor is not valid.

The number of effects used in the evaporation system was determined by an economic analysis of the evaporator-heater system. That is, for a given initial and final concentration of sugar, reactor feed water temperature, and flash condition,

the optimum use of the potential heat source was made to mini-
mize the required capital investment of the evaporator heater
system and the utility cost of heating oil. It was found that
for initial and final concentrations of 2 and 12%, the optimum
number of stages would be 6. This optimum number does not vary
with feed capacity, but it will vary with the degree of concen-
tration necessary. At 4% to 12% the number of stages was de-
termined to be 5. This increase in initial concentration would
correspond to a decrease in the hydrolysis liquid to solid ratio.
Six effects were used in the plant design and cost estimates;
this would allow one unit to be used in standby if maintenance
problems develop.

Equipment Design Information

Evaporators:

   Standard vertical-tube evaporators.

   Heat transfer area determined by flow capacity.

   Constructed with cast iron shell and copper tubes.

Condenser:

   Standard shell and tube construction.

   Cooling flow through tubes.

   Constructed of carbon steel.

   Atmospheric pressure.

Condensing Chamber:

   Volume based on 2 minutes residence time.

   Standard steel construction.

   Design pressure 150 psi.

Direct Fired Heater:

   Cylindrical construction.

   Carbon steel tubes.

   Design pressure 500 psi.

In Line Mixer:

   Carpenter 20 steel.

   Nettco Flomix is recommended (Nettco Corp., Everett, Mass.)

Centrifuge:

   Sharples Super O - Hydrator continuous operation.

   Ordinary steel construction.

   Pressurized at 150 psi.

Pumps - Water:

   Motorized centrifugal pumps

   Carbon steel construction.

Pumps - Slurry:

   Moyno slurry pump.

5.4 Design Calculations

     The basic design calculations were generalized so that a computer program with variable plant inputs could be written. The inputs to the program consist of:

   1. Total plant refuse processed.

   2. Fractional input of paper

   3. Percent cellulose in paper

   4. Fraction garbage in refuse

   5. Fraction of refuse separated before hydrolysis

   6. Fraction of inerts in hydrolysis feed

   7. Liquid to solid ratio for hydrolysis

8. Recycle ratio

9. Acid concentration

10. Reaction temperature

11. Time to maximum yield

12. Chemical yield of glucose.

The separable portion of refuse was assumed to be that which can be separated in the hydropulper system (metals, plastics, stones, dirt, etc.). The garbage portion of refuse flows into the hydrolysis reactor with the paper. Although the majority of the garbage, organic plant waste, will be decomposed, it was assumed that fifty percent would not be hydrolyzed. This portion would add to the inert portion of the hydrolysis recycle stream and therefore give a conservative estimate for the reactor size and final glucose concentration. The inert fraction would include the clay paper additives in addition to the unhydrolyzable portion of the garbage.

A. Material Balance (Appendix IV)

The following assumptions were made in making the material balance:

1) Specific volume of paper slurry 62.4 lb/ft^3

2) The liquid content leaving the pre-hydrolysis screw press will be 50%.

3) 66 Be' sulfuric acid (93% H_2SO_4)

4) Solid stream from centrifuges will contain 50% moisture.

5) Degree of refuse separation described previously in 5.4

6) Lime slurry contains 50% liquid.

A computer program print out of a material balance and a generalized flow sheet follows in Table 5-1 and Figure 5-5.

Table 5-1

MATERIAL BALANCE
REPRESENTATIVE 250 TON PLANT

```
? 250
INPUT FRACTION PAPER,GARBAGE,SEPARABLES IN WASTE
? .6,.15,.25
INPUT FRATION CELLULOSE IN PAPER
? .8
INPUT TIME TO MAX YIELD IN MIN
? 1
INPUT CELLULOSE FRACTION CONVERTED AND SUGAR PRODUCED
? .75,.55
INPUT FRACT ACID,SOLID TO LIQUID,REACTION TEMP CENT
? .004,.1,230
INITIAL FRACTION INERTS 0.28125
INPUT I1,INERT RATIO FINAL
? .4
DO YOU WANT MATERIAL FLOW BALANCE YES OR NO
? YES
```

SEPARATION SYSTEM

SEPARATOR	IN	OUT T/D	IN	OUT T/HR
WASTE	250	187.5	10.4167	7.8125
WATER	12500	375	520.833	15.625

****

REACTOR	IN	OUT T/D	IN	OUT T/HR
CELLULOSE	131.875	32.9687	5.49479	1.3737
WATER	2183.75	2173.22	90.9896	90.551
ACID	9.39247	9.39247	0.391353	0.391353
SUGAR	0	79.7844	0	3.32435
D SUGAR	0	29.0125	0	1.20885
S INERTS	52.75	52.75	2.19792	2.19792
L INERTS	33.75	33.75	1.40625	1.40625

****

FLASH	IN T/D	OUT T/D	IN T/HR	OUT T/HR
WATER	2173.22	1917.73	90.551	79.9053

****

CENTRIFUGE #1	IN	LIQUID OUT	SOLID STREAM	TONS/HR
CELLULOSE	1.3737	0	1.3737	
WATER	79.9053	76.3336	3.57161	
ACID	0.391353	0.385087	6.26631 E-3	
SUGAR	3.32435	3.17657	0.147781	
D SUGAR	1.20885	1.15512	5.37386 E-2	
S INERTS	2.19792	0	2.19792	
L INERTS	1.40625	1.34374	6.25136 E-2	

********************BLEED AND RECYCLE*******************

MATERIAL	BLD-T/D	REC-T/D	BLD-T/HR	REC-T/HR
CELLULOSE	21.0937	11.875	0.878906	0.494792
S INERTS	33.75	19.	1.40625	0.791667
WATER	54.8437	30.875	2.28516	1.28646
ACID	9.62221 E-2	5.41695 E-2	4.00925 E-3	2.25706 E-

PLUS SMALL AMOUNTS OF SUGAR AND LIQUID INERTS

****

Table 5-1 (Continued)

NEUTRALIZER	IN T/D	OUT T/D	IN T/HR	OUT T/HR
WATER	1841.44	1843.14	76.7266	76.7973
ACID	9.24208	0	0.385087	0
CASO4	0	12.8257	0	0.534406
CO2	0	4.14951	0	0.172896
LIME	9.4307	0	0.392946	
SUGAR	76.2376	76.2376	3.17657	3.17657
D SUGAR	27.7228	27.7228	1.15512	1.15512
L INERTS	32.2497	32.2497	1.34374	1.34374

****

CENTRIFUGE 2	IN	LIQ OUT	SOL OUT	TONS/HR
WATER	76.7973	76.2629	0.534406	
CASO4	0.534406	0	0.534406	
CO2	4.14951	0	0	
SUGAR	3.17657	3.17565	9.21027 E-4	
D SUGAR	1.15512	1.15478	3.34919 E-4	
L INERTS	1.34374	1.34335	3.89608 E-4	

****

REACT WATER T/HR AT TEMP
81.8906 T/HR   244.561 DEG CENT 472.209 DEG F

TEMP TO HEATER DEG F AND C   329.809   165.45

EVAPORATORS
STEAM FROM FLASH USED 2.9652 TONS/HR

EFFECT	VAPOR	TONS/HR
1	4.86472	
2	6.58327	
3	7.98176	
4	9.1766	
5	10.0442	
6	10.9322	

Figure 5-5

MATERIAL BALANCE SHEET
REPRESENTATIVE PLANT 250 T WASTE/DAY

REACTOR INPUT T/HR	
CELLULOSE	5.38
WATER	101.74
ACID	0.44
SOL INERTS	3.23
LIQ INERTS	1.56

REACTOR OUTPUT T/HR	
CELLULOSE	1.345
WATER	101.31
ACID	0.44
SUGAR	3.26
DECOMP SUGAR	1.18
SOLID INERTS	3.23
LIQ INERTS	1.56

WATER	18.63 T/HR
WASTE	7.81 T/HR

FROM SEPARATION SYSTEM

REACTOR
446°F
400 psi

REC STREAM	T/HR		
		SUGAR	3.26
CELLULOSE	1.35	DEC SUGAR	1.18
WATER	69.41	SOL INERTS	3.23
ACID	0.43	LIQ INERTS	1.56

CENTRIFUGE
130 psi

FLASH CHAMBER
350°F
135 psi

RECYCLE	T/HR
CELLULOSE	0.69
SOLID INERT	1.67
WATER	2.36
ACID	5.4E-3
TRACE SUGAR	—

LIQUID STR	T/HR
WATER	84.83
ACID	0.426
SUGAR	3.00
DECOMP SUGAR	1.124
LIQ INERTS	1.48

CaCO₃ 0.435 T/HR

93% H₂SO₄ 0.432 T/HR

NEUTRALIZER

CENTRIFUGE
135 psi

	T/HR
WATER	85.3
CaSO₄	0.59
CO₂	0.19
SUGAR	3.00
DECOMP SUGAR	1.124
LIQ INERTS	1.48

SOLID	T/HR
WATER	0.59
CaSO₄	0.59
SUGAR	8.9E-4
D SUGAR	8.2E-4
L INERT	4.2E-4

LIQ STR	T/HR
WATER	84.75
SUGAR	3.00
D SUGAR	1.123
L INERTS	1.48

HEATER
467°F

CONDENSING CHAMBER
326°F

FUEL OIL

FEED WATER

EVAPORATORS

240°F	260°F	282°F	304°F	327°F	350°F
25 psi	35 psi	57 psi	74 psi	100 psi	135 psi

PRODUCT	T/HR
WATER	26.3
SUGAR	3.00
DEC. SUGAR	1.12
LIQ INERTS	1.48

B. Reactor Design and Recycle Calculation

The design of the reactor vessel is determined by the flow capacity, flow velocity, and required residence time. The total flow through the reactor is found by a recycle material balance on the reactor system.

The recycle calculation is performed on the solid portion of the refuse. It is only necessary to consider the cellulose and inert portion of the stream. The soluble portion of non-cellulosic materials and liquid will be separated by the continuous centrifuge and therefore will not be included in the recycle loop.

Let C_1 = fresh feed of cellulose Tons/hr

I_1 = fresh feed of inerts Tons/hr

C_2 = recycled cellulose Tons/hr

R_1 = entering ratio of inerts to cellulose

R_2 = exit ratio of inerts to cellulose

B = amount of cellulose bled off Tons/hr

Y = fractional conversion of cellulose

Y_1 = fraction yield of sugar

The final ratio of inerts to cellulose at the exit of the reactor will be:

$$R_2 = \frac{R_1(C_1 + C_2)}{Y(C_1 + C_2)} = \frac{R_1}{Y}$$

At steady state the amount of inerts entering the reactor will equal the amount of inerts bled off.

$$I_1 = R_2 \cdot B$$

A material balance around the bleed point requires that the

$$(1 - Y)(C_1 + C_2) = (C_2 + B)$$

$$C_2 = \frac{B - (1-Y)C_1}{Y}$$

Thus once values for R_1 and Y are set the total amount of cellulose and inerts in the reactor can be determined.

The total amount of solid material in the reactor will include, in addition to the cellulose and inerts, the non-hydrolyzable portion of garbage (G). Total solids will be:

$$S = G + C_1 + C_2 + R_1(C_1 + C_2)$$

From the solid to liquid ratio, L, the necessary liquid flow rate is found to be $W = LxS$ and the total weight of material will be $M = S + W$ Tons/hr. With the assumed value of 62.4 lb/ft^3 the total volumetric flow rate can be determined (Q). This value in conjunction with the residence time T determine the reactor volume, $V = QxT$. The necessary cross sectional area and length can be found from this volumetric flow, residence time, and flow velocity of 1 ft/sec.

C. Energy Balance

The heat load to the system is a function of plant capacity, liquid to solid ratio, recycle ratio, reaction temperature, and preheated feed water temperature. The first three of these are directly associated with the required liquid flow stream in the reactor (W). The temperature of this stream (T_1) is set by the reaction temperature. The preheat temperature (T_2) is calculated by an energy balance on the flash and evaporator section.

$$T_2 = \frac{V\lambda}{WCP} + \sum_{C=1}^{6} \frac{T_e C_e + FT_f}{\sum_{C=1}^{6} C_e + F}$$

Where V = vapor from flash chamber, lb/hr

λ = latent heat of vapor, BTu/lb.

W = water flow rate to reactor, lb/hr

C_p = heat capacity, 1 $\frac{BTu}{lbF°}$

T_e = temperature from effect e °F

C_e = condensate from effect e $\frac{lb}{hr}$

T_f = make up feed temperature °F

F = make up feed flow lb/hr

The required heat load to the system will then be

$$Q = (T_1 - T_2) W C_p$$

This is supplied by the direct fired heater with oil at $1.5E5 \frac{BTu}{gal}$ with 80% conversion efficiency.

D. Flash Chamber Design

The amount of material vaporized in the flash chamber can be determined by an adiabatic enthalpy balance where: The enthalpy of the feed equals the combined enthalpy of the vapor and liquid stream leaving the chamber.

$$F H_i^L = V H_o^V + L H_o^L \qquad \text{enthalpy balance}$$

$$F = V + L \qquad \text{mass balance}$$

$$F H_i^L = V H_o^V + (F - V) H_o^L$$

$$\frac{V}{F} = \frac{H_i^L - H_o^L}{H_o^V - H_o^L} \qquad \text{fraction flashed}$$

For a flash from 230°C to 177°C

$$\frac{V}{F} = 0.117$$

The size of the flash chamber is determined by the cross

of the chamber is usually between 7 and 12 ft.[19], to prevent

splashing and therefore liquid entrainment. The allowable vapor

flow rate (G) lb/hr.ft^2 is determined by an empirical correla-

tion based on a decontamination factor, DF = weight vapor/

weight of entrained liquid. From Reference (20) the recom-

mended flow rate for DF = 10,000 at 300°F is 200 lb/hr.ft^2.

The recommended flash temperature is 350°F, therefore it is

necessary to use the empirical correlation found in Perry[19].

$$G = C^1 \sqrt{\rho \, (\rho_\ell - \rho_g)}$$

With G = lb/hr.ft^2 of vapor

  ρ_g = vapor density lb/ft^3 at flash temp.

  ρ_ℓ = liquid density lb/ft^3 at flash temp.

  C^1 = empirically correlated factor

  C^1 = 80 at DF of 10,000

For T = 350°F

  G = 320 lb/hr.ft^2

For a total flow rate of 2 x 10^5 lb/hr the cross sectional area

required is 69 ft^2 and the total volume is 8300 ft^3. This volume

will result in a vapor residence time of ≈ 0.7 minutes. For the

computer program a residence time of 2 minutes was used to cal-

culate a nominal flash chamber volume. This will give a con-

servative estimate of the volume required for the preliminary

design.

E. Evaporator Design

The design procedure for feed forward multi-effect evapo-

ration systems was taken from Kern[21]. In such a design the

temperatures and pressures in the first and last effects are

fixed. It is usually assumed that equal areas will be used and

that under such conditions the pressure difference between effects will be approximately equal. The equal area restriction is imposed, partially, because it is less expensive to build a system with equal area effects. From these pressures the saturated liquid temperature can be found. The actual temperature and pressure drop in the system will adjust itself during operation according to the actual heat transfer coefficient in each stage. The steam supply for the first effect is taken from the flash chamber and the vapor formed in each effect is used to evaporate the liquor in the subsequent effect. This liquor will boil at a lower temperature than the condensing vapor because its saturation pressure is lower than the vapor's, due to the staged pressure drop.

The steam and surface requirements for the multi-effect evaporation system are computed by performing a heat balance across each effect and an overall material balance on the system.

$$W_S \lambda + W_f C_f (T_f - T_1) = W_1 \lambda_1 \qquad \text{Heat balance 1st effect}$$

$$W_{i-1} \lambda_{i-1} + (W_f - \sum_{n=1}^{i} W_n) C_{i-1} (T_{i-1} - T_i) = W_i \lambda_i \qquad \begin{array}{l}\text{Heat balance on} \\ \text{subsequent effects}\end{array}$$

$$E = \sum_{n=1}^{K} W_n \qquad \text{Material balance}$$

$$A_1 = \frac{W_S \lambda_S}{U_i (T_S - T_1)} \qquad \text{Required surface area}$$

$$A_i = \frac{W_{i-1} \lambda_{i-1}}{U_i (T_{i-1} - T_i)}$$

where C_f = specific heat of feed BTu/lb°F

T_F = feed temperature °F

W_F = feed lb/hr

T_S = saturation temperature of steam °F

W_S = steam to first effect lb/hr

E = total required evaporation lb/hr

C_i = specific heat of liquor in effect i BTu/lb°F

T_i = boiling point of liquor in effect i °F

W_i = vapor removed in effect i lb/hr

λ_i = latent heat of vapor i BTu/lb

A_i = area of effect i ft^2

U_i = heat transfer coefficient for effect i BTu/hr.ft^2 °F

Therefore for a system composed of K effects there will be K + 1 unknowns, the required steam input and K vapor rates, and K + 1 equations. These equations were solved by matrix inversion in a variable input computer program. If the areas are not equal the pressure drops, and therefore temperature differences, are adjusted until they are equal.

It was assumed that the boiling point rise due to solute content will be negligible. This assumption was based on information obtained from Kern[21] which indicated that over the range of 0 to 20°Brix ($\approx$ % weight sugar) the BPR was approximately 1°. It was further assumed that the specific heat of the solution would be 1 BTu/lb°F. Over the same range of concentration C_p varies from 1 to 0.9.

The heat transfer coefficient in each stage will be controlled by the temperature, temperature difference, the viscosity of the liquor, and scale formation in the effect. The standard method of calculating an overall heat transfer coefficient from the individual resistances is not used in practice. Most information concerning the heat transfer coefficients is obtained from operating experience with the given type of effects.

Reference (19) gives a range of experimental values for vertical tube evaporation with natural water circulation of 200 - 500 BTu/hr.ft^2°F. Kerr[19] gives data for operational transfer coefficients obtained with a feed forward system used in concentrating cane sugar to 50° Brix. The transfer coefficients are from 100 to 450 over a temperature range of 220 to 120°F. Kern[21] also presents data for concentrating cane sugars from approximately 13 to 50°Brix with $\Delta T = 23$°F and a temperature range of 274 to 180°F.

The proposed system for concentrating the hydrolysis sugars operates with a $\Delta T \approx 23$°F, temperatures from 350 to 212°F, and sugar concentrations from 2 to 12%. Since other solids will be mixed with the sugars, the actual concentrations will be from approximately 4 to 24%. Given the previously mentioned experimental data and the above specifications, a range of coefficients from 500 to 250 was used in the design calculations. The data in Table 5-2 were used in the design of the multi-effect system.

Table 5-2

EVAPORATOR DESIGN DATA

Steam Chest	Press, psia	Temp F°	L, BTu/lb	U, BTu/hr ft²
1	135	350	870	500
2	100	327	889	480
3	74	304	905	450
4	57	282	924	410
5	35	260	939	370
6	25	240	952	250
To CONDENSER	14.7	212	970	500

6. PLANT ECONOMICS

Many of the design parameters for plant operation cannot
be determined without an economic evaluation of the hydrolysis
plant. That is, variables such as recycle rate, acid concen-
tration, reaction temperature, and residence time must be set
such that the manufacturing cost of glucose is minimized. A
knowledge of the effect of total refuse input and its compo-
sition on the manufacturing cost must also be determined, be-
fore a decision can be made concerning the economic potential
of refuse disposal by paper hydrolysis. It would require a
great amount of labor to perform an overall economic analysis
such as this, without the use of a plant-simulating computer
program.

The previously described generalized material flow program
(Section 5.4) generates the information necessary to size the
individual plant components. The size of each component can
then be used to determine its purchased and installed cost. From
these costs, the total fixed capital investment is calculated.
The material balance is also used to determine the total manufac-
turing cost per pound of glucose.

6.1 Capital Costing Procedure (Appendix IV)

Estimates of equipment costs, not including the hydropulper
system, were taken from a recent article by C.E. Guthrie[22].
The equipment cost information in this article included, in ad-
dition to purchase costs, the size exponential factor for each
piece of equipment and a direct material and labor factor used
to determine the total installed cost. The M & L factor includes:

piping, concrete, steel, instruments, electric material, insulation, paint, and labor necessary to install the component. The hydropulper system cost was estimated by the Black Clawson Co. for an 80 ton/day capacity system with an 0.6 factor for scale-up. The cost information in Reference (22) was for mid-1968 and a 6% escalation was used to predict the capital investment for mid-1969.

To arrive at a value for the final fixed capital investment, a percentage of the installed equipment cost was used to determine the additional plant cost.

Building Cost = 20% of IEC (Installed Equipment Cost)
  Outdoor-indoor type construction

Freight & Taxes = 8% of IEC

Construction = 17.8% of IEC

Engineering = 10% of IEC

Contingency & Contractor Fee = 18% of Direct Plant Cost

Working Capital = 15% of Direct Plant Cost

The above percentages were taken from Reference (23) and are accepted values used in preliminary cost estimations.

A printout of the equipment sizes and cost for a nominal 250 ton plant are shown in Figure 6-1. The manufacturing costs in this example represent 24 hours of continuous operation. Given any set of initial conditions for plant operation, the computer program will calculate the presented information. In this manner, it is possible to determine the total manufacturing cost per pound of sugar for any municipality with its own local plant operating cost and refuse composition. In order to use this program to evaluate a plant for any location, see Appendix IV.

Figure 6-1

CAPITAL & MANUFACTURING   COST ANALYSIS
REPRESENTATIVE 250 TON PLANT

DO YOU WANT EQUIPMENT SIZE AND COST YES OR NO
? YES
*»*****»*COST ANALYSIS******************

EQUIPMENT	SIZE			P COST	IN COST
HOPPER	27000	FT^3		9732.57	10705.8
CONVEYOR	100	FT		9978.68	16165.5
HYDROPULP	250	TONS/DAY		133363.	213381.
REACTOR	47.6612	FT^3		9089.98	13332.
ACID STORAGE	121078.	GAL		5668.84	10487.4
FLASH CHAM	97.2111	FT^3		10461.5	13782.6
CENT 1	283.956	GAL/MIN		79387.6	127020.
NEUT	304.302	GAL/MIN		3711.69	5938.7
LIME ST	2218.99	FT^3		1026.93	1129.62
CENT 1	304.302	GAL/MIN		17643.9	28230.2
HEATER	2.33224 E+7	BTU/HR		74047.8	120698.
OIL ST	43900.9	GAL		8939.09	16537.3
EVAP	1521.98	FT^2		349953.	664911.
COND	1291.5	FT^2		10628.1	24869.7
COND POT	87.49	FT^3		3101.27	6202.53

PUMP	FT^3/HR	H.P.	P.C.	I.C.
	500.801	2.73062	1190.92	2870.12
	12019.2	65.5349	6217.17	14983.4
	751.202	27.3062	3943.51	9503.86
	6.85696	0.311563	660.805	1592.54
	412.326	14.9881	2013.16	4851.72
	937.577	34.0809	4425.2	10664.7
	18.4916	0.168042	279.412	673.382

TOTAL PURCHASED EQUUIPMENT COST 790192. DOLLARS
TOTAL INSTALLED EQUIPMENT COST 1.39764 E+6 DOLLARS
BUILDING COST   279529. DOLLARS
FREIGHT AND TAXES   111811. DOLLARS
CONSTRUCTION COST   248781. DOLLARS
ENGINEERING COST   139764. DOLLARS

DIRECT PLANT COST   2.17753 E+6 DOLLARS
CONTINGENCY AND CONTRACTOR FEE   391955. DOLLARS

FIXED CAPITAL INVESTMENT   2.56948 E+6 DOLLARS

WORKING CAPITAL   385423. DOLLARS

(continued)

Figure 6-1   (continued)

```
***************MANUFACTURING COST********************
INPUT DUMPING FEE PER TON
? 4
input cost for disposal of waste per ton
? 3
INPUT INTEREST RATE AND YEARS OF OPERATION
? .04,20
RAW MATRIALS
ACID            9.24208        TONS/DAY        295.747
LIME            9.4307         TONS/DAY        113.168
UTILITIES
WATER           150902.        GALS            37.7256
ELECT           12984.3        KILOWATTS       162.303
oil             4390.09        gal             439.009
WASTE DISPOSAL  86.0937        TONS/DAY        258.281
LABOR           72             HRS             216
SUPER           24             HRS             84
FRINGE BEN                                     45.
MAINTAIN        0              0               356.873
SUPPLIES        0              0               26.7655
FIXED CHARGES
TAXES           0              0               142.749
INSURANCE       0              0               71.3745
cap return                                     603.964
GENERAL COST
PAY OVER        0              0               71.7655
LAB             0              0               71.7655
PLANT OVER      0              0               239.218

TONS /DAY OF GLUCOSE 75.7071
TOTAL COST/DAY NO DUMP FEE      3235.71 DOLLARS

COST/TON OF GLUCOSE NO DUMP  42.7398 DOLLARS
COST/LB OF GLUCOSE NO DUMP    2.13699 E-2 DOLLARS

TOTAL COST/DAY WITH DUMP FEE  2235.71 DOLLARS
COST/TON WITH DUMP FEE        29.531 DOLLARS
COST/LB WITH DUMP FEE         1.47655 E-2 DOLLARS

TIME: 6.365 SEC.
READY
```

6.2 Manufacturing Cost Estimation

The amount of raw material required for a given plant size is calculated from the material balance. The raw materials purchase prices were taken from a June 16, 1969 edition of the Oil, Paint and Drug Report in which the current prices f.o.b. New York are given for all major chemicals.

Utility costs were calculated from rates given in Ref. (24) for 1967. These rates will vary with the given plant location. Mid-range values were used for calculation purposes.

Labor costs were based on three men operating the equipment with one supervisor, and three shifts. This amounts to one man per plant section with one overall supervisor. Labor rates are reported in U.S. Department of Labor publications and a yearly index for such rates is given in Reference (24).

Other direct costs such as fringe benefits, maintenance, and repairs are calculated on a percentage basis, as are the indirect costs of payroll overhead, laboratory and plant overhead. These percentages were taken from References (23) and (24).

The fixed charges such as capital return, taxes, and insurance are all based on the fixed capital investment. The charges for the original capital investment depend upon the source of the capital investment. It was assumed that these charges would be 4% for 20 years if the plant is built by the municipality, and 10% for 20 years if by private industry. From these interest rates and years of operation an overall capital recovery factor can be determined. The taxes and insurance are a percentage of the fixed capital investment. Table 6-1 gives the values used for calculating the direct, indirect, and fixed cost of manufacturing.

Table 6-1

MANUFACTURING COST ANALYSIS

Direct Cost

    Raw Materials

H_2SO_4 66%	$32.30/ton
$CACO_3$	$13.50/ton

    Utilities

Oil	$ 0.10/gal.
Water	$0.25/1000 gal.
Electricity	$0.010/KWHR

    Labor

3 Laborers	$3.00/hr.
Supervisor	$3.50/hr.

Maintenance (Materials & Labor)	5% of F.C.I.
Supplies	13% of Maintenance Material
Fringe Benefits	15% of Labor Cost

Indirect Cost

Payroll Overhead	15% of Total Labor Cost
Laboratory	15% of Total Labor Cost
Plant Overhead	50% of Total Labor

Fixed Charges

    Capital Investment

Municipal	4%, 20 years
Private	10%, 20 years
Taxes	2% of FCI
Insurance	1% of FCI

In addition to these operating costs there will be the cost of disposing of unhydrolyzed waste from the plant and possible credit for disposing of the original waste. The charge for disposing of plant waste will be lower than that associated with raw refuse disposal since it is compact and already separated. For calculation purposes, it will be assumed to cost $3.00; approximately the lower limit of incineration cost. A dumping fee of $4.00 was used to demonstrate the effect of waste disposal credit on the total manufacturing cost. As stated earlier, the dumping fee is the charge for waste disposal assigned to the municipality by the plant. It can vary from zero to a value which is just under the cost of the next best means of disposal.

6.3 Manufacturing Cost Analysis

The operational plant variables such as temperature, acid concentration, liquid to solid ratio, and recycle ratio, must be set such that the sugar manufacturing cost is minimized. The reaction temperature and acid concentration effect on sugar cost are independent of the recycle ratio but not the liquid to solid ratio. If a lower liquid to solid ratio is used, then an increase in acid concentration will not increase the total acid cost as appreciably as it would at a higher ratio. It is not possible to determine what the lowest feasible liquid to solid ratio is without data from a flow reactor experimental apparatus. It has been shown by Saeman et al[26] that values as low as 3 to 1 produce consistent hydrolysis yields. The hydrolysis plant relies on thorough mixing of the pre-pulped cellulosic material and acid solution prior to passage through the flow reactor. Due to such consideration, a middle range value of 10 to 1 was

chosen for the liquid to solid ratio. A study of the acid
concentration and temperature effects on the operating cost was
conducted for a hypothetical 250 ton plant with 40 and (0%
paper contents. The cellulose content of paper (amorphous and
crystalline) was set at 80%. The expected sugar yields were
taken from the experimental analysis section of this report.

A study of the sugar manufacturing price was performed for
ranges of temperature from 220 - 240°C and acid concentrations
of 0.2 to 1%. It is believed that extrapolating yields for
acid concentrations outside of this range would not be possible.
Not enough information concerning the exact effect of the acid
catalysis on yield is known to allow this. Above 240°C the
reaction residence time is below 10 seconds. Such short resi-
dence times give little margin for process control and it would
be unrealistic to consider such conditions for plant operation.
The manufacturing costs for the conditions considered are pre-
sented in Table 6-2. These costs range from 8.5 to 2.7¢/lb.
The costs with a dumping fee credit of $4.00 range from 7.3 to
2 cents/lb. The lowest cost occurs at a 1% acid concentration
and a 230°C reaction temperature.

The optimum recycle rate for these, 230°C, 1% and 60% paper,
was found to be a 0.4 ratio of inerts to cellulose in the reactor.
A range of 0.3 to 1 was studied and minimum cost occurred at 0.4.
The optimum recycle setting varies with reaction conditions,
yield, L/S ratio, and plant capacity. It would therefore be
impossible to set a value which would be optimal for any given
hydrolysis plant.

Table 6-2

EFFECT OF ACID CONCENTRATION AND TEMPERATURE ON MANUFACTURING COST

COST ¢ lb.

% Paper	Acid Concentration	Temperature °C		
		220°	230°	240°
40	.2	8.5¢	7.4¢	6.2¢
60	.2	6.0	5.4	4.4
40	.5	5.0	4.7	4.3
60	.5	3.7	3.2	2.8
40	1.	4.8	4.2	*
60	1.	3.3	2.7	*

*Not feasible (reaction time too short)

The effect of overall plant capacity on the manufacturing cost of sugar was studied for various refuse compositions. Table 1-2 demonstrated that a wide range of municipal refuse compositions can be expected. Three different refuse compositions: 40% paper, 30% garbage, 30% separables; 50% paper, 17% garbage, 33% separables; 60% paper, 15% garbage, 25% separables, all with paper containing 75% cellulose, were used to determine the manufacturing cost/lb. sugar. In this manner the expected cost can easily be determined for the various types of communities. A basis of 5 lb. of refuse per capita per day was used in calculating population from total plant capacity. Figure 6-2 presents this calculation and Figure 6-3 shows the approximate fixed capital investment for such plants. Operational variables used in these calculations were 230°C, 1% acid, and a 10 to 1 liquid to solid ratio. Although the recycle ratio was not optimized for each plant size, it was held in a suboptimum range. In this range the recycle ratio had little effect on total cost and was close to the actual optimum value.

Figure 6-2 also shows the range of sugar cost which would result from using blackstrap molasses as a raw material for a fermentation process. Blackstrap molasses is the waste syrup from a sugar cane crystallization process. It is the most widely used fermentation raw material and therefore would be the most competitive sugar containing raw material. Blackstrap molasses contains approximately 55% sugar by weight including sucrose, glucose, and fructose. Since this molasses is an agricultural commodity, its selling price fluctuates a great

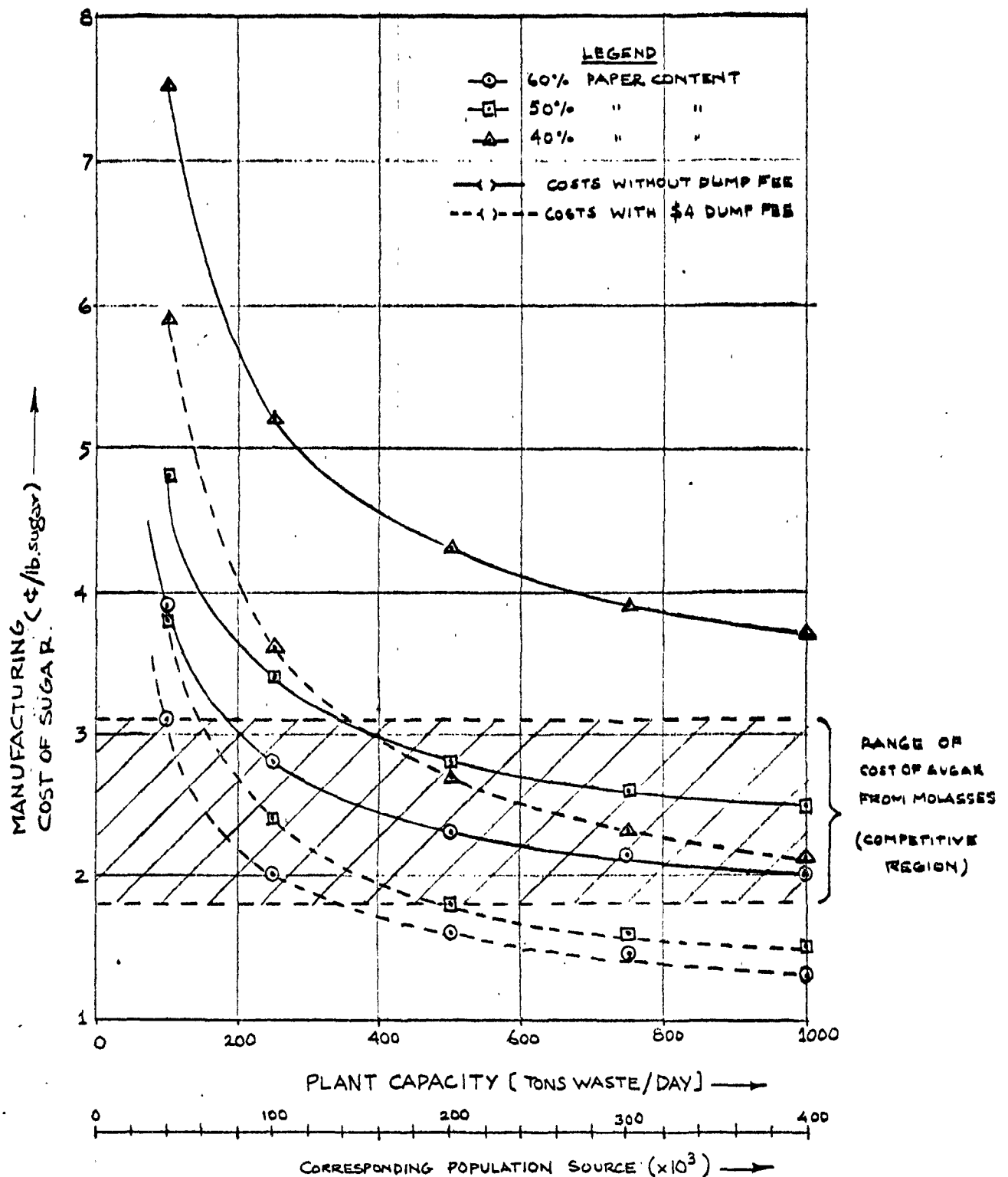## Figure 6-2

SUGAR COST versus PLANT CAPACITY

Figure 6-3

CAPITAL COST versus PLANT CAPACITY
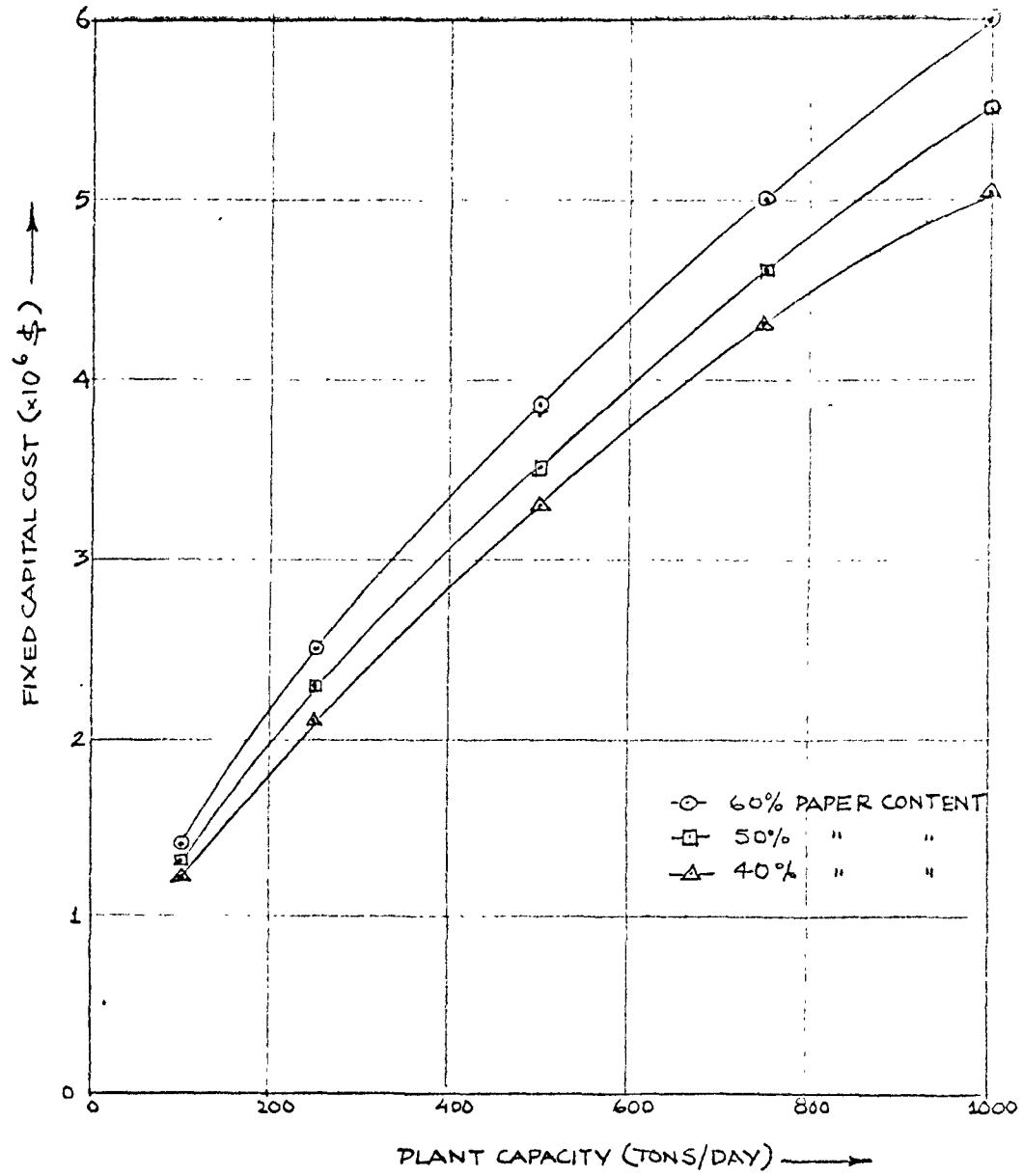
deal. The Commodity Year 1968 Book[27] gives the selling price for molasses up to February 1968, and the ranges for 1966, 1967, and 1968 are 11 to 12, 17 to 18.75, and 17 cents/gallon. This fluctuation in selling price greatly affects the ability of a process to produce a fermentation product at a constant market price, which is one of the main reasons for the switch from fermentation to synthetic production of many products. Hydrolysis of refuse would produce sugar at a more constant cost and over the years the actual production price should decrease, since the trend is toward a higher level of refuse paper composition. The main advantage of using molasses is its high sugar concentration which allows it to be used for any fermentation process, with economical shipment of the raw material over long distances.

Plants which operate at cost below that of molasses can be considered as producing a saleable raw material. It is noticed that in some cases it would be necessary to charge a credit for the refuse processed to operate in a competitive range. In the case of a municipality this would require absorbing some of the cost of production. If the necessary charges are below the existing cost of waste disposal, then it would be of an economic advantage to build a hydrolysis plant. If the plant is owned by a private industry then it would require that the plant charge the community a set cost for disposing of its refuse.

The quoted prices given in the graph are for a capital return factor based on 4% interest for 20 years. If owned privately, a factor of 10% for 20 years would have to be used. With this value the cost per pound increases approximately 0.2 cents/lb. Another factor which is not shown in this graph

is the liquid to solid ratio effect. A 10 to 1 ratio was used
for the calculations but this is not necessarily the lowest
possible ratio. It was found for a 500 ton plant opera:ing
with 50% paper that, at a 7 to 1 ratio, the manufacturing price
drops from 2.8 cents/lb. to 2 cents per lb., and correspondingly
an increase to 13 to 1 increases the cost to 3.4 cents/lb. This
points out the dramatic effect the liquid to solid ratio has on
overall production cost.

For the conditions used, it is therefore shown that the
following plants could produce a 12% aldohexose solution which
would be competitive with molasses on a cost/lb. sugar basis:
a 40% paper composition would reach the competitive range at
400 tons with a dumping charge; a 50% paper composition would
be competitive at the 400 ton level without a dumping charge
and at the 200 ton capacity with a dumping charge; a 60%
paper composition would be competitive at the 200 ton level
with no dumping fee and the 100 ton level with a dumping fee.
The minimum expected costs at 1000 tons capacity, 60% paper,
with and without a dumping credit, are 2 and 1.3 cents/lb.
respectively. These values are well below the average cost
associated with molasses of $\approx$2.5 cents/lb. of sugar.

The lowest predicted disposal price for the most economical
incineration process is approximately $3.00/ton, presently
$\approx$$4.00/ton. Although sanitary landfill can undercut this cost
in some areas, there are many cities which have no available
close land sites which enable them to even approach $3.00/ton.
In such municipalities, with refuse paper contents greater than
50%, refuse hydrolysis would be a means to cut disposal cost and
produce sugar at a competitive market price with molasses.

6.4 The Marketability of a Glucose Solution

It is assumed that the sugars produced by the hydrolysis are fermentable. This seems to be a valid assumption since the aldohexose sugars of glucose and mannose, which are produced, are the same sugars used in most fermentation processes. It has also been proven by Saeman et al[28] that these same sugars obtained by wood hydrolysis are fermentable. In some cases contamination of the fermentation product occurs, such as by the SO_2 in spent sulfite liquors. Such difficulties are not foreseen with the hydrolysis plant product which, in addition to being free of such inorganics as SO_2, should be free of micro organism contamination due to the high temperatures of the reaction.

The total U.S. consumption of blackstrap molasses in 1967 was 700 million gallons. Approximately 300 million gallons were used in the industrial production of drugs, citric acid, vinegar, and ethanol. This indicates that approximately one million tons of such sugars were consumed in processes which could equally as well use the product of a hydrolysis plant. This does not necessarily mean that a greater market is not available for the raw sugar solution produced by hydrolysis, since at a lower price than molasses, this product may reopen the markets that have since been closed by synthetic processes. The main draw-back to producing sugar solutions by hydrolysis is the low concentrations produced. That is, at concentrations of 10 to 15% (molasses is approximately 55%) the cost of shipment to distant areas may preclude its ability to compete with molasses prices. Consideration must therefore be given to building a

plant, which uses the hydrolysis plant product as a raw material, in conjunction with the hydrolysis plant. The construction of a fully integrated source and consumption plant has t1e advantage of cutting the overall cost of production for both the raw sugar and the final product of ethanol, citric acid, etc. The construction of such a plant with the final product of ethanol was suggested by Porteous.

Ethanol or ethyl alcohol was originally totally produced by fermentation of molasses, but as of 1954, synthetic processes using ethylene hydrolysis and hydration began to replace fermentation. Presently the only large fermentation plant in existence is operated by Publicker Industries, Philadelphia, Pa. This change of processes was due to the variable price of black-strap molasses and the low price of ethylene. Of the possible products which can be produced by fermentation, ethanol has the largest available market; approximately 520 million gallons were produced in 1963. As of June 16, 1969, ethanol was selling at $0.52/gallon. There are a myriad of uses for ethanol as both a raw material and as a solvent. If the selling price were reduced, there would most likely be a much larger demand for ethanol.

Browning[8] states that sugar must be produced at approximately one-third the cost of ethylene before fermentation would be competitive with synthetic ethanol production. This applies to the production of ethanol by private industry where a margin of profit is expected. Using the current selling prices of ethylene, 3.25¢/lb., this requires that sugar be produced at 1.08¢. Even with a dumping fee of $4.00, the lowest predicted

sugar cost is 1.3¢. This stringent requirement indicates that
it would be very difficult to persuade a private concern to
build and operate an ethanol producing refuse disposal plant
under the present cost considerations. It should be kept in
mind that these costs are based on the current knowledge of
the system, and that a decrease in cost could result if it were
found that a flow reactor could operate at a lower liquid to
solid ratio. It is believed that if a municipality were will-
ing to build and operate an ethanol plant, it could dispose of
its refuse without charge. Since such a plant would not have
to operate at a profit, its sole manufacturing criterion would
be to produce ethanol at the break-even point. This would re-
quire that the municipality enter the chemical sales field but
this factor should not dissuade the municipality from such an
advantageous means of refuse disposal.

An estimate of the ethanol manufacturing cost can be ob-
tained by a cost analysis performed on the raw material required
for 1000 gallons of ethanol[29], and an updated investment cost
per unit of capacity. The cost associated with the sulfuric
acid used to adjust the pH is excluded, since the pH can be
fixed by the degree of neutralization in the hydrolysis plant.
Since ethanol production by fermentation is a dying art, the
latest capital cost per year capacity was $78 in 1950. This
value is presumably high, since in most cases[30] the actual
cost increase over such a long period of time is below that
indicated by cost indexing methods. This smaller increase is
primarily due to the technological advancements in the manufac-
ture of process equipment and materials. A value of $100/ton

year would be considered more realistic. Using this value,
the indirect and direct cost of manufacturing are calculated
on a percentage basis as indicated in Section 6.1. Table 6-3
contains the ethanol by fermentation cost estimation.

The manufacturing price of ethanol is calculated as
$0.52/gallon. This result implies that ethanol could be pro-
duced at a value equal to the existing selling price. There-
fore for a 500 ton plant with 50% paper, ethanol production
would be an economical use for the refuse produced sugars. It
is also seen from these results why private industry would not
be willing to enter the hydrolysis-ethanol industry with the
predicted sugar cost. The overall capital cost for a 500 ton
hydrolysis plant and a 5.4 million gallons ethanol plant would
be 5.2 million dollars. The expected profit before taxes with
a $4.00 disposal charge would be 8.4 hundred thousand dollars,
which is only a 16% return on the original investment. The
fixed manufacturing cost included a capital recovery factor
which calculated both the yearly cost necessary to recover the
original capital investment and an interest charge of 4% per
year; therefore all calculated percentage returns on investment
are in addition to this 4% charge. Vilbrandt and Dryden[23]
indicate that a 45% return is expected before taxes on a high
risk venture such as this. An alternative would be the construc-
tion of only the ethanol plant by the chemical company, which
results in a return of 49%, since the capital investment does
not include the municipal built hydrolysis plant. This return
would require the municipality to absorb the necessary dumping
fee charge. It has been pointed out that a break-even point
with no dumping fee could be obtained by total plant operation
by the city. Therefore, construction of the total plant by the
community would be the most logical decision.

Table 6-3

ETHANOL PRODUCTION BY FERMENTATION

COST ANALYSIS

FERMENTATION PLANT (5.4 million gal/year) $1.7 million

RAW MATERIALS (excluding sugar)

$(NH_4)_2SO_4$	225 lbs.	$ 2.85
Steam	750,000 lbs.	37.50
Process Water	150,000 gals.	15.00
Cooling Water	630,000 gals.	31.50
Electricity	1600 KWHR	16.00
		$102.85

LABOR

2 Laborers	$144.00
1 Supervisor	84.00
	$228.00

MAINTENANCE (Material & Labor)	$235.00
SUPPLIES	26.00
FRINGE BENEFITS	34.00
PAYROLL OVERHEAD	34.00
LABORATORY	34.00
PLANT OVERHEAD	114.00

FIXED CHARGES

Capital Return 4%, 20 years	$350.00
Taxes	98.00
Insurance	47.00
	$495.00

MANUFACTURING PRICE, NOT INCLUDING SUGAR $1302.85/DAY

COST GAL., NOT INCLUDING SUGAR $0.087/GAL.

SUGAR COST (Basis 500 ton Refuse, 50% Paper)

15.3 lbs. sugar/gal.	
$0.028/lb, No Dumping	$0.43/gal.
$0.018/lb. at $4.00 dumping	$0.275/gal.

TOTAL MANUFACTURING PRICE

NO DUMPING FEE	$0.518/gal.
WITH $4.00 DUMPING FEE	$0.362/gal.
CURRENT SELLING PRICE	$0.52/gal.

The capital investment for the total process would be 5.2 million dollars. Although this investment is very high, it can be justified by the savings incurred by the zero disposal cost. If the municipality were presently paying $4.)0/ton for disposal, a hypothetical profit of $720,000 would result. This is approximately a 14% return on the investment which is well above any other expected returns for a city run operation. These calculations have been made on an assumption of a 50% paper composition; if the actual plant paper were higher there would be an additional profit due to the ethanol production. The conclusion drawn from this preliminary cost analysis of ethanol production is that such a process must be considered as a possible user of hydrolysis sugars.

Chapter 7 describes other chemicals which may be possible sources of demand for the hydrolysis plant product. With these chemicals, as well as ethanol, a market study must be made to determine whether expanding markets exist for the product. The necessity of such a study is illustrated by the magnitude of ethanol production capable of a 500 ton refuse plant, which could produce approximately 5.5 million gallons per year. Although the existing ethanol demand could absorb the production from a small number of such plants, it could not withstand the impact which would occur if every city of over 200,000 people began producing ethanol.

Although refuse hydrolysis is not a panacea for the refuse disposal problem, it does possess the potential to alleviate the problem in many municipalities. Cities which produce

refuse high in paper content and in large quantities have
various alternatives open to them: 1) own and operate a com-
bination hydrolysis-chemical plant, 2) produce sugar by hy-
drolysis with sales to a local chemical producer, and 3) entice
private industry into establishing a combination plant in the
community. The final decision will be determined by the
ability of the municipality to raise the necessary original
capital investment and the competitive nature of the product.

7. GLUCOSE AS A POTENTIAL RAW MATERIAL

The production of ethanol by glucose fermentation has been outlined in Section 6.4. As stated in that section, glucose can be used in most processes which use molasses as a raw material. Thus if the glucose solution from the hydrolysis process is sold at a lower price than molasses on a cost/lb sugar basis, then it may have potential as a raw material for production of chemicals other than ethanol. Such processes which use molasses are described in the following sections. The pertinent information which must be considered when evaluating such processes are: competitive processes which do not require molasses (synthetic), the existing market, yield of product per lb. of sugar, and the selling price of the product.

It is not known a priori what the effect of producing a given product at a lower price will be on the market demand. It is possible that additional markets or uses will be established, thus increasing the demand for the product. Such information can only be obtained through a thorough market analysis. It is essential that such information be obtained since it would be foolish to attempt to produce a product for an already saturated market.

The following information for the various chemicals is taken from Reference (29). Most market and cost information are for the year 1963.

7.1 Monosodium Glutamate

Monosodium glutamate is a food flavoring produced by the fermentation of glucose with "micrococcus glutamicus". It requires a 15% glucose solution and produces approximately 0.27

pounds of monosodium glutamate per lb. of glucose. The production is on the increase with approximately 31 million pounds being produced in 1963. As of June 16, 1969 its selling price was $0.47/lb. Although synthetic processes are being developed, fermentation was the only economical means as of 1963.

7.2 Citric Acid

Citric acid is produced strictly by fermentation and is primarily used in the beverage industry. A 15 to 20 percent sugar solution is fermented by "aspergillus niger". Approximately 118 million pounds were produced in 1963 and sold at $0.34/lb. One pound of citric acid is produced for approximately two pounds of sugar.

7.3 Butanol

Butanol was originally produced by fermentation of a 5% sugar solution but has since been synthetically produced from acetaldehyde. The yield is 20% by weight of original sugar. Three hundred million pounds were produced in 1963. The present selling price is $0.13/lb. It is used as a solvent and a raw material for butyl acetate, resins, and plasticizers.

7.4 Lactic Acid

Lactic acid is primarily used in the food industry and its market is small -- 5 million pounds/year in 1963. It is produced by fermentation of a 15% glucose solution with an 85% yield, or by the hydrolysis of lactonittrite. The synthetic process was just under development in 1963. Its current selling price if $0.17/lb for a 50% technical grade solution.

7.5 Sorbital and Oxalic Acid

Sorbital and oxalic acid can also be produced from a glucose solution but they require a 50% and 60% solution. Such high

concentrations would require extensive evaporation of the hydrolysis plant sugars. It is therefore unlikely that such products could economically be produced from these sugars.

7.6 Conclusions

Of the above chemicals, monosodium glutamate and citric acid have the greatest potential for economic production with refuse produced sugars. Both can use low sugar concentrations, approximately 15%, which could be economically produced by a refuse hydrolysis plant. In addition, the only available means of producing these chemicals is by fermentation, thus eliminating competition from synthetic processes. The present market, as in the case of all fermentation products, may not be large enough to absorb the added production of many new plants, but this cannot be unequivocally stated without further market research. All such possible uses for sugar must be considered, since the final solution will lie in establishing many such outlets for the refuse sugars.

8. RECOMMENDATIONS FOR FUTURE WORK

Although sufficient experimentation was conducted to establish the economic potential of the process, there is still additional experimentation which must be done on a small scale before a pilot plant can be built. This work includes the study of the effect of metal ions on the hydrolysis reaction, the ability to react a slurry at low liquid to solid ratios, and the fermentability of the sugars produced. This experimentation would lead to a more accurate pilot plant design, thus increasing the probability of successfully producing a product at a marketable cost.

8.1 Metal Ion Effect on Hydrolysis

When metal ions were present, low sugar hydrolysis yields occurred. Such ions were found to interfere with the O-toluidine sugar test resulting in false, low yields. Although it is believed that such ions do not interfere with the actual hydrolysis, this hypothesis has not been proven. An analysis procedure, using ethylene diamine tetra acetic acid to nullify the reactivity of metal ions, is being developed. With such a procedure a sample containing metal ions can be hydrolyzed and analyzed for sugar content with and without addition of the EDTA solution. If the metal ions only affect the sugar test, the hydrolyzed solution containing EDTA should show higher yields than the solution without EDTA. Moreover, if the iron containing hydrolyzed solution treated with EDTA gives yields comparable with hydrolyzed solutions from paper without iron, then this would be positive evidence that metal ions do not interfere with the actual hydrolysis.

Since almost any alloy metals used in constructing the
hydrolysis reactor will corrode to some degree, it is essential
to determine whether metal ions actually affect the hydrolysis
reaction. In addition, if metal ions do not affect the hydrol-
ysis, waste acids could be used as the acid catalysis. Waste
pickling acids from the steel industry, which contain metal
ions, may then be used in the hydrolysis process, thereby
reducing the manufacturing cost of sugar.

8.2 Flow Reactor

It is essential that a model flow reactor system be built.
The enormous effect of the liquid to solid ratio on the manu-
facturing cost has been shown. A flow reactor system must be
tested in order to determine what the minimum feasible liquid
to solid ratio is for both the hydrolysis reaction and the
equipment used. A flow reactor is also needed to produce sugar
in large quantities from actual refuse. This would enable a reason-
able scale of sugar fermentation, and thus determine whether
refuse contains any materials which would contaminate fermen-
tation.

8.3 General Plant Considerations

The main manufacturing cost of the hydrolysis plant is the
oil necessary to heat the slurry to the reaction temperature.
If a system other than evaporation could be used to concentrate
the sugars, a more efficient heat recovery system could be
designed. Reverse osmosis can be used to concentrate sugar
solutions, and future experimentation may prove that it is more
economic than evaporation.

Presently there is no internally proposed method for hy-
drolysis waste disposal. It may prove economic to burn the
residual waste and use the generated heat as an additional

preheat source. Before this can be proposed, it is necessary to determine the BTu potential of the waste. In addition to hydrolysis waste, outlets for scrap metals should be determined and possible uses for $CASO_4$ explored.

8.4 Sugar as a Raw Material

Chapter 7 listed chemicals other than ethanol which can be produced by sugar fermentation. Although the production of ethanol seems to be economically feasible, a cost and market analysis should also be performed on these other chemicals. It may be found that there would be a larger economic advantage in producing some other chemical. If such a feasibility study indicates an existing economic potential for another chemical, then an experimental program based on this chemical should be established.

9. SUMMARY AND CONCLUSIONS

A survey of existing municipal refuse disposal processes showed that high temperature incineration is one of the impo:·tant conventional disposal methods, and the projected disposal cost of such a plant can be around $3/ton. The main component of refuse was found to be paper, 40 to 60%, and, as shown by Porteous, the paper content of refuse is increasing.

Porteous' process for refuse disposal, which utilizes the refuse paper content as a raw material for sugar production by acid hydrolysis, was studied. Experimentation was conducted to determine a kinetic model for paper hydrolysis which was then compared with Saeman's model for wood cellulose hydrolysis. Saeman's predicted $A \xrightarrow{K_1} B \xrightarrow{K_2} C$ irreversible reaction model was found to accurately describe the reaction, but the determined rate constants were found to differ from those predicted by Saeman. Yields, approximately 75% of those predicted by Porteous with Saeman's kinetics, were obtained.

A hydrolysis plant design, using the experimentally determined kinetics, was proposed. Modifications of Porteous' original design included, a hydropulper separation and pretreatment system adopted for use from those used in the waste paper pulping industry, a recycle stream for the continuous flow reactor system, and a multi-effect evaporation system for concentrating the sugar solution.

A generalized computer program with variable refuse tonnage, refuse composition, and operating conditions, was

used to size the individual plant components and calculate the total plant and manufacturing cost. A 1% acid solution and a 230°C reaction temperature, yielding 51% cellulose-sugar conversion, were found to be the most economical hydrolysis conditions. The manufacturing cost of a 12% sugar solution for various refuse compositions and plant capacities was calculated and compared to the market price of molasses sugars on a cost/lb. sugar basis. This comparison showed that under the proposed operating conditions cities with populations greater than 200,000 with refuse containing 50% paper, and 100,000 people with refuse containing 60% paper, could produce sugar by acid hydrolysis at a cost comparable to the existing market price of molasses and at a zero refuse disposal cost to the city. Moreover, a preliminary economic study showed that ethanol could be economically produced by fermentation of the sugars. Other potential uses for the sugar solutions include the production of monosodium glutamate and citric acid.

Porteous' economic study indicated that a 250 ton refuse hydrolysis and ethanol fermentation plant could make $4.00/ton profit with refuse containing 60% paper, and $0.77/ton profit with refuse containing 40% paper. Although this study showed that the hydrolysis process was not as economically attractive as originally conceived, it still indicated that this method of refuse disposal could eliminate the refuse disposal cost for many U.S. cities.

Before the final step of establishing a pilot plant is taken, it was recommended that a small scale flow reactor be built. Such a reactor would be able to confirm the predicted isothermal yields and produce sugars in large enough quantities for fermentation experimentation.

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Appendix I

QUANTITATIVE SACCHARIFICATION

Quantitative saccharification is an analytical technique which hydrolyzes cellulose to glucose with a minimum amount of glucose decomposition. Reference (9) from which the procedure was taken, indicates that chemical yields of greater than 95% can be achieved.

Procedure:

A ground cellulosic sample of 0.35 grams is weighed and mixed with 5 ml. of 72% sulfuric acid that has been cooled to 15°C. This mixture is placed in a water bath at 30°C. This temperature is maintained for 45 minutes and during this time the sample is stirred at 5 to 10 minute intervals. After the required time, the mixture is diluted in an Erlenmeyer flash with 140 ml. of water. The diluted solution is autoclaved for one hour at 15 psi. This yield will be the maximum potential aldohexose yield of the sample $\frac{\text{weight aldohexose}}{\text{weight sample}} \times 100$. For a pure cellulose sample the potential glucose yield should be 111.1%.

Appendix II

SUGAR TEST
(EXPERIMENTAL WORK BY WILLIAM ELLSWORTH, SENIOR CHEMIST)

Two methods of measuring the sugar content of the hydrolysis product were compared: spectrophotometry and ferricyanide oxidation. The latter test measures the total reducing power of the solution including partially decomposed sugars. The first technique measures only the aldohexose sugars which are the sugars of interest since they are fermentable. All glucose yields found in this report have been obtained by use of the O-toluidine colorimetric test.

It was found that metal ions cause a false reading to occur with the colorimetric test, but that decomposed sugars have no effect on the test results. A summary of the test procedures and the experimental study done on the O-toluidine test follows.

A. Spectrophotometry:

Principle: Aldohexoses react with O-toluidine reagent to form a green colored complex. The solution is then put in a spectrophotometer. The color follows Beers Law, i.e. color is proportional to concentration of sugar up ro 1000 mg%, where mg% equals number of milligrams per hundred milliliters of solution.

Procedure:

(1) 0.1 ml of sugar solution is mixed with 6 ml of reagent.

(2) Mixture placed for 8 minutes in a boiling water bath, then cooled to room temperature.

(3) Read in spectrophotometer at 630 mu.

(4) % sugar found from calibration curve. Calibration is done using standard glucose solutions.

Reagent: 60 ml O-toluidine + 1.5 ml thiourea. Dilute this to 1000 ml with glacial acetic acid.

References:

This method is a modification of several in the literature:

(1) Nature, Vol. 183, p. 108, 1959

(2) Clin. Chem. Acta, Vol. 7, p. 140, 1962

(3) Clin. Chem. 8, p. 215, 1962

B. Oxidation with Ferricyanide:
I & EC: Analytical Edition, Vol. 9 (1937), p. 228

In this test, sugar is oxidized using ferricyanide. Excess ferricyanide is titrated with ceric sulfate.

Procedure:

(1) 5 ml of sugar solution (not containing more than 3.5 mg sugar) + 5 cc of alkaline ferricyanide. Solution is placed in boiling water bath for 5 minutes, then cooled.

(2) Add 5 ml of 5% H_2SO_4 to above solution. Titrate against 0.01% ceric sulfate using setopaline-C indicator.

Comparison of Results

Method A estimates only the glucose, whereas Method B estimates all kinds of sugars -- pentose, etc.

Comparison of results:

% Sugar (gms sugar/100 grams paper)

	Test A	Test B
Method A	28.81	29.83
Method B	31.55	31.87

C. Analysis of Spectrophotometric Test Reliability

1. Determination of Effect of Ferrous Ion

This test was run by taking a standard glucose solution and adding ferrous sulfate to it to give various concentrations of iron.

Run	Experimental Result	Percent Error
1) Standard Solution	120 mg %	-
2) Solution + 0.01% $FeSO_4$	88	26.6
3) Solution + 0.1% $FeSO_4$	46	61.6
4) Solution + 0.5% $FeSO_4$	44	63.4
5) Solution + 1.0% $FeSO_4$	39	67.5

Ferrous sulfate was chosen because iron makes up about 50% of Carpenter 20 CB3 and is the most reactive metal in it.

The results show that even a very small amount of ferrous ion causes a low reading.

2. Determination of Effect of Carpenter 20 CB3 on Tests.

A 1.6g (1/2" of 1/4" tubing) piece of CB3 plus 20 ml of 0.5% H_2SO_4 was put into the constant temperature bath at 268°C. It was left for 30 minutes and then the 15 ml of it that hadn't boiled out of the glass liner was diluted to 41 ml.

A 102 mg% standard solution was used in this and the rest of the experiments.

Run	Experimental	Expected	Error
1) Standard Solution (SS)	106 mg %	102 mg %	3.9%
2) 2 ml of SS + 2 ml H_2O	49	51	3.9%
3) 2 ml of SS + 2 ml test	42	51	17.6%
4) 5 ml of SS + 2 ml H_2O	72	73	1.4%
5) 5 ml of SS + 2 ml test	69	73	5.5%
6) 10 ml of SS + 2 ml H_2O	85	85	0.0%
7) 10 ml of SS + 2 ml test	79	85	7.1%

A similar test gave almost the same results.

This experiment definitely indicates that, at high temperatures over an extended period of time, the 0.5% H_2SO_4 dissolves enough iron to affect the glucose test. The fact that when the test solution was added to the standard glucose solution the glucose concentration indicated was always lower than when just water was used, is consistent with experiment #1. The fact that the error goes down with increasing dilution of the test solution is also in agreement.

3. Paper Hydrolysis with No Metal Contact to determine the effect of decomposed sugars in the glucose test.

The paper hydrolysis was carried out using 20 ml of 0.5% H_2SO_4 + 0.2g of paper in a glass lined reactor. It was put into the bath at 265°C for 15 minutes, then diluted to 50 ml with H_2O.

Run	Experimental	Expected	Error
1) Hydrolysis product (HP)	51 mg %	-	-
2) 5 ml of HP + 5 ml SS	80	77 mg%	3.9%
3) 5 ml of HP + 10 ml SS	85	84	1.2%
4) 5 ml of HP + 25 ml SS	95	94	1.1%
5) 5 ml of HP + 50 ml SS	93	97	4.1%
6) 5 ml of HP + 75 ml SS	101	99	2.0%
7) 2 ml of HP + 2 ml H_2O	24	25.5	0.6%
8) 2 ml of HP + 5 ml H_2O	13	14.6	1.1%
9) 2 ml of HP + 2 ml SS	79	77	2.6%

These results indicate some error, but it is probably within experimental error. See the next experiment.

4. Test to determine the overall accuracy of the dilution
   method of checking the glucose test.

Run	Experimental	Expected	Error
1) 2 ml of SS + 2 ml H_2O	45 mg %	51 mg %	11.8%
2) 5 ml of SS + 5 ml H_2O	50	51	2.0%
3) 5 ml of SS + 10 ml H_2O	34	34	0.0%
4) SS alone	101	102	1.0%
5) SS alone	106	102	3.9%

See also runs 2, 4, and 6 of experiment #2.

The average percent error of these eight runs is 3.0%.
There is some dilution error in these tests, and also some error
in the glucose determinations.

5. Conclusion

The test is accurate to 3 - 4 percent, and is more consistent
if all the tests are performed simultaneously than if they are
done separately. Care must be taken that no ferrous ion is in
the solution.

From other references it was learned that the amount of time
that the samples are heated is crucial, and that any metal ion
affects the tests.

It has also been determined that allowing the sample to sit
in the test tube with the O-toluidine solution for a short time
before heating it does not affect the test appreciably.

NONISOTHERMAL HYDROLYSIS RESULTS

TEMPERATURE TIME HISTORY AND YIELD

0.2% Acid Runs
0.5 gram Samples
20 ml Liquid

Observations: Base temp. = 100°C.   The body of
table reads temp. in °C.

Run No.-	1	2	3	4	5	6	
Time (Min.)							Temp.
0	100	100	100	100	100	100	
1	120	119	120	122	121	121	
2	138	139	139	143	140	141	
3	153	154	155	157	156	156	
4	167	167	169	171	171	170	
5	179	179	180	183	183	182	
6	183	189	191	195	194	192	
7		200	201	204	204	202	
8		202	209	214	212	210	
9			211	222	220	217	
10					228	224	
11					233	230	
12						235	
13						237	
14							
Yield w/w % paper	1.4	5.9	7.8	8.7	12.8	11.8	
Time Quenched (Min.)	5.4	7.2	8.2	9	11	12.4	

Observation: Temp. to time curve for run was:

$$\theta = A + BT + CT^2 + DT^3 + ET^4$$

A = 99.9254
B = 23.0599
C = -1.78918
D = 0.105227
E = -3.11787 E-3

TEMPERATURE TIME HISTORY & YIELD

0.5% Acid Runs   0.2 gram samples   20 ml of Liquid

Temperature °C

Run No.:	1	2	3	4	5	6	7	8	9	10	11
Time (Min.)											
0	100	100	100	100	100	100	100	100	100	100	100
1	124	122	121	120	122	121	123	121	120	123	122
2	143	139	140	139	140	139	142	139	139	144	143
3	160	155	157	155	157	155	160	155	155	160	155
4	174	168	171	168	171	170	172	170	170	173	169
5	178	180	183	180	182	180	183	183	181	185	182
6		190	193	191	192		192+	193+	191	195	193
7			202	200	201			203	200	203	203
8			210	208	209			210	208	210	211
9				215	216				215	216+	218
10				221	222+				220	223	224
11					229					229	229
12					231						232
13											
Yield w/w Paper	5.06	15.25	23.12	28.87	11.5	6.87	12.5	22.75	24.0	9.5	8.25
Time Quenched	4.6	6.8	8.7	10.2	11.5	4.8	6.8	8.7	10.5	11.5	11.5

Least square curve fit for the above data gave a fourth order polynomial fit as

$$\theta = A + BT + CT^2 + DT^3 + ET^4$$

θ = Temp in °C   T = Time in min.

A = 99.9458
B = 23.6488
C = -1.82949
D = 8.98731E-2
E = -2.06728E-3

Error Sum of Sq. = $1.8E-1$

TEMPERATURE TIME HISTORY & YIELDS

1% Acid Runs
0.5 gram Samples
20 ml of Liquid

Run No.:	1	2	3	4	5	6	7	8.	
Time (Min.)									Temperature °C
0	100	100	100	100	100	100	100	100	
1	118	119	119	119	119	119	119	119	
2	127	137	127	137	137	137	137	137	
3	152	152	153	152	152	152	152	152	
4	165	165	165	165	165	165	165	165	
5	175	177	177	177	177	177	177	177	
6		183	186	187	188	187	188	187	
7			191	197	197	197	197	197	
8				202	203	203	203	204	
9					205	210	210	211	
10						.	219	219	
11							220	224	
13								227	
Yield w/w paper	9.97	11.85	19.70	30.60	31.30	31.56	19.08	3.0	
Time Quenched	4.8	5.6	6.6	7.6	8.2	8.6	10.4	11.6	

Observation: Temp. to time curve for run was:

$$\theta = A + BT + CT^2 + DT^3 + ET^4$$

A = 99.6517
B = 21.3828
C = −1.52206
D = 7.43993E-2
E = −0.001729

COMPUTER PROGRAMS

A. HOOKE-JEEVES SEARCH AND RUNGE-KUTTA NUMERICAL
    INTEGRATION

Used for calculating parameters of Arrhenius' equations
which best fit the data of the non-isothermal analysis.

The Hooke-Jeeves search was originally written for two
dimensions by Steve Smith, Tuck-Thayer, 1967. It was modi-
fied for four dimensions and incorporated with a 4th order
Runge-Kutta integration routine written by Professor Converse,
Thayer School of Engineering. A program flow sheet and
internal program documentation are given to help explain its
operation.

HOOKE JEEVES SEARCH

INPUT
Yields & Times

INITIALIZATION

Set X_i's i=1 to 4 (Arrhenius Parameters)
Set D_i's i=1 to 4 (Step Sizes)
Set L = Search Convergence Criterion

Let $B_i = X_i$

Calculate Sum Sq Error With
$X_i = B_i + D_i$
$X_i = B_i - D_i$
Save Suboptiumum X_i's

To Runge Kutta
Subroutine

Reset B_i ◄── YES ── If $X_i <> B_i$

NO

Decrease D_i's

MINIMUM OF
FUNCTION ◄── YES ── If Sum of D_i's<L ── NO
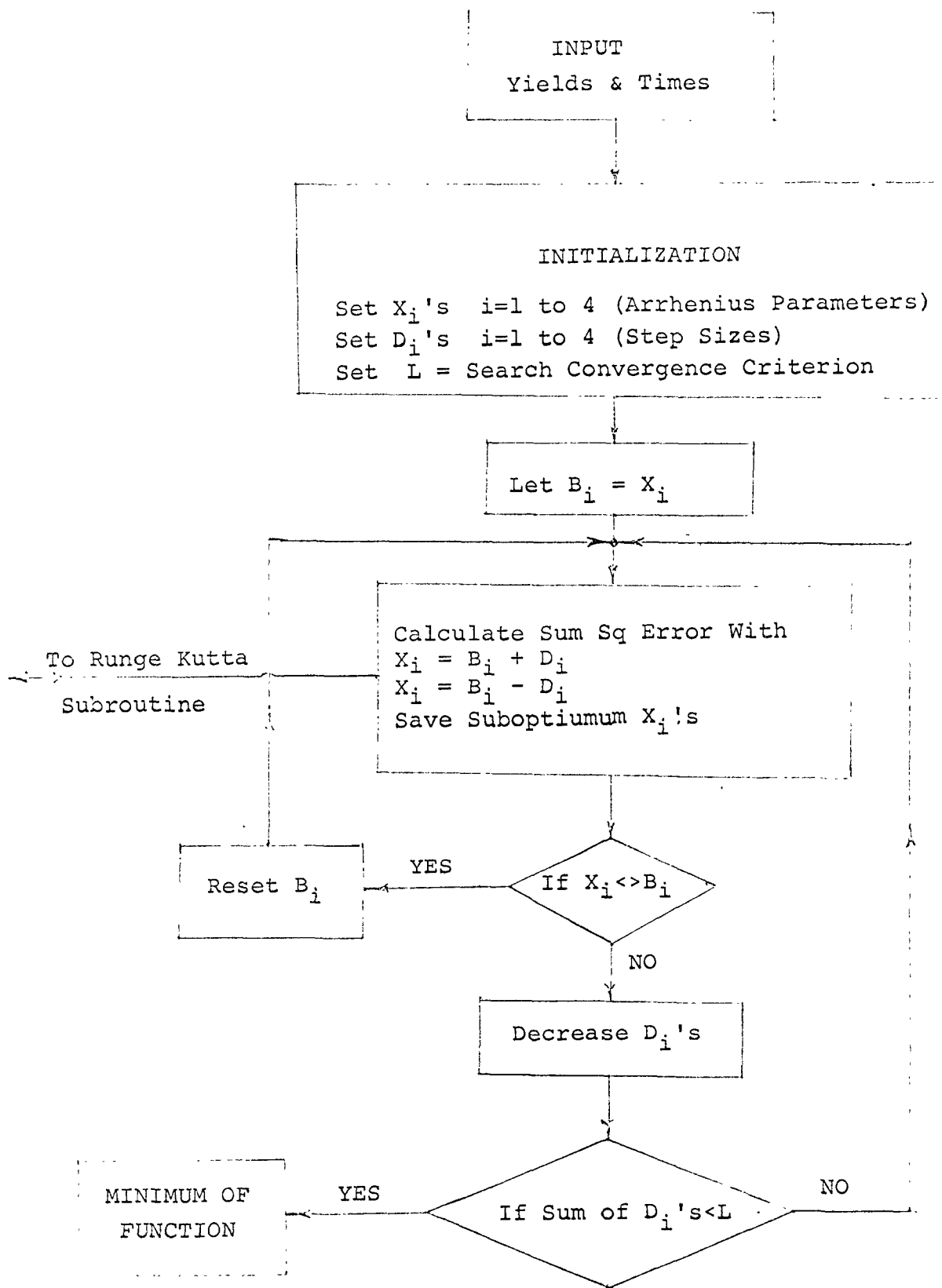
From Hooke-Jeeves Search

```
┌─────────────────────────────────┐
│   RUNGE KUTTA SUBROUTINE        │
└─────────────────────────────────┘
```

```
┌─────────────────────────────────────────┐
│ INITIALIZATION                           │
│ Set X(1)  = Cellulose content            │
│     X(2)  = Sugar content                │
│      t_o  = Time of initial conditions   │
│      t_1  = Time of final conditions     │
└─────────────────────────────────────────┘
```

```
        ┌─────────────────────┐
        │   Fourth Order      │
        │   RUNGE KUTTA       │
        └─────────────────────┘
```

```
┌───────────────────────────────┐
│ EQUATIONS                     │
│ Temp T = f(t)                 │
│     K_1 = g'(X_1, X_2, T)     │
│     K_2 = g''(X_3, X_4, T)    │
│   X(1) = h'(K_1, t)           │
│   X(2) = h''(K_1, K_2, t)     │
└───────────────────────────────┘
```

$$\text{Temp } T = f(t)$$
$$K_1 = g'(X_1, X_2, T)$$
$$K_2 = g''(X_3, X_4, T)$$
$$X(1) = h'(K_1, t)$$
$$X(2) = h''(K_1, K_2, t)$$

NO ◄──── ◇ If $t > t_1$ ◇

YES

```
┌───────────────────────────────┐
│ Calculate:                    │
│ Sum of Squares                │
│ Error of fit                  │
└───────────────────────────────┘
```

To Hooke-Jeeves Search

TAR

```
1 REM This program calculates the 4 parameters of 2 Arrhenius
2 REM equations which best fit the curve of a non-isothermal
3 REM kinetic analysis.
50 PRINT "INPUT NUMBER OF TIME POINTS"
52 INT T9=7
60 PRINT "INPUT TIME(MIN), YIELD(FRACT) "
62 FOR N= 1 TO T9
64 READ T(N),Y(N)
65 NEXT N
66 DATA 5.6,.11,6.6,.1995,7.6,.306,8.2,.313,8.6,.3156
68 DATA 10.2,.1908,11.6,.03
100   REM  THIS PROGRAM DOES A HOOKE-JEEVES PATTERN SEARCH AS
110   '     DESCRIBED IN SECTION 7-08 OF WILDE AND BEIGHTLER,
120   '     "FOUNDATIONS OF OPTIMIZATION," PP. 307-310.  PRESENTLY THE
130   '     PROGRAM IS LIMITED TO FOUR INDEPENDENT VARIBLES,X1,X2,X3,X4
140   '     *****************DATA REQUIRED*****************************
150   '     STATEMENT 250      LET X1= INITIAL VALUE OF 1ST PRE-EXPOTENTIAL
160   '     STATEMENT 260      LET X2= INITIAL VALUE OF 1ST ACT ENERGY
170   '     STATEMENT 270      LET X3=INITIAL VALUE OF 2ND PRE-EXPOTENTIAL
180   '     STATEMENT 280      LET X4= INITIAL VALUE OF 2ND ACT ENERGY
190   '     STATEMENT 290      LET D1 = INITIAL VALUE OF X1 STEP SIZE
200   '     STATEMENT 300      LET D2 = SAME X2
210   '     STATEMENT 310      LET D3 = SAME X3
220   '     STATEMENT 320      LET D4 = SAME X4
230   '     SUB ROUTINE 1490   RUNGE-KUTTA INTEGRATION
240   '     *****************END OF DESCRIPTION*******************
250 LET X1=600000 'ACTUALLY 6E19 SEE LINE 2334
260 LET X2=45000
270 LET X3=24000 'ACTUALLY 2.4E14 SEE LINE 2335
280 LET X4=32800
290 LET D1=1E5' GIVE LARGE SEARCH MARGIN
300 LET D2=1000' KEEP IN FEASIBLE RANGE
310 LET D3=1E4' GIVE LARGE SEARCH MARGIN
320 LET D4=1000' KEEP IN FEASIBLE RANGE
330 LET P1=0
340 LET P2=0
350 LET P3=0
360 LET P4=0
370 DIM P(300,4)
380 LET P(0,1)=X1
390 LET P(0,2)=X2
400 LET P(0,3)=X3
410 LET P(0,4)=X4
420  GO SUB 1490
430  LET F0=F
440   '*********************************************************************
450 FOR I= 1 TO 290
460  GO SUB 1490
470  IF F>F0 THEN 500
480  LET F0=F
```

SEAR   (continued)

```
490   GO TO 540
500   LET P1=X1
510   LET P2=X2
520   LET P3=X3
530   LET P4=X4
540   LET X0 = X1
550   LET X1=X1+D1
560   GO SUB 1490
570   IF F>F0 THEN 600
580   LET F0 = F
590   GO TO 670
600   LET X1=X0
610   LET X1=X1-D1
620   GO SUB 1490
630   IF F> F0 THEN 660
640   LET F0= F
650   GO TO 670
660   LET X1 = X0
670   LET X0=X2
680   LET X2= X2+D2
690   GO SUB 1490
700   IF F> F0 THEN 730
710   LET F0 = F
720   GO TO 800
730   LET X2= X0
740   LET X2= X2-D2
750   GO SUB 1490
760   IF F>F0 THEN 790
770   LET F0=F
780   GO TO 800
790   LET X2= X0
800   LET X0= X3
810   LET X3= X3+D3
820   GO SUB 1490
830   IF F>F0 THEN 860
840   LET F=F0
850   GO TO 930
860   LET X3=X0
870   LET X3= X3-D3
880   GO SUB 1490
890   IF F>F0 THEN 920
900   LET F0= F
910   GO TO 930
920   LET X3= X0
930   LET X0= X4
940   LET X4= X4+D4
950   GO SUB 1490
960   IF F> F0 THEN 990
970   LET F0=F
980   GO TO 1190
```

SF R   (continued)

```
990 LET X4= X0
1000 LET X4= X4-D4
1010 GO SUB 1490
1020 IF F>FO THEN 1050
1030 LET FO=F
1040 GO TO 1190
1050 LET X4=XO
1060 '    ***********END OF ABOVE DESCRIBED ROUTINE***************
1070 '    THE FOLLOWING TWO TESTS DETERMINE IF THE NEW BASE POINT OR
1080 '    ANY OF ITS SURROUNDING PERTURBATIONS ARE BETTER THAN THE LAST
1090 '    BASE POINT.  IF NOT THEN A NEW BASE POINT MUST BE CALCU-
1100 '    LATED USING A SMALLER STEP SIZE.
1110 IF P1<>X1 THEN 1190
1120 IF P2<>X2 THEN 1190
1130 IF P3<> X3 THEN 1190
1140 IF P4<> X4 THEN 1190
1150 LET X1= P(I-1,1)
1160 LET X2= P(I-1,2)
1170 LET X3= P(I-1,3)
1180 LET X4= P(I-1,4)
1190 LET P(I,1)=X1
1200 LET P(I,2)=X2
1210 LET P(I,3)=X3
1220 LET P(I,4)=X4
1230 '    THE FOLLOWING FOUR STATEMENTS CALCULATE AND ASSIGN
1240 '    VALUES TO THE NEW BASE POINT.
1250 FOR J= 1 TO 4
1260 LET P(I+1,J)=2*P(I,J)-P(I-1,J)
1270 NEXT J
1280 LET X1= P(I+1,1)
1290 LET X2= P(I+1,2)
1300 LET X3=P(I+1,3)
1310 LET X4= P(I+1,4)
1320 LET Z9=D1+D2+D3+D4
1321 IF Z9<100 THEN 1430
1330 '    THE NEXT FOUR STATMENTS REDUCE THE STEP SIZE IF THE PRECEEDING
1340 '    SEARCH DID NOT FIND A NEW MINIMUM.
1350 FOR J= 1 TO 4
1360 IF P(I+1,J)<>P(I,J) THEN 1420
1370 NEXT J
1380   LET D1=D1/2
1390   LET D2=D2/2
1400   LET D4= D4/2
1410   LET D3= D3/2
1420   NEXT I
1430   PRINT "MINIMUM OF FUNCTION IS"FO
1440 PRINT "COORDINATES ARE"X1;X2;X3;X4
1450 PRINT " FINAL STEP SIZES ARE"D1;D2;D3;D4
1452 FOR J= 1 TO T9
1453 PRINT SQR(E(J)),Y(J)
```

SEAR   (continued)

```
1454 NEXT J
1460 PRINT
1470 PRINT"IT";I
1480 GOTO 2500
1490 ' THIS IS START OF RUNGE-KUTTA
1491 IF X1<0 THEN 1530' PUT RESTRAINT ON SEARCH VARIABLES
1493 IF X2<0 THEN 1530
1494 IF X3<0 THEN 1530
1495 IF X4<0 THEN 1530
1500 GOTO 1540
1510 REM
1530 LET F=F+100
1531 PRINT"01"
1532 GOTO 2400
1540 REM
1640 LET H=.2' INTEGRATION STEP SIZE IN MINUTES
1700 REM
1840 LET N=2' NUMBER OF EQUATIONS
1845 LET T1=T(T9)+.2
1860 LET X(1)=.8' INITIAL CONDITION ON POTENTIAL SUGAR YIELD
1862 LET X(2)=.1'INITIAL CONDITION ON SUGAR CONTENT
1960 LET T=4.8' TIME OF ABOVE CONDITIONS
1970 GO SUB 2330
1980 FOR J=1 TO N
1990 LET L(1,J)=H*G(J)
2000 LET X(J)=X(J)+L(1,J)/2
2010 NEXT J
2020 LET T = T + H/2
2030 GO SUB 2330
2040 FOR J= 1 TO N
2050 LET L(2,J)=H*G(J)
2060 LET X(J)=X(J)-L(1,J)/2+L(2,J)/2
2070 NEXT J
2080 GO SUB 2330
2090 FOR J= 1 TO N
2100 LET L(3,J)=H*G(J)
2110 LET X(J)=X(J)-L(2,J)/2+L(3,J)
2120 NEXT J
2130 LET T = T + H/2
2140 GO SUB 2330
2150 FOR J= 1 TO N
2160 LET X(J)=X(J)-L(3,J)+(L(1,J)+2*L(2,J)+2*L(3,J)+H*G(J))/6
2170 NEXT J
2310 IF T > T1 THEN 2360 ' END OF INTEGRATION
2311 FOR J=1 TO T9' PICK OUT ERROR OF EACH POINT
2312 IF ABS(T-T(J))>.01 THEN 2317
2313 LET E(J)=(X(2)-Y(J))^2
2314 IF E(J)>500 THEN 2341
2317 NEXT J
2320 GOTO 1970
```

SEAR   (continued)

```
2330' C WILL BE ABSOLUTE TEMP -TIME FUNCTION
2331 LET C=273+99.6517+21.3828*T-1.52206*T^2+7.4399E-2*T^3
2332 LET C=C-1.729E-3*T^4
2333' ARRHENIUS FUNCTIONS FOLLOW
2334 LET K1= X1*1E14*EXP(-X2/(1.98*C))
2336 LET K2= X3*1E10*EXP(-X4/(1.98*C))
2337' CONSTRAINTS ON K1,K2
2338 IF K1>20 THEN 2341
2340 IF K2<20 THEN 2345
2341 LET F=F+10
2342 GOTO 2400
2344 ' DIFFERENTIAL EQUATIONS FOLLOW
2345 LET  G(1)=-K1*X(1)
2346 LET G(2)=-K2*X(2)+K1*X(1)
2350 RETURN
2355' CALCULATE SUM SQUARE ERROR
2360 LET F=0
2370 FOR J= 1 TO T9
2380 LET F=F+E(J)
2381 NEXT J
2382 LET J5=J5+1
2383 IF J5=100 THEN 2395
2384 IF J5=160 THEN 2395
2385 IF J5=200 THEN 2395
2386 IF J5=250 THEN 2395
2387 IF J5=350 THEN 2395
2388 IF TIM>320 THEN 2395
2389 GOTO 2400
2395 PRINT F,X1,X2,X3,X4
2396 FOR J=1 TO T9
2397 PRINT SQR(E(J)),Y(J)
2398 NEXT J
2399 PRINT "I",I
2400 IF J=100 THEN 2402
2401 GOTO 2405
2402 PRINT J
2405 RETURN
2500 END
```

B. HYDROLYSIS PLANT SIMULATION PROGRAM
by R. Fagan

The hydrolysis plant simulation program can be used to calculate the manufacturing cost of sugar for any city with local refuse composition and local operational cost. Internal documentation is given to aid the reader in following the program. The inputs to the system are either external or internal. External inputs are requested by the program at run time, and internal inputs must be changed before run time.

Line Number

External Inputs

230 - 270	Refuse tonnage and composition
270 - 500	Plant operational variables
	A. yield
	B. reactor residence time
	C. acid concentration & temperature
	D. solid to liquid ratio
	E. recycle ratio
3790	Dumping credit
3810	Waste disposal charge
3830	Interest rate and years of operation

Internal Inputs

1820-3010	Equipment cost parameters
3332	Equipment cost update %
3370-1442	Factors for calculating total fixed capital cost from installed equipment cost
3570-3780	Manufacturing raw material cost and indirect manufacturing cost factors

Outputs

850-1590	Material balance
3070-3250	Equipment size and cost
3450-3544	Fixed capital investment
3900-4165	Manufacturing cost analysis

By inserting these variables, an economic feasibility study can easily be performed on any city which might wish to use acid hydrolysis to dispose of its refuse.

```
COST3

100 DIM S(30),P(30),I(30)
110 DIM H(30)
120 DIMT(30)
130 LET A$(1)="CELLULOSE"
140 LET A$(2)="WATER"
150 LET A$(3)="ACID"
160 LET A$(4)=" SUGAR"
170 LET A$(5)="D SUGAR"
180 LET A$(6)="S INERTS"
190 LET A$(7)="L INERTS"
200 LET A$(8)=" LIME"
210 LET A$(9)="SEPARABLES"
220 REM *******MATERIAL BALANCE**************
230 PRINT"INPUT TOTAL TONS WASTE"
240 INPUT S' TOTAL TONS/DAY WASTE
250 let j1=s
260 PRINT "INPUT FRACTION PAPER,GARBAGE,SEPARABLES IN WASTE"
265 INPUT F1,F4,F3
270 PRINT"INPUT FRATION CELLULOSE IN PAPER"
272 INPUT F2
273 LET F5=1-F2
280 PRINT"INPUT TIME TO MAX YIELD IN MIN"
290 INPUT T5
300 PRINT"INPUT CELLULOSE FRACTION CONVERTED AND SUGAR PRODUCED"
310 INPUT Y1,Y2
311 LET Y3=1-Y1
320 PRINT"INPUT FRACT ACID,SOLID TO LIQUID,REACTION TEMP CENT"
330 INPUT C2,C1,T
340 LET C2=C2*100/93'CORRECT FOR 93% ACID
360 LET P= F1*S
370 LET C= F2*P' CELL
380 LET M=F3*S' SEP
390 LET G= F4*S' GAR
400 LET K= F5*P' CLAYS
410 LET S1= S-M' SOLIDS TO REACTOR
420 LET I= .5*( G+K)' TOTAL INERTS TO SYSTEM
430 LET L= S1/C1' TONS/DAY
440 LET X= L-S1' WATER ADDED AFTER HYDRO
450 LET T1= ((L+S1)*T-2*S1*20)/X' REQUIRED TEMP
460 LET A1= C2*L' TONS/DAY ACID
470 REM*************RECYCLE PROBLEM*******************
480 PRINT"INITIAL FRACTION INERTS";I/C
490 PRINT"INPUT I1,INERT RATIO FINAL"
500 INPUT I1
510 LET R4= I1/Y3' RATIO INERTS TO CELL OUT
520 LET B= I/R4' TOTAL CELL BLEED
530 LET R= (B-Y3*C)/(Y3-1)' RECYCLED CELL
540 LET R1= C+R' TOTAL CELL   IN REACTOR
542 REM
543 REM
```

COST3   (continued)

```
550 LET R2= Y3*R1' TOTAL CELL LEFT
560 LET R3= 1.1*Y2*R1' TOTAL WEIGHT SUGAR FORMED
570 LET S3= I+C+R+I1*(C+R)' TOTAL SOLIDS IN REACTOR
580 LET W= S3/C1' TOTAL WATER REQ
590 LET A3= C2*W' TOTAL ACID REQ
600 LET W1=W-L-R-R4*R'ADDITIONAL WATER TO RECYCLE
610 LET F=V9*W+.1*(D+G1)
620 LET A4=A3-A1-A3/(W-F)*(R+R4*R)'ADDED ACID
630 REM G1= GLUCOSE  OUT WITH WATER
640 LET G1= R3-R3/(W-F)*(R2+I1*R1)
650 LET D= (1-Y3-Y2)*R1*1.1' TOTAL DECOMPOSED SUGAR IN WASTE
660 LET D1= D-D/(W-F)*(R2+I1*R1)
670 LET D2= I-I/(W-F)*(R2+I1*R1)
680 LET W4=W-.1*(D+G1)
690 LET W5=W4-V9*W
700 LET T2=((W1+2*(R*R4+R))*T-2*(R*R4+R)*177)/W1
705 LET T2=(T1*X+T2*W1)/W'TEMP OF  IX WATER CENT
710 LET A5=A3-A4-A1' ACID OUT WITH SOLIDS
720 LET S7= Y2*C*1.1' SUGAR PRODUCED IF NO RECYCLE
730 LET W9=W5-R2-R1*I1
740 LET N6= W9+(A3-A5)/98*18' WATER OUT OF NEUT
750 LET N7=N6-(A3-A5)/98*136
760 LET L9=(A3-A5)/98*100'LIME NEEDED
770 LET G2=(A3-A5)/98*136*(G1/(N6+L9))
780 LET G3= G1-G2' SUGAR TONS/DAY OUT OF  PLANT
790 LET E9=B+R4*B+M/2'TONS PER DAY OF SOLID WASTE
800 PRINT"DO YOU WANT MATERIAL FLOW BALANCE YES OR NO"
810 INPUT M$
820 IF M$="NO" THEN 1580
830 PRINT"SEPARATION SYSTEM"
840 PRINT
850 PRINT"SEPARATOR","IN","OUT T/D","IN","OUT T/HR"
860 PRINT "WASTE",S,S-M,S/24,(S-M)/24
870 PRINT A$(2),S/.02,(S-M)/.5,(S)/.02/24,(S-M)/.5/24
880 PRINT
890 PRINT "***************************************************"
900 PRINT
910 PRINT"REACTOR","IN","OUT T/D","IN","OUT T/HR"
920 PRINT A$(1),R1,Y3*R1,R1/24,Y3*R1/24
930 PRINT A$(2),W,W4,W/24,W4/24
940 PRINT A$(3),A3,A3,A3/24,A3/24
950 PRINT A$(4),Z9,R3,Z9,R3/24
960 PRINT A$(5),Z9,D,Z9,D/24
970 PRINT A$(6),I1*R1,I1*R1,I1*R1/24,I1*R1/24
980 PRINT A$(7),I,I,I/24,I/24
990 PRINT
1040 PRINT
1050 PRINT"***************************************************"
1060 PRINT
1070 PRINT"FLASH","IN T/D","OUT T/D","IN T/HR","OUT T/HR"
```

COST3   (continued)

```
1080 PRINT A$(2),W4,W5,W4/24,W5/24
1090 PRINT
1100 PRINT"*****************************************"
1110 PRINT
1120 PRINT "CENTRIFUGE #1","IN","LIQUID OUT","SOLID STREAM","TONS/HR"
1130 PRINT A$(1),R2/24,0,R2/24
1140 PRINT A$(2),W5/24,W9/24,(W5-W9)/24
1150 PRINT A$(3),A3/24,(A3-A5)/24,A5/24
1160 PRINT A$(4),R3/24,G1/24,(R3-G1)/24
1170 PRINT A$(5),D/24,D1/24,(D-D1)/24
1180 PRINT A$(6),I1*R1/24,Z9,I1*R1/24
1190 PRINT A$(7),I/24,D2/24,(I-D2)/24
1200 PRINT"***************BLEED AND RECYCLE*****************"
1210 PRINT "MATERIAL","BLD-T/D","REC-T/D","BLD-T/HR","REC-T/HR"
1220 PRINT A$(1),B,R,B/24,R/24
1230  PRINT A$(6),R4*B,R4*R,R4*B/24,R4*R/24
1240 PRINT A$(2),B+R4*B,R+R4*R,(B+R4*B)/24,(R+R4*R)/24
1250 PRINT A$(3),A5*(B/(R+B)),A5*(R/(R+B)),A5/24*(B/(B+R)),A5/24*(R/(R+B))
1260 PRINT"PLUS SMALL AMOUNTS OF SUGAR  AND LIQUID INERTS"
1270 PRINT
1280 PRINT"*****************************************"
1290 PRINT
1300 PRINT"NEUTRALIZER","IN T/D","OUT T/D","IN T/HR","OUT T/HR"
1310 PRINT A$(2),W9+L9,N6+L9,(W9+L9)/24,(N6+L9)/24
1320 PRINT A$(3),A3-A5,Z9,(A3-A5)/24,Z9
1330 PRINT"CASO4",Z9,(A3-A5)/98*136,Z9,(A3-A5)/98*136/24
1340 PRINT"CO2",Z9,(A3-A5)/98*44,Z9,(A3-A5)/98*44/24
1350 PRINT A$(8),(A3-A5)/98*100,Z9,(A3-A5)/98*100/24
1360 PRINT A$(4),G1,G1,G1/24,G1/24
1370 PRINT A$(5),D1,D1,D1/24,D1/24
1380 PRINT A$(7),D2,D2,D2/24,D2/24
1390 PRINT"*****************************************"
1400 PRINT
1402 LET U7=(N6+L9)/24-(A3-A5)/98*136/24
1404 LET U9=(A3-A5)/98*136/24
1405 LET U8=U9
1406 LET Y9=(A3-A5)/98*136/24'T/HR OF CASO4 PRODUCED
1410 PRINT"CENTRIFUGE 2","IN","LIQ OUT","SOL OUT","TONS/HR"
1420 PRINT A$(2),(N6+L9)/24,U7,Y9
1430 PRINT"CASO4",U9,Z9,U9
1440 PRINT"CO2",(A3-A5)/98*44,0,0
1450 PRINT A$(4),G1/24,G1/24-Y9*(G1/(N6+L9))/24,Y9*(G1/(N6+L9))/24
1460 PRINT A$(5),D1/24,D1/24-Y9*(D1/(N6+L9))/24,Y9*(D1/(N6+L9))/24
1470 PRINT A$(7),D2/24,D2/24-Y9*(D2/(N6+L9))/24,Y9*(D2/(N6+L9))/24
1480 PRINT
1530 PRINT "*****************************************"
1540 PRINT
1550 PRINT"REACT WATER T/HR AT TEMP"
1560 PRINT (X+W1)/24;"T/HR",T2;"DEG CENT";(T2-100)*9/5+212;"DEG F"
1580 LET S4= (S3/24+S3/C1/24)*2000*1/70' FT^3 HR IN REACTOR
```

COST3   (continued)

```
1590 LET E1= G3/24
1600 REM*************EQUIPMENT PARAMETERS*******************
1610 LET F1= W*2000/24/62.4'FT^3/HR OF FLOW TO FLASH
1620 LET F2= F1/.134' GAL/HR TO FLASH
1630 LET S5= S4/.134' GAL/HR THROUGH REACTOR
1640 LET C5= (S3-I)/24' TONS SOLID/HR TO 1ST CENT
1650 LET C6= W5/24*1000*2/70'FT^3/HR TO CENT OF WATER
1660 LET N1=W9*2000/24/62.4'FT^/HR TO CENT1
1670 LET N2= N1/.134' GAL/HR TO CENT 2
1680 LET N3= (A3-A5)/98*100/24' TONS/HR OF LIME TO CENT
1690 LET N8= N7*2000/63/24' FT^3 /HR TO EVAP
1700 LET N9=N8/.134'GAL/MIN
1710 LET S3= S1
1720 LET P1= S3/.02*1000*2/24/62.4' FT^3 TO PUMP 1 TO PULPER
1730 LET E2= E1/(N7*2000/24)' FRACTION SUGAR IN LIQUID
1740 LET P2= W1*2000/62.4/24'FT^3/HR TO 1ST MIX
1750 LET P3= L*2000/62.4/24' FT^3/HR TO FRESH REFUSE
1760 LET P4=(A1+A4)*2000/24/(62.4*1.8)'FT^3/HR OF ACID
1770 LET P5= (S3/.02-S3/.5)*1000*2/24/62.4'FT^3/HR PULP RECYCLE
1780 LET P6= P1-P5' FRESH WATER TO PULPER
1790 LET H1= P2+P3' THROUGH HEATER AND COND
1800PRINT
1810 PRINT
1820 REM*************EQUIPMENT COST*****************
1830 REM STORAGE HOPPER 3 DAY CAPACITY
1840 REM ASSUME REFUSE IS 500 LB/YD^3
1850 LET S(1)= 3*S*2000/500*9'FT^3
1860 LET P(1)=S(1)^.9
1870 LET I(1)=1.1*P(1)
1880 REM CONVEYOR 18 INCH PULLEY MAGNETIC TYPE
1890 LET S(2)=100'FT
1900 LET P(2)= S(2)^.65*450*S/250+1000
1910 LET I(2)= P(2)*1.62
1920 LET H(2)=1
1930 REM SEPARATION HYDROPULPER SYSTEM
1940 REM
1950 LET S(3)= S1'TONS/DAY
1960 LET P(3)=(S(3)/80)^.6*8E4
1970 LET I(3)= P(3)*1.6
1980 LET H(3)=20*S/24
1990 REM REACTOR COST
2000 REM VERTICAL TUBULAR REEACTOR MADE OF CARPENTER 20 STEEL
2010 REM AND DESIGNED FOR A 500 PSIA PRESSURE
2020 LET S(4)= S4*T5/60'TOTAL VOLUME OF REACTORR IN FT^3
2030 LET E(4)= (S(4)/62.8)^.65*2500
2040 LET C(4)= (S(4)/62.8)^.65*2500*3*1.45-E(4)
2050 LET P(4)= C(4)+E(4)
2060 LET I(4)= E(4)*3.03+C(4)
2070 REM  H2SO4 STORAGE
2080 REM 10 DAY SUPPLY OF ACID
```

COST3   (continued)

```
2090 LET S(5)=(A1+A4)*10*2000/(1.83*62.4)*74.8'GAL
2100 LET P(5)=(S5/1E5)^.63*15000
2110 LET I(5)=P(5)*1.85
2120 REM FLASH CHAMBER 2 MIN RESIDENCE TIME
2130 LET S(6)= F1/60*2'FT^2
2140 LET P(6)= (S(6)/62.8)^.65* 2500
2150 LET C(6)= P(6)* 1.05*3-P(6)
2160 LET I(6)= P(6)* 2+C(6)
2170 LET P(6)= C(6)+P(6)
2180 REM CENTRIFUGE  ONE
2190 LET S(7)= C6/(.134*60)' GAL MIN OF WATER TO CENT
2195 IF S(7)>350 THEN 2220
2200 LET P(7)= (S(7)/350)^.6*9E4
2210 LET I(7)= P(7)* 1.6
2211 LET X7=1
2212 LET H(7)=S(7)
2213 GOTO 2230
2220 REM
2222 LET P(7)=9E4+((S(7)-350)/350)^.6*9E4
2223 LET I(7)=P(7)*1.6
2224 LET X7=2
2225 LET H(7)=S(7)
2230 REM CONTINUOS FLOW NEUTRALIZER
2250 REM IN LINE MIXER
2260 REM DESIGN 150 PSI
2270 LET S(8)=N1/.134/60'GAL/MIN
2280 LET P(8)=(S(8)/500)^.6*5000
2300 LET I(8)=P(8)*1.6
2305 LET H(8)=S(8)/500*5
2310  REM LIME STORAGE
2370 LET S(9)=(A3-A5)*100/98*2000*10/85'FT^3 FOR 10 DAYS
2330 LET P(9)=S(9)^.9
2340 LET I(9)=1.1*P(9)
2350 REM CENTRIFUGE 2
2360 LET S(10)= N2/60' GAL MIN
2370 LET P(10)=(S(10)/375)^.6*2E4
2380 LET I(10)= P(10)* 1.6
2390 LET H(10)=(S(10)/375)*100'H.P.
2400 REM AUX DIRECT FIRED HEATER
2410 GOSUB 4170
2411 LET K5=(K4-212)*5/9+100
2420 REM T2&T1
2422 PRINT"TEMP TO HEATER DEG F AND C",K4,K5
2423 PRINT
2425 PRINT"EVAPORATORS"
2426 PRINT"STEAM FROM FLASH USED";W(1,1)/2000;"TONS/HR"
2427 PRINT"EFFECT","VAPOR","TONS/HR"
2428 FOR J=2 TO 7
2429 PRINT J-1,W(J,1)/2000
2430 NEXT J
```

COST3   (continued)

```
2431 LET  S(11)=(X+W1)*(T2-K5)*9/5*2000/24'BTU/HR
2440 LET  P(11)= (S(11)/5E6)^.85*20000
2450 LET  I(11)= P(11)*1.63
2460 REM  OIL AND OIL STORAGE BASED ON  1.5E5 BTU/GAL
2470 LET  O=(S(11)/1.5E5/.85)'GAL/HR AT 85 % EFF
2480 LET  O1= O*24' GAL/DAY
2490 LET  S(12)= O1*10' GAL FOR 10 DAYS
2500 IF S(12)>4E4 THEN 2540
2510 LET  P(12)= (S(12)/1E4)^.30*1600
2520LET  I(12)= P(12)* 1.4
2530 GOTO 2560
2540 LET  P(12)= (S(12)/3E5)^.63*3E4
2550 LET  I(12)= P(12)* 1.85
2560 REM  ******PUMPS*******
2570 REM  ** FRESH WATER TO PULPER
2580 REM  OUT PSI= 60
2590 LET  S(13)= P6' FT^3/HR TO PULPER
2600 LET  H(13)= 60* S(13)*7.27E-5
2610 LET  P(13)= (S(13)/.134/60*60/1000)^.52*600
2620 LET   H(13)= H(13)/.8
2630 LET  I(13)= P(13)*2.41
2640 REM    PULPER RECYCLE PUMP
2650 LET  S(14)= P5
2660 LET  P(14)= (S(14)/.134/60*60/1000)^.52*600
2670 LET  H(14)= 60*S(14)*7.27E-5
2680 LET  I(14)= P(14)*2.41
2690 LET  H(14)= H(14)/.8
2700 REM  MOYNO SCREW PUMP FROM PULPER  TO REACTOR
2710 LET  S(15)= (S1+2*S1)*2000/24/62.4'FT^3/HR
2720 LET  H(15)= 400*S(15)*7.27E-5
2730 LET  P(15)= (S(15)/.134/60*400/1000)^.52*600
2740 LET  H(15)= H(15)/.8
2750 LET  I(15)= P(15)*2.41
2760 REM  H2S04 FEED PUMP
2770 REM  CONTROLLED VOLUME PUMP
2780 LET  S(16)= P4
2790 LET  H(16)= 500* S(16)*7.27E-5
2800 LET  P(16)=(S(16)/.134/60*500/1000)^.7*1200
2810 LET  H(16)= H(16)/.8
2820 LET  I(16)= P(16)*2.41
2830 REM  REACTOR MOYNO RECYCLE PUMP
2840 LET  S(17)= (W1+R+R4*R)/62.4*2000/24
2850 LET  H(17)= S(17)*500*7.27E-5
2860 LET  P(17)= (S(17)/.134/60*200/1000)^.52*600
2870 LET  I(17)= P(17)*2.41
2880 REM  FEED WATER TO HEATER PUMP
2890 LET  S(18)=(P+W(1,1))/62.4'FT^3/HR
2900 LET  H(18)=S(18)*400*7.27E-5/.8
2910 LET  P(18)=(S(18)/.134/60*400/1000)^.52*600
2920 LET  I(18)= P(18)*2.41
```

COST3   (continued)

```
2930 REM MOYNO SCREW FOR LIMEE
2940 LET S(19)= 2*N3/85*2000
2950 LET H(19)= S(19)*100/.8*7.27E-5
2960 LET P(19)=(S(19)/.134/60*100/1000)^.52*600
2970 LET I(19)= P(19)*2.41
2980 REM 6 STAGE EVAPORATION SYSTEM
2982 LET P(20)=S(20)^.53*1200*6
2983 LET I(20)=P(20)*1.9
2990 REM CONDENSER
2993 LET P(21)=(S(21)/1000)^.65*9000
2995 LET I(21)=P(21)*2.34
3000 LET P(22)=(S(22)/62.8)^.65*2500
3010 LET I(22)=P(22)*2
3015 PRINT
3016 PRINT
3017 PRINT"DO YOU WANT EQUIPMENT SIZE AND COST YES OR NO"
3018 INPUT Y$
3019 IF Y$="NO" THEN 3290
3070 PRINT"*********COST ANALYSIS*****************"
3080 PRINT"EQUIPMENT","SIZE","    ","P COST","IN COST "
3090 PRINT"HOPPER",S(1),"FT^3",P(1),I(1)
3100 PRINT"CONVEYOR",S(2),"FT",P(2),I(2)
3110 PRINT"HYDROPULP",S,"TONS/DAY",P(3),I(3)
3120 PRINT"REACTOR",S(4),"FT^3",P(4),I(4)
3130 PRINT"ACID STORAGE",S(5),"GAL",P(5),I(5)
3140 PRINT"FLASH CHAM",S(6),"FT^3",P(6),I(6)
3150 PRINT"CENT";X7,S(7),"GAL/MIN",P(7),I(7)
3160 PRINT"NEUT",S(8),"GAL/MIN",P(8),I(8)
3170 PRINT"LIME ST",S(9),"FT^3",P(9),I(9)
3180 PRINT"CENT 1",S(10),"GAL/MIN",P(10),I(10)
3190 PRINT"HEATER",S(11),"BTU/HR",P(11),I(11)
3200 PRINT"OIL ST",S(12),"GAL",P(12),I(12)
3210 PRINT"EVAP",S(20),"FT^2",P(20),I(20)
3220 PRINT"COND",S(21),"FT^2",P(21),I(21)
3230 PRINT"COND POT",S(22),"FT^3",P(22),I(22)
3240 PRINT
3250 PRINT"PUMP","FT^3/HR","H.P.","P.C.","I.C."
3260 FOR I= 13 TO 19
3270 PRINT"    ",S(I),H(I),P(I),I(I)
3280 NEXT I
3290 LET P=0
3300 LET T=0
3310 FOR I= 1 TO 22
3320 LET P= P+P(I)
3330 LET T= T+I(I)
3340 NEXT I
3350 PRINT
3352 LET P=P*1.06 '6% ESCALATION FOR MID 1969
3353 LET T= T*1.06 '6% ESCALATION
3360 PRINT
```

COST3   (continued)

```
3370 PRINT"TOTAL PURCHASED EQUUIPMENT COST";P;"DOLLARS"
3380 PRINT"TOTAL INSTALLED EQUIPMENT COST";T;"DOLLARS"
3390 LET B= .2*T
3400 LET F=.08*T'FREIGHT AND TAXES
3410 LET C= .178*T'CONSTRUCTION
3420 LET E=.10*T'ENGINEERING
3430 LET D=T+B+F+C+E
3440 LET C1=.18*D'CONTINGENCY AND CONTRACTORS FEE
3442 LET Y8= .15*(D+C1)
3450 PRINT"BUILDING COST                      ";B;"DOLLARS"
3460 PRINT"FREIGHT AND TAXES                  ";F;"DOLLARS"
3470 PRINT"CONSTRUCTION COST                  ";C;"DOLLARS"
3480 PRINT"ENGINEERING COST                   ";E;"DOLLARS"
3490 PRINT
3500 PRINT"DIRECT PLANT COST                  ";D;"DOLLARS"
3510 PRINT"CONTINGENCY AND CONTRACTOR FEE     ";C1;"DOLLARS"
3520 PRINT
3530 PRINT"FIXED CAPITAL INVESTMENT           ";D+C1;"DOLLARS"
3540 PRINT
3544 PRINT"WORKING CAPITAL                    ";Y8;"DOLLARS"
3550 PRINT
3560 PRINT"***************MANUFACTURING COST********************"
3570 LET A=(A1+A4)*32'COST OF ACID
3580 LETL= (A3-A5)/98*100*12'COST OF LIME
3590 LET W= G3/.12'TONS OF WATER UESED
3600 LET W2=W*2000/62.4/.134'GALS
3610 let w3=w2/1000*.25'cost of water
3620 LET O3=O1*0.1'OIL COST
3630LET H=0
3640 FOR I= 1 TO 22
3650 LET H= H+H(I)
3660 NEXT I
3670 LET E=H*24*.7487'KILOWATT HOURS
3680LET E1=E*1.25*.010'COST PER DAY WITH 25% SURPLUS
3690 LET L1=3*3*24'LABOR 3 MEN 24HR AT 3.00
3700 LET L2=3.5*1*24'SUPERVISION
3710 let f=.15*(l1+l2)'fringe benefits
3720 LET M=(D+C1)*.05/360'MAIN AND REPAIRS AT 5% OF FCI
3730 LET S=.15*M/2'SUPPLIES 15% OF  MAIN
3740 LET F1=.02*(D+C1)/360'TAXES 2 % OF FCI
3750 LET F2=.01*(D+C1)/360'INSURANCE
3760 LET P=.15*(L1+L2+M/2)'PAYROLL OVERHEAD
3770 LET P2= P'LAB WORK
3780 LET P3=.5*(L1+L2+M/2)'PLANT OVERHEAD AT 50% OF LABOR
3790 PRINT"INPUT DUMPING FEE PER TON"
3800 input d1
3810 print"input cost for disposal of waste per ton"
3820 INPUT D2
3830 PRINT"INPUT INTEREST RATE AND YEARS OF OPERATION"
3840 INPUT R1,R2
```

COST3   (continued)

```
3842 LET  C2=(R1*(1+R1)^R2)/((1+R1)^R2-1)
3850 LET  C=C2*(D+C1+Y8)/360
3860 REM  CAPITAL RETURN
3870 let  t=a+l+w3+o3+el+l1+l2+f+m+s+f1+f2+p+p2+p3+c
3880 LET  T=T+D2*E9
3890 let  T1=t-j+d1
3900 PRINT"RAW MATRIALS"
3910 PRINT"ACID",A1+A4,"TONS/DAY",A
3920 PRINT"LIME",(A3-A5)/98*100,"TONS/DAY",L
3930 PRINT"UTILITIES"
3940 PRINT"WATER",W2,"GALS",W3
3950 PRINT"ELECT",E,"KILOWATTS",E1
3960 print "oil",O1,"gal",O1*0.1
3970 PRINT"WASTE DISPOSAL",E9,"TONS/DAY",D2*E9
3980 PRINT"LABOR",72,"HRS",L1
3990 PRINT"SUPER",24,"HRS",L2
4000 print"FRINGE BEN","","",f
4010 PRINT"MAINTAIN",Z9,Z9,M
4020 PRINT"SUPPLIES",Z9,Z9,S
4025 PRINT"FIXED CHARGES"
4030 PRINT"TAXES",Z9,Z9,F1
4040 PRINT"INSURANCE",Z9,Z9,F2
4050 print"cap return","","",c
4055 PRINT"GENERAL COST"
4060 PRINT"PAY OVER",Z9,Z9,P
4070 PRINT"LAB",Z9,Z9,P2
4080 PRINT"PLANT OVER",Z9,Z9,P3
4090 PRINT
4095 PRINT"TONS /DAY OF GLUCOSE";G3
4100 PRINT"TOTAL COST/DAY NO DUMP FEE    ";T;"DOLLARS"
4110 PRINT
4120 PRINT"COST/TON OF GLUCOSE NO DUMP ";T/G3;"DOLLARS"
4130 PRINT"COST/LB OF GLUCOSE NO DUMP   ";T/G3/2000;"DOLLARS"
4140 PRINT
4145 PRINT"TOTAL COST/DAY WITH DUMP FEE ";T1;"DOLLARS"
4150 PRINT"COST/TON WITH DUMP FEE       ";T1/G3;"DOLLARS"
4160 PRINT"COST/LB WITH DUMP FEE        ";T1/G3/2000;"DOLLARS"
4165 GOTO5160
4166 REM***************EVAPORATOR CALCULATION******************
4170 LET  N=6
4180 DIM  B(7,7),W(7,1),F(7,1),R(7,7)
4190 MAT  B=ZER
4270 FOR  I= 0 TO N
4280 READ T(I),L(I)
4290 LET  X(I)=T(I)
4300 NEXT I
4310 LET  C1=G3/N7
4320 LET  C2=.12
4330 LET  F= N7*2000/24
4340 FOR  I= 1 TO N+1
```

COST3   (continued)

```
4350 READ U(I)
4360 NEXT I
4370 LET G=(X+W1)*2000/24
4380 DATA 350,870,327,889,304,905,282,924,260,939,240,952,212,970
4381 DATA 500,480,450,410,370,250,500
4400 LET WO=F
4410 LET S8=F*C1'SOLIDS IN FEED
4420 LET P=S8/C2'PRODUCT RATE
4430 LET E= WO-P' LBS/HR EVAPORATED IN TOTAL SYSTEM
4440 FOR I= 1 TO N
4450 LET T(I)= X(I-1)-X(I)
4460 NEXT I
4470 LET B(1,1)= L(0)
4480 LET B(1,2)= -L(1)
4490 LET B(1,3)=0
4500 LET B(1,4)=0
4510 LET B(2,1)=0
4520 LET B(2,2)= L(1)-T(2)
4530 LET B(2,3)=-L(2)
4540 LET B(2,4)=0
4550 LET B(3,1)=0.
4560 LET B(3,2)= -T(3)
4570 LET B(3,3)=L(2)-T(3)
4580 LET B(3,4)=-L(3)
4590 IF N>3 THEN 4640
4600 LET B(4,1)=0
4610 LET B(4,2)=1
4620 LET B(4,3)=1
4630 LET B(4,4)=1
4640 LETF(N+1,1)=E
4650 FOR I= 1 TO N
4660 LET F(I,1)= -WO*T(I)
4670 NEXT I
4680 IF N=3 THEN 4810
4690 FOR J=4 TO N
4700 LET B(J,1)=0
4710 FOR I= 2 TO J-1
4720 LET B(J,I)=-T(J)
4730 NEXT I
4740 LET B(J,J)=L(J-1)-T(J)
4750 LET B(J,J+1)=-L(J)
4760 NEXT J
4770 LET B(N+1,1)=0
4780 FOR I= 2 TO N+1
4790 LET B(N+1,I)=1
4800 NEXT I
4810 MAT R= INV(B)
4820 MAT W= R*F
4830  REM CALCULAT AREAS
4840 FOR I= 1 TO N
```

COST3   (continued)

```
4850 LET A(I)= W(I,1)*L(I-1)/(U(I)*T(I))
4860 NEXT I
4870 LET G2= W(N+1,1)*L(N)/140
4880 LET T4= 212-70
4890 LET T5= 2
4900 LET T6= (T4-T5)/(LOG(T4/T5))
4910 LET A(N+1)=W(N+1,1)*L(N)/(U(N+1)*T6)
4920 PRINT
4930 PRINT
4940 FOR I= 1 TO N
4950 LET Z8=Z8+W(I,1)*X(I-1)
4960 LET Z7=Z7+W(I,1)
4970 NEXT I
4980 LET K1=(Z8+W(7,1)*212+P*212)/(Z7+W(7,1)+P)
5050 LET S(22)=(X+W1)*2000/62.4*2/24/60
5055 LET K2=(W*V9*2000/24-W(1,1))*870/((X+W1)*2000/24)
5056 LET K4=K1+K2'F DEG   INTO HEATER
5057 LET Y=0
5080 FOR I= 1 TO N
5090 LET Y= Y+A(I)
5100 NEXT I
5110 LET Y2= Y/N
5152 LET S(20)=Y2
5153 LET S(21)=A(N+1)
5157 RETURN
5160 END
```

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