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Process Design and Optimization of Cellulose Hydrolysis

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(M. S. thesis)

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ABSTRACT

The primary concern of this work is the economic optimization of a process for the hydrolysis of waste cellulosic material to fermentable sugars. Hydrolysis is performed enzymatically, utilizing the cellulase enzyme complex produced by Trichoderma viride. Using corn stover as a substrate, a system was designed to provide 14% hydrolyzate sugars (70% fermentable) at an estimated cost of 6.84¢/pound of sugar, a 43% cost reduction over previous designs. Optimal residence time for hydrolysis was found to be 62 hours, resulting in a 34% conversion of raw material to sugars. Total fixed capital investment for the process is estimated to be $17.13 x 10^6.

The kinetics of cellulose hydrolysis were modeled through the use of a modified Michaelis-Menten equation, making computer simulation of batch hydrolyses possible. Additional studies on the accessibility of cellulose were performed, and the feasability of a counter-current processing scheme was investigated.

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Chapter 1 INTRODUCTION

Today's man is a child of mechanistic society. While technology has made life easier for man, it has also made him dependent, and this dependence may best be typified by man's desire for mobility.

With the advent of the personal automobile in the United States, there became an increasing demand for a supply of liquid fuel. This gave birth to what is now the largest industry on earth, the petrochemical industry. But all resources are limited, and the age of petroleum is drawing to an end. Man, however, cannot break free of his dependence on the automobile, for in today's society without mobility there is no life.

For this reason, it is immediately important to develop new sources of liquid fuels. This work is part of a long term project to develop an alternative liquid fuel from cellulosic materials. It is concerned primarily with the optimization of a process to hydrolyze cellulose to sugars that are readily fermentable to ethanol.

Ethanol has demonstrated its capability of reducing the load that is now placed upon petroleum in several ways. Research in Brazil[1] has shown that alcohol may be mixed with gasoline for use in conventional internal combustion engines. This provides a direct utilization as a fuel. In a slightly more subtle way, alcohol may be used as the feedstock for a variety of materials and a component in a number of commercial products.[2] Ethanol for this purpose is currently produced by the catalytic hydration of ethylene obtained from petroleum.

The primary reason that alcohol is not currently produced on a large scale from cellulose is economics. In the United States,

where the price of petroleum has been sufficiently controlled, ethanol produced from cellulose is not currently competitive with that produced from petroleum. Given time, it will be found that this process will become much more attractive.

Emphasis of this work is placed on the use of engineering knowledge to design and optimize economically the process for the conversion of acid pretreated corn stover to hydrolyzate sugars. The design is strictly controlled withn existing engineering technology -- in an attempt to determine a true measure of the process. Process improvements will undoubtedly be forthcoming in due course from research in progress here and elsewhere.

REFERENCES FOR CHAPTER 1

1. Hammond, A. L., Science, 195, 564 (Feb. 1977).

2. Considine, D. M. (ed), Chemical and Process Technology Encyclopedia, McGraw-Hill, NY, 423 (1974).

Chapter 2 BACKGROUND

Cellulose is one of the truely renewable resources. It has been estimated that 146 billion tons of biomass, plant life containing cellulose, are produced on the earth each year.[1] This cellulose is a polymeric form of the sugar glucose, and it has been shown[2] that it is possible to enzymatically hydrolyze cellulose to the monomer by use of a cellulase enzyme system produced by the fungus Trichoderma viride.

However, all cellulosic substances are not readily amenable to enzymatic hydrolysis. There exist varying quantities of lignin, amorphous and crystalline cellulose, and other materials, depending on the substrate, which interfere with the enzyme accessibility to the system. Table 2-1 gives the composition for a representative substrate, corn stover.[3] For this reason, various pretreatments are being studied in an attempt to increase accessibility prior to the enzyme hydrolysis step.

One of the most promising economical pretreatments to date is with dilute sulfuric acid. Table 2-2 shows the effect of this pretreatment on the agricultural residue, corn stover.[3] It can be seen that by this pretreatment, conversion has risen from 26% to 60%, thereby vindicating this approach. Materials thus treated, may then be sent through a processing scheme to effectively convert the cellulose to glucose.

TABLE 2-1

ANALYSIS OF CORN STOVER

	PERCENT
GLUCAN	35.1
MANNAN	0.25
GALACTAN	0.75
XYLAN	13.0
ARABINAN	2.8
TOTAL CARBOHYDRATE	51.9
LIGNIN	15.1
ASH	4.3
EXTRACTIVES	5.5
UNIDENTIFIED (ORGANIC)	18.0
PROTEIN	4.0
TOTAL	98.8

TABLE 2-2

COMPARISON OF ACID TREATMENT HYDROLYSIS CASE

ORIGINAL SOLID		
GLUCOSE (EQUIVALENTS)	39.0	
XYLOSE	14.8	
OTHER HEX	1.1	
OTHER PENT	3.2	
TOTAL	58.1	
ENZYMATIC HYDROLYSIS WITHOUT ACID TREATMENT		
GLUCOSE	11.2	
CELLOBIOSE	0.5	
XYLOSE	3.0	
ARABINOSE	0.6	
TOTAL	15.3	CONVERSION 26%
ENZYMATIC HYDROLYSIS WITH ACID TREATMENT		
GLUCOSE	15.7	
CELLOBIOSE	1.1	
XYLOSE	0.8	
ARABINOSE	0.1	
TOTAL	17.6	
ACID TREAT LIQUOR		
GLUCOSE	1.9	
CELLOBIOSE	1.0	
XYLOSE	12.2	
ARABINOSE	2.4	
TOTAL	17.5	TOTAL CONVERSION 60%

A diagram of such a scheme as proposed by Wilke[3] et al. is shown in Figure 2-1.

Agricultural residues are first milled to reduce size and allow fluidization. The substrate is then pretreated with a dilute solution of sulfuric acid, washed to neutrality, and contacted with the existing hydrolyzate sugar stream to recover enzyme remaining in solution. The solids are then fed to a series of mixed tanks for enzymatic hydrolysis. Enzyme is produced separately by fermentation of Trichoderma viride. The cellulase enzyme is extracellular, allowing removal of the cells before enzyme is fed to the hydrolysis stages. The sugar solution is then evaporatively concentrated and utilized in an ethanol fermentation by Saccharomyces cerevisiae. The alcohol is distilled to 95 wt% for a final product.

Economic designs[3,4,5,6] of this process have suggested that while this process is desirable, it is not cost effective. These designs, however, were based on intuitively selected specifications and necessitated several simplifying assumptions. Through the use of a kinetic model, it is possible to eliminate these assumptions, and by application of computer technology to easily calculate a large number of design systems. In such a manner as the major thrust of this work, it is hoped that the optimum process may be found.

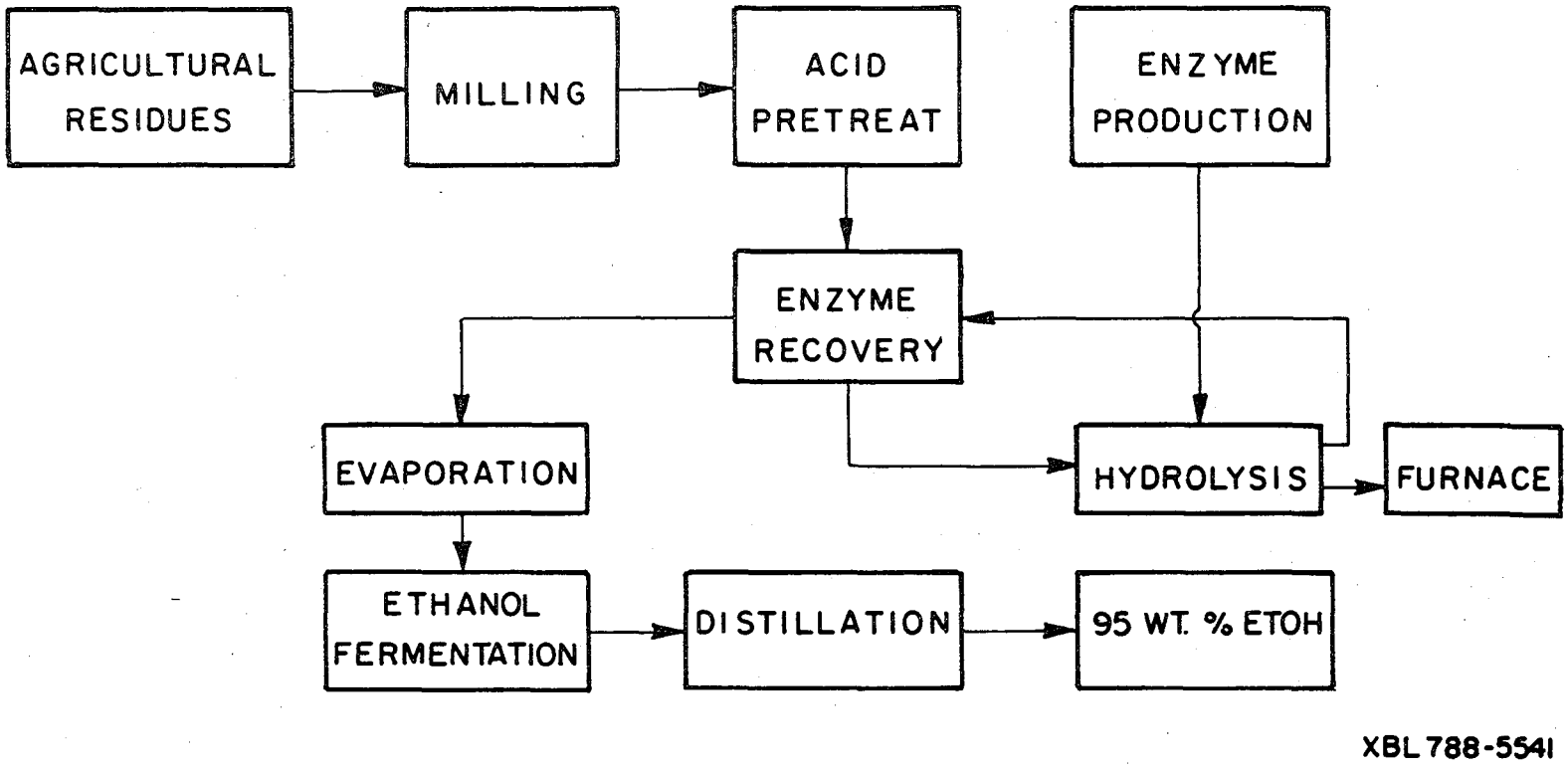

Fig. 2.1. Cellulose processing scheme.

REFERENCES FOR CHAPTER 2

1. Riley, G. A., Am. Sci., 32, 129, (Apr. 1964).
2. Mandels, M. and Weber, J., Advan. Chem. Ser., 95, 391, (1969).
3. Wilke, C. R., Yang, R., Sciamanna, A. F. and Frietas, R. P., Evaluation and Process Development Studies for Conversion of Biomass to Sugars and Ethanol, UC-LBL-7847, June 1978.
4. Cysewski, G. R. and Wilke, C. R., Biotech. and Bioeng., 18, 1297, (1976).
5. Wilke, C. R., vonStockar, U., Yang, R., Cysewski, G. R., Biotech. and bioeng., 18, 1315, (1976).
6. Mitra, G. and Wilke, C. R., Biotech. and Bioeng. Symp. No. 5, 253, (1975).

Chapter 3 ANALYTICAL PROCEDURES

3.1 DNS Sugar Assay

The amount of sugar in a given sample may be determined by measurement of the number of reducing groups in that sample. The standard method for this determination is the dinitrosalicyclic acid (DNS) method.[1] For purposes of this work, the method outlined below was used as a standard technique with slight variations in dilutions as required to maintain sensitivity.

1. Clarify sample by centrifugation at 10000 RPM for 10 minutes.
2. To 1.0 ml of sample 3.0 ml of DNS reagent are added and the mixture is stirred vigorously in a Vortex mixer.
3. Heat mixture in a boiling water bath for 5 minutes.
4. Cool in ice bath for 5 minutes.
5. Dilute the 4.0 ml mixture with 20.0 ml of water, mixing well by inverting the tube several times.
6. Measure absorbance of diluted sample at 600 nm and a 0.03 mm slit width.
7. Determine sugar concentration from curve prepared from standard solutions of glucose in the range of 0.5 to 2.5 grams/liter.

It should be noted that with the DNS reagent all reducing substances are determined. This can include glucose, cellobiose, xylose, arabinose, and other compounds with reducing groups.

DNS Reagent is prepared as follows:

1. Mix 300 ml of 4.5% of 4.5% NaOH (13.5 gm NaOH/300 ml) and 800 ml of 1% 3,5-dinitrosalicylic acid and 255 gm of Rochelle Salt (Na-K-tartrate 4 H_2O).

2. To 10 gm of crystalline phenol, add 22 ml of 10% NaOH. Add water to dissolve. Dilute to 100 ml and mix.

3. To 69 ml of solution in (2), add 6.9 gm sodium bisulfate and add to 3,5-dinitrosalicylic acid solution.

4. Mix well and keep in tightly stoppered bottle.

3.2 Filter Paper Activity

Cellulase is a complex enzyme system which contains several components. These may be summarized[2] as:

(1) C_1, β-1,4 glucan cellobiohydrolases which are required for the hydrolysis of highly ordered solid cellulose.

(2) C_x, endo-β-1,4 glucanases whose actions are of random nature but are generally more reactive with internal linkages; and exo-β-1,4 glucanases which successively remove single glucose units from the non-reducing end of the cellulose chain.

(3) β-Glucosidases, which vary in specificity but are highly active on cellobiose.

Although techniques exist for the assessment of the activity of these relative components in a given enzyme system, it is not within the scope of this research to become involved in the isolation and characterization of the individual components. Rather, it is the nature of the combined actions of a system of enzymes that is relevant. Therefore, the activity of this crude enzyme system is commonly measured against filter paper to given an overall evaluation of its hydrolytic strength.

The method of determining Filter Paper Activity (FPA) as used in this work is as follows:

1. 1.0 ml of enzyme sample is added to 1.0 ml of 0.05 M acetate buffer (pH 5.0).
2. To this mixture a 1x6 cm strip (50 mg) of Whatman #1 filter paper that has previously been coiled is added.
3. Incubate in a 50 C static water bath for 60 minutes.
4. Remove from water bath and cool in ice bath for 5 minutes.
5. Pipet 1 ml of solution from mixture making sure to avoid removing any of the filter paper residue.
6. Determine the reducing sugars by the DNS method.
7. The concentration of sugar in mg/ml multiplied by the dilution factor of 2 is the FPA.

3.3 Determination of Hydrolysis Sugars by Gas Chromatography

At times it is useful in the consideration of process development to determine the exact composition of the hydrolysis sugars mixture. In the case of these sugars proceeding to an ethanol fermentation, it is really important only to be concerned with the levels of glucose and cellobiose. Both of these requirements may be satisfied by the use of gas chromatography. Since the material to be studied is non-volatile, volatile derivatives must be prepared -- but otherwise standard GC technique is used.

Preparation of the sugar derivatives is as follows:[3]

1. Centrifuge hydrolysis sample and decant liquid.
2. Boil liquid in 100 C bath for 20 minutes, then freeze until chromatography is to be performed.

3. Transfer 1.0 ml of this liquid to a small vial and freeze dry.
4. To the freeze dried residue, add 1.0 ml of a dimethyl sulfoxide solution containing 5.0 g/l of 2-hydroxypyridine and 2.0 g/l of myo-inositol (this is an internal standard).
5. Place sample in 40 C oven and allow to equilibrate for 6 hours.
6. After equilibration, add 0.5 ml of silylating reagent and mixed with Vortex mixer (the reagent is prepared by adding 2 parts by volume of hexamethyl disilazane (HMDS) and 1 part by volume of chlorotrimethyl silane (TMCS)).
7. Allow to stand for 30 minutes, mix again and allow to stand for an additional 30 minutes.
8. Two phases will form. Discard the lower phase and add to the upper phase an equal volume of water, and mix.
9. Two phases will again form. Discard the lower phase and add a small portion of anhydrous sodium sulfate to dry the sample.
10. The sample is now ready for injection into the gas chromatograph.

Sugar derivatives prepared in this manner will produce two curves for each of the sugars. These curves may be integrated and compared to the inositol standard to determine the amounts of each sugar present in the original sample.

REFERENCES FOR CHAPTER 3

1. Summer, J. B. and Somers, G. E., Laboratory Experiments in Biological Chemistry, Academic Press, NY, (1944).

2. King, K. W. and Vessal, M. I., Adv. in Chem. Series, 95, 7, (1969).

3. Frietas, R. P., Personal Communication, Univ. of Calif.-Lawrence Berkeley Laboratory.

Chapter 4 PRODUCTION OF CELLULASE ENZYME

4.1 Media Formulation

A lyophilized culture of Trichoderma Viride QM 9414 was obtained from the American Type Culture Collection. The culture was transferred to a potato dextrose agar slant and maintained under refrigeration until use.

The composition of the medium was based upon the standard media developed by Mandels and Reese,[1] with modifications suggested by Sternberg.[2] Carbon to nitrogen ratio was increased from the value of 6.25 that had typically been used to 8.0. Solka Flock, a purified wood cellulose, was used as the carbon source and Tween 80 was added to enhance enzyme production.[3] A slightly more complex trace elements solution was also used. Details of both media and trace element solution are given in Tables 4-1 and 4-2.

4.2 Fermentation

The cellulase enzyme was produced by batch fermentation in the 30 liter fermenter schematically represented in Figure 4-1. Temperature was controlled at 28°C, and pH was controlled only to prevent it from falling below 3.35. Filter sterilized air was injected at a sufficiently low rate to prevent excessive foaming, and agitation was provided to keep the solids suspended and well mixed. Antifoaming agent (AF 60, General Electric Company) was added as needed.

The fungus had first grown in a one liter innocullum chamber which had itself been inoculated directly from the slant culture, and contained the same media as the larger fermentor. After four

TABLE 4-1

MEDIA FOR CELLULASE FERMENTATION

COMPONENT	CONCENTRATION (g/l)
Solka Floc	20.0
$(NH_4)_2SO_4$	3.48
KH_2PO_4	2.0
Urea	0.3
$CaCl_2 \cdot 2H_2O$	0.4
$MgSO_4 \cdot 7H_2O$	0.3
Proteose Peptone	1.552
Tween 80	2.0
Trace Metals Solution	1.0 ml/l

TABLE 4-2

TRACE ELEMENT SOLUTION

COMPONENT	CONCENTRATION (g/l)
H_3BO_3	2.0
$CoSO_4 \cdot 7H_2O$	0.2
$CuSO_4 \cdot 5H_2O$	0.8
$ZnSO_4 \cdot 7H_2O$	2.0
$MnSO_4 \cdot H_2O$	0.6
KI	0.2
$FeSO_4 \cdot 7H_2O$	0.4
$Al_2(SO_4)_3$	0.6

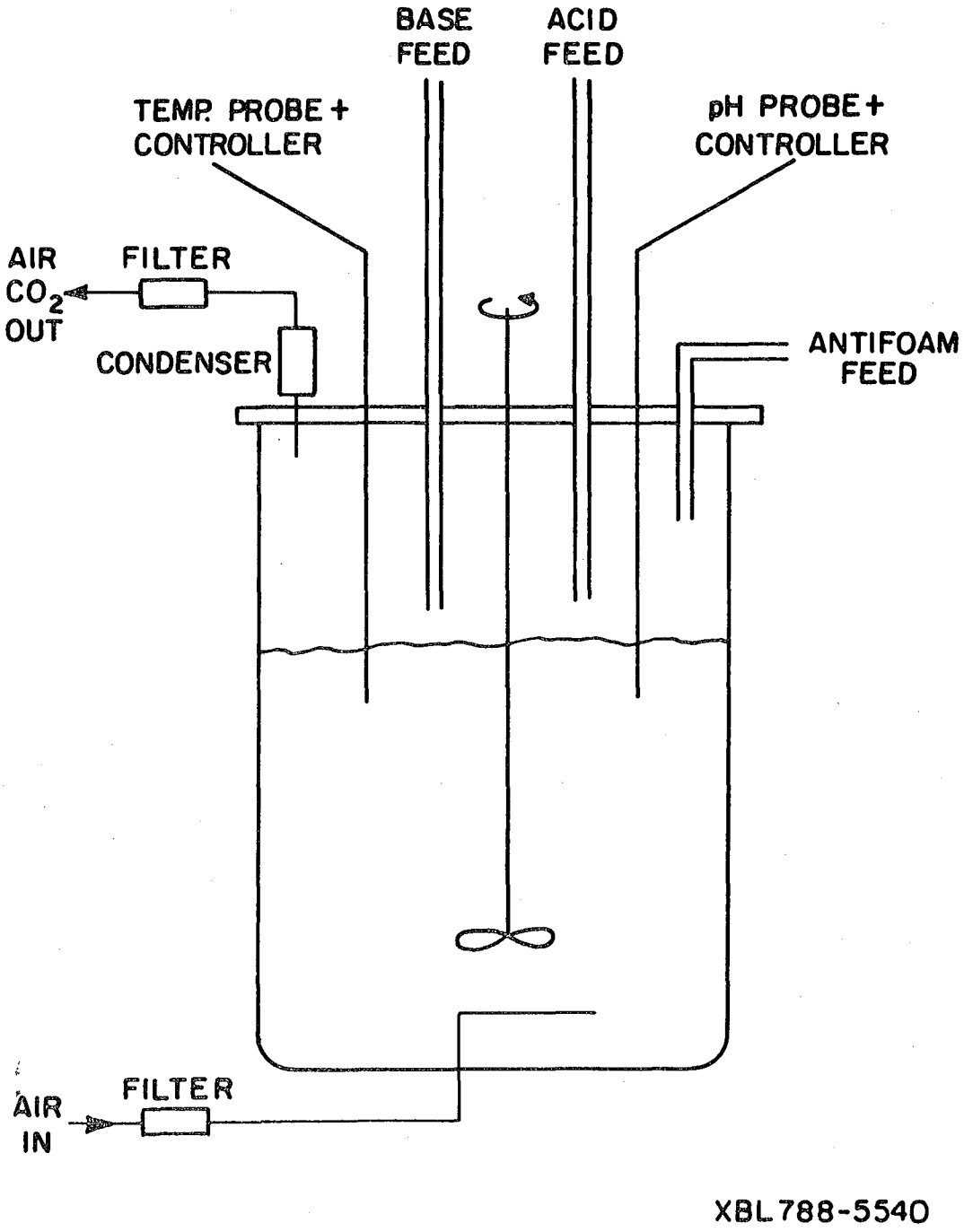

Fig. 4.1. Batch fermentor.

days growth, this one liter culture was used to inoculate the 30 liter fermentor. Filter Paper Activity of the inoculum was 2.4.

The media was sterilized in place by the direct injection of steam, and pH after sterilization was 6.05. Sternberg[2] has indicated that the effects of pH on the production of cellulase are significant. When left uncontrolled, the pH may fall to 2.4 and under these conditions growth is slow[4] and cellulase enzymes are inactivated.[5] It has also been shown[2] that as the pH rises, so does the level of β-glucosidase production. For this reason, the pH of the system was allowed to rise. The pH trace for the 118 hour fermentation may be seen in Figure 4-2.

The cellulase enzyme was harvested at the end of 118 hours, when the pH had risen to 5.5. Filter Paper Activity at this time was measured to be in excess of 7.0. Mycellia was removed by filtration through glass wool, and 0.01% Merthiolate (Eli Lilly Co.) was added to prevent contamination. The enzyme solution was then stored at 2 to 4°C.

4.3 Cellulase Activity

Although no specific attempt will be made in this work to accurately assess the relative strengths of the various components in the cellulase complex, work performed by Long and Sciamanna[6] indicate that the activity of the major individual components in this enzyme solution are each about three times that of activities normally produced (measured in International Units). However, even though initial activity was on the order of 6.7 to 7.0 FPA, there was a decay over a period of months to 5.6 FPA, where the enzyme appeared to stabilize.

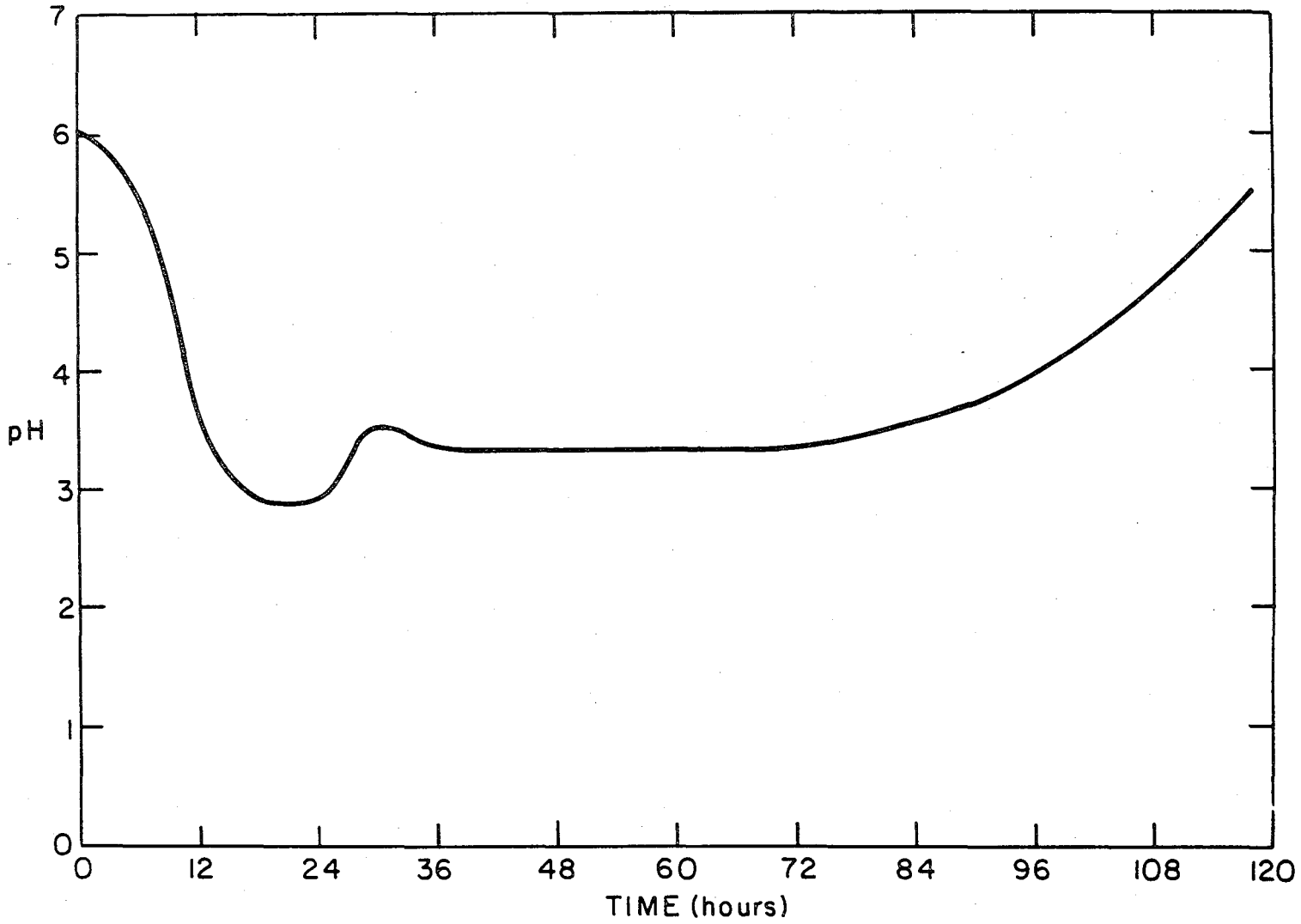

Fig. 4.2. Fermentation pH trace.

Activity of the cellulase enzyme mixture with dilution tends to the non-linear. This may be due to synergistic effects of the enzyme or to the varying rates of hydrolysis of the crystalline and amorphous regions in the filter paper. The dilution curve for this particular cellulase complex is shown in Figure 4-3.

For purposes of modeling, it is important to determine some relationship between the Filter Paper Activity of a solution and the amount of protein in the solution. Data for this purpose was taken from work performed by Yang[7] and data specifically determined for this enzyme by Long and Sciamanna.[6] A plot of protein concentration versus FPA is shown in figure 4-4. This was fit to a logarithmic curve to give the relationship:

$$FPA = 3.293 + 1.399 \ln(E)$$

where E is the enzyme concentration in grams per liter.

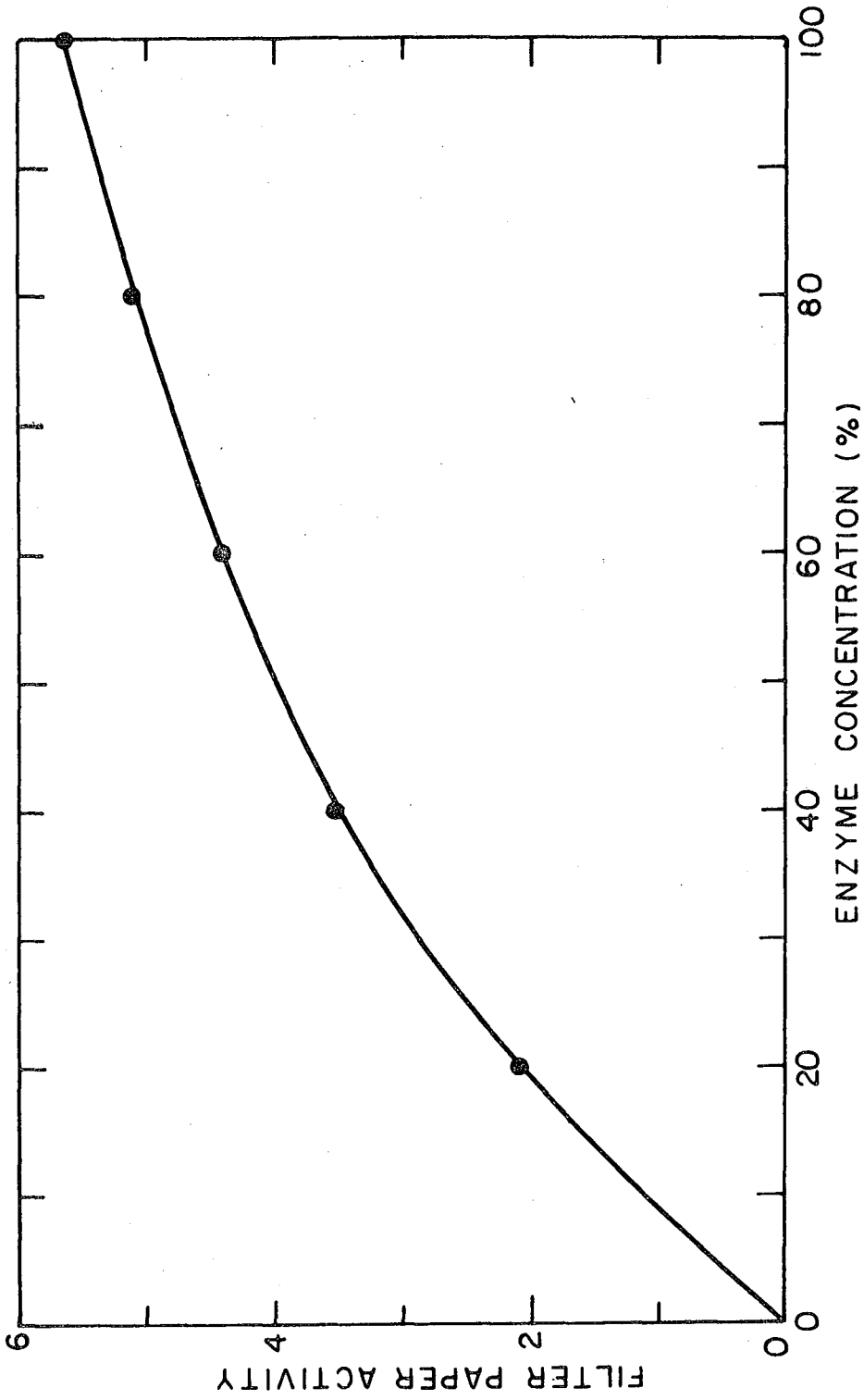

Fig. 4.3. FPA vs enzyme dilution.

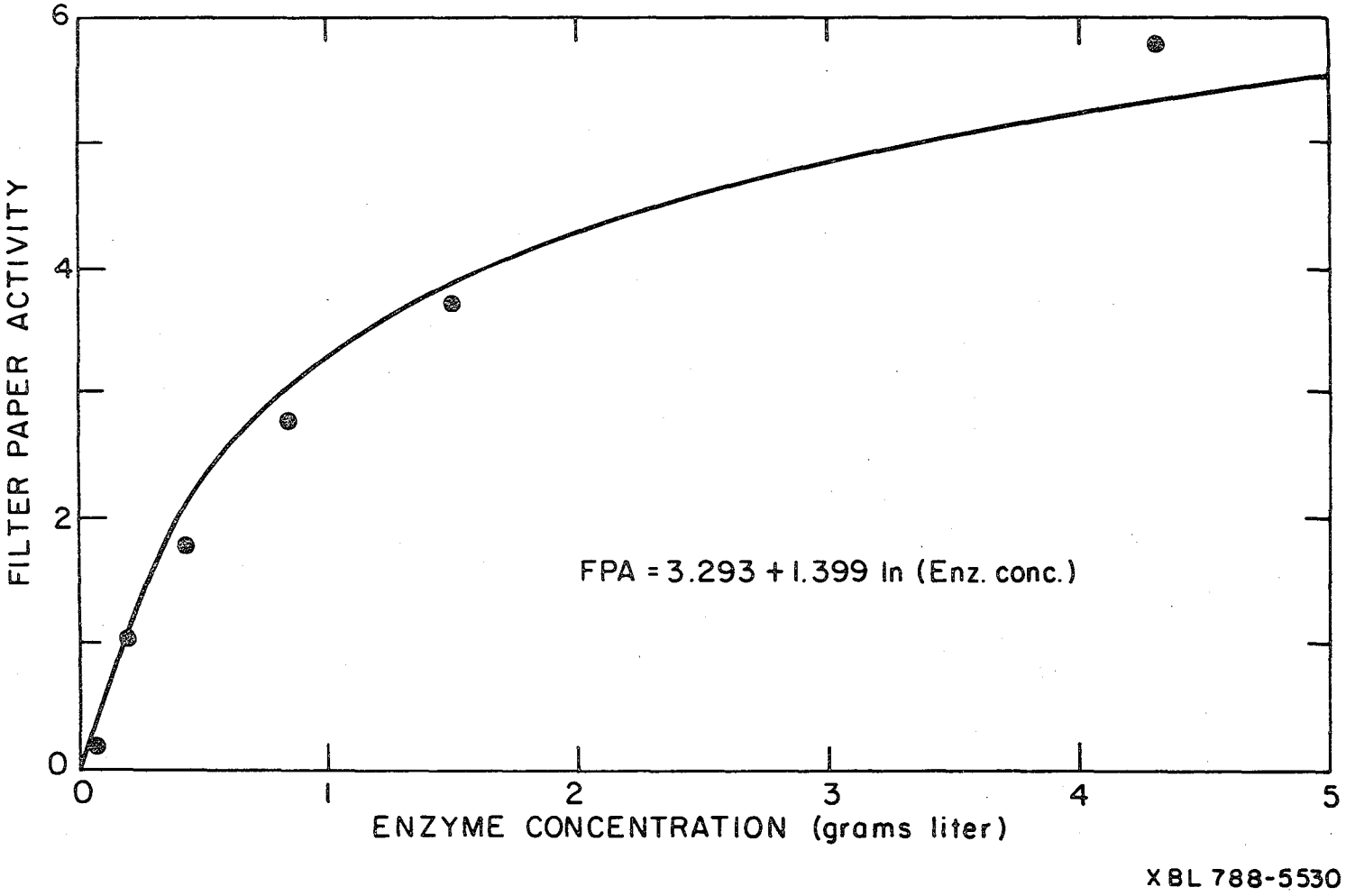

Fig. 4.4. FPA vs enzyme concentration.

REFERENCES FOR CHAPTER 4

1. Mandels, M. and Reese, E. T., J. Bacteriol., 73, 269, (1957).

2. Sternberg, D., Biotech. and Bioeng., 18, 1751, (1976).

3. Reese, E. T. and Maguire, A., Develop. Ind. Microbiol., 12, 212, (1971).

4. Brown, D. E., Halstead, D. J., and Howard, P., Symposium on the Enzymatic Conversion of Cellulose, Bailey, Enari, Linko, eds., SITRA, Helsinki, Finland, 137, (1975).

5. Sternberg, D., Appl. Environ. Microbiol., 31, 648, (1976).

6. Sciamanna, A. F. and Long, W., Personal Communication, Univer. of Calif.-Lawrence Berkeley Laboratory.

7. Wilke, C. R. and Yang, R., Applied Polymer Symp., 28, (1975).

Chapter 5 ACCESSIBILITY OF CELLULOSE

5.1 Theory

Because of the dual nature of crystalline and amorphous cellulose, it is expected that as the hydrolysis proceeds, the mode of attack by the cellulase enzyme complex upon the cellulosic substrate will vary. This may be due to the changing availability or accessibility of active sites for the binding of the various cellulase proteins, and the possibility of absorption of these proteins onto binding sites that offer no further progression along the cellulose chain.

The hydrolysis of cellulose by the cellulase enzyme complex may be viewed as a heterogeneous catalytic reaction. Thus the reaction occurs in three sequential steps: (1) adsorption of the enzyme on the substrate; (2) catalytic actions at the surface of the substrate; and (3) the release of product to the surrounding solution. However, because of the complexity of the cellulase enzyme mixture, step two, the catalytic reactions are not well defined. It is important, therefore, to gain some quantitative view of these actions in the hope that more insight may be gained.

5.2 Experimental Methods and Results

By studying the production of sugar from cellulose complexes of varying composition, it is possible to gauge the nature of the changing accessibility of the substrate. To obtain substrates that are increasingly difficult to hydrolyze, the raw material may be exposed to the cellulase system for varying lengths of time prior to the actual period of experimentation. In theory, this would effectively reduce the number of active sites for enzyme attack and allow some insight

to be gained on the effect of varying quantities of crystalline and amorphouse cellulose. Newsprint (Wall Street Journal; cellulose content 72%; -20 mesh) was chosen as a typical substrate for these tests.

Hydrolysis was run at a temperature of 45 C in four well stirred stages, each with a residence time of 12 hours. At the completion of each 12 hour period, the liquid and solid were filter separated, with the solid being returned to the vessel while the liquid was sent to the next stage. In all each portion of the liquid had a residence time of 48 hours, four contacts with solids of the same strength -- 12 hours long. This method of contacting is schematically represented in Figure 5-1. The solid lines indicate the flow of liquid through the systems, while the numbers within the circles represent the length of time the solids have previously been exposed to the enzyme solution (F indicates fresh substrate).

The results of this experiment are shown in Figures 5-2 through 5-5. It can be seen that the components of the enzyme system are adsorbed rapidly on the surface of the substrate, thereby producing the high initial hydrolysis rate (Fig. 5-2). During the subsequent stages of hydrolysis, it is seen that little release of free sugars occurs, and it may be inferred that the majority of the enzymes have been adsorbed onto the initial substrate, thereby decreasing the possible catalytic effect. There is a further implication that at some point in the catalytic process, enzyme is bound to an active site that is resistant to catalytic activity. This causes a decrease in the activity of the solution and a loss of usable enzyme from the system. The following figures (Fig. 5-3 to 5-5) show that it requires progressively

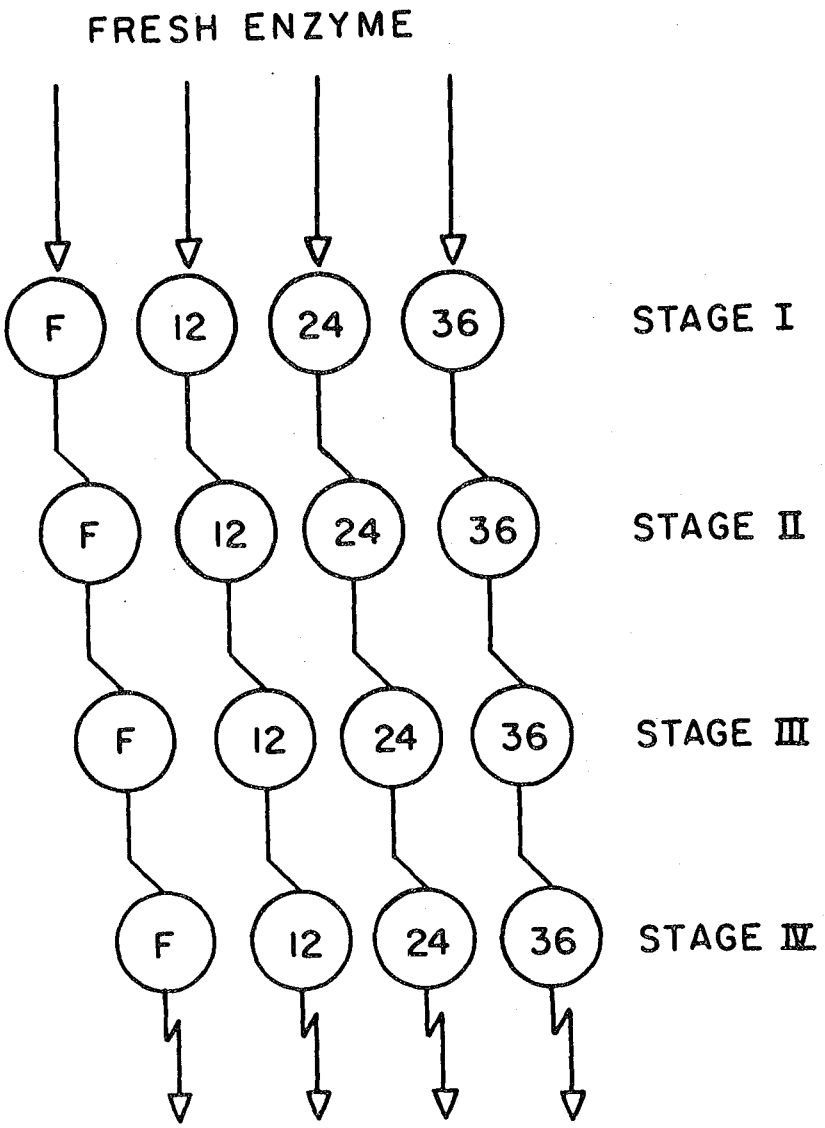
FRESH ENZYME
F
12
24
36
STAGE I
F
12
24
36
STAGE II
F
12
24
36
STAGE III
F
12
24
36
STAGE IV
SPENT ENZYME
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Fig. 5.1.

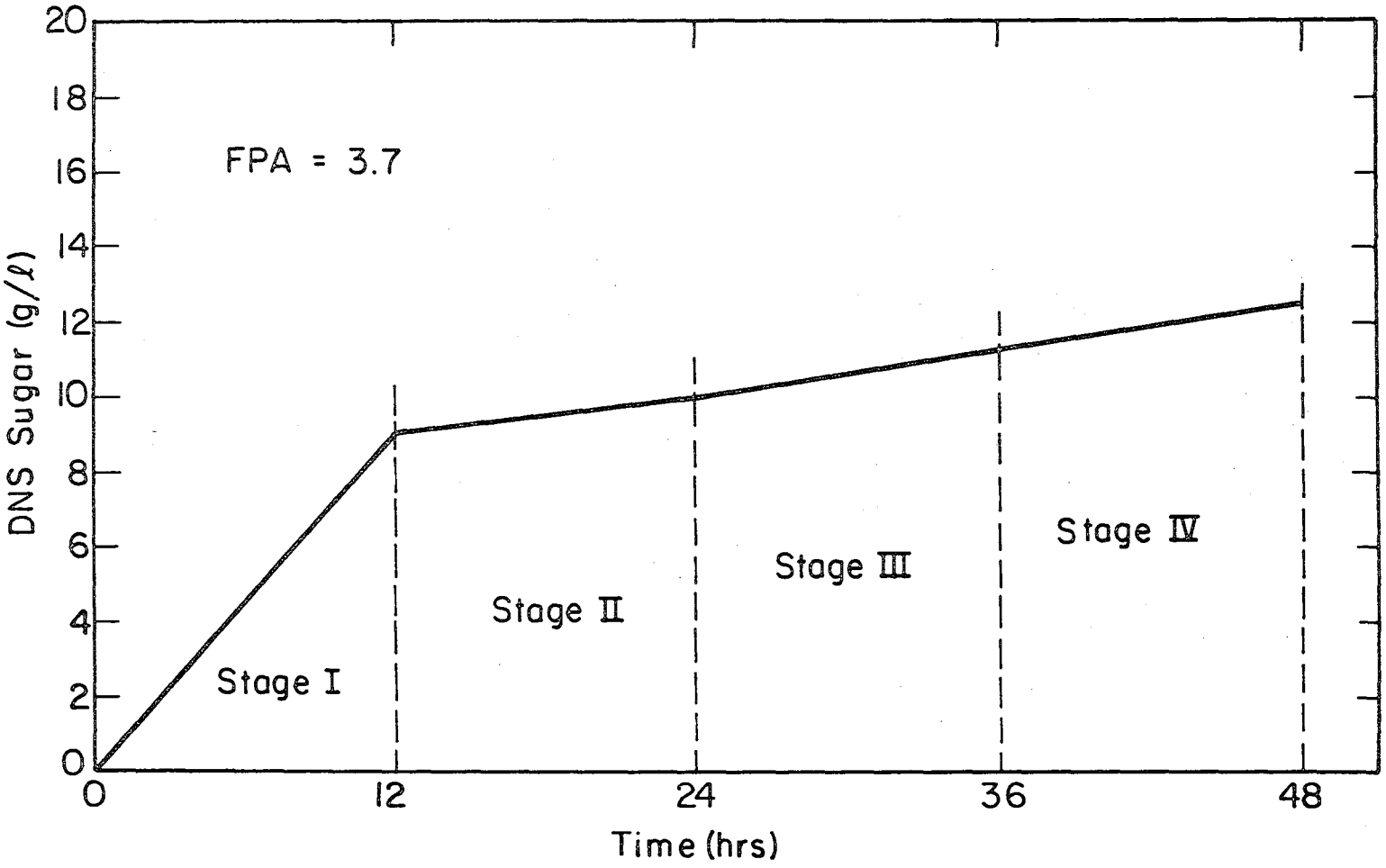

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Fig. 5.2. 4-Stage hydrolysis of fresh substrate.

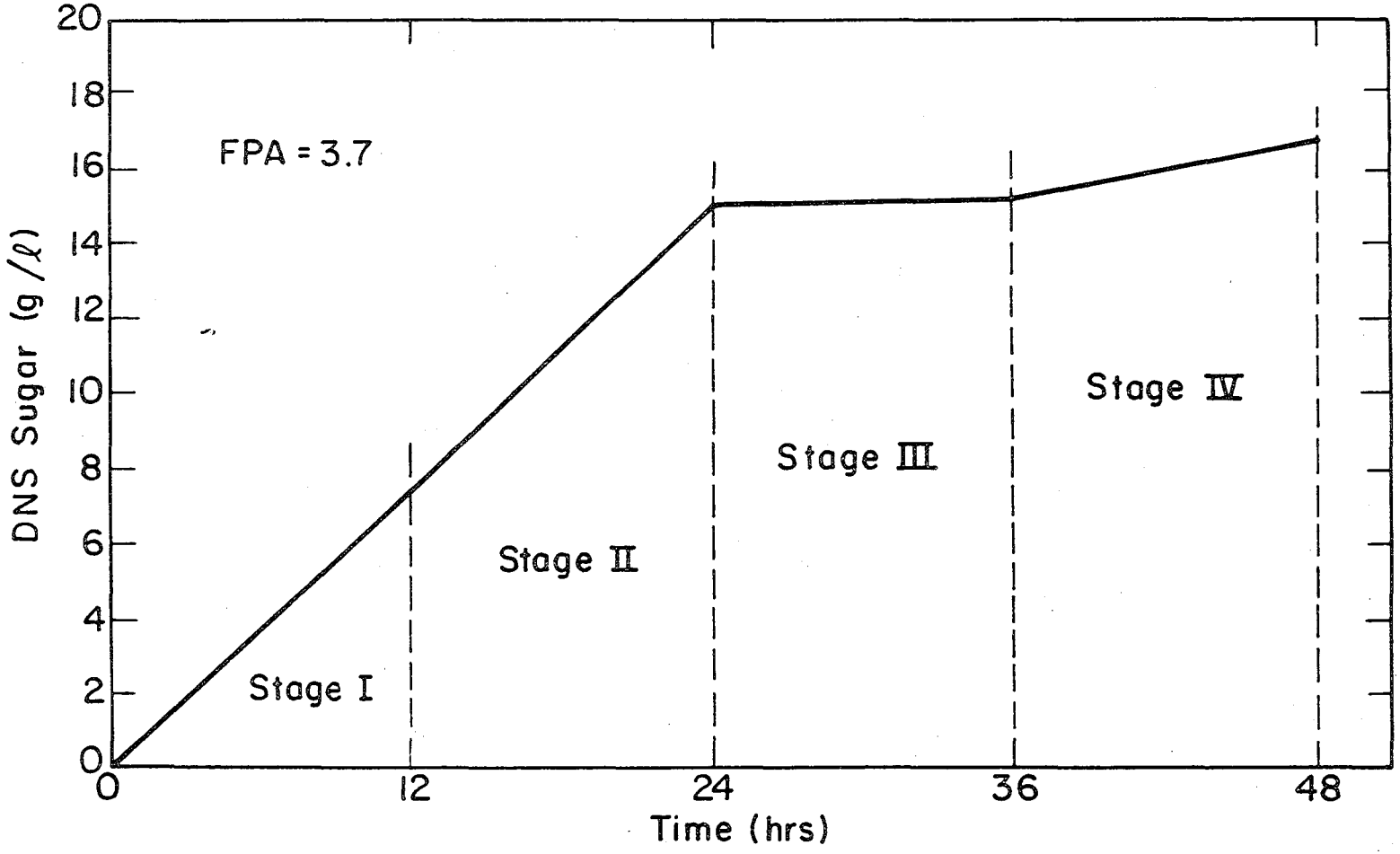

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Fig. 5.3. 4-Stage hydrolysis of 12 hr substrate.

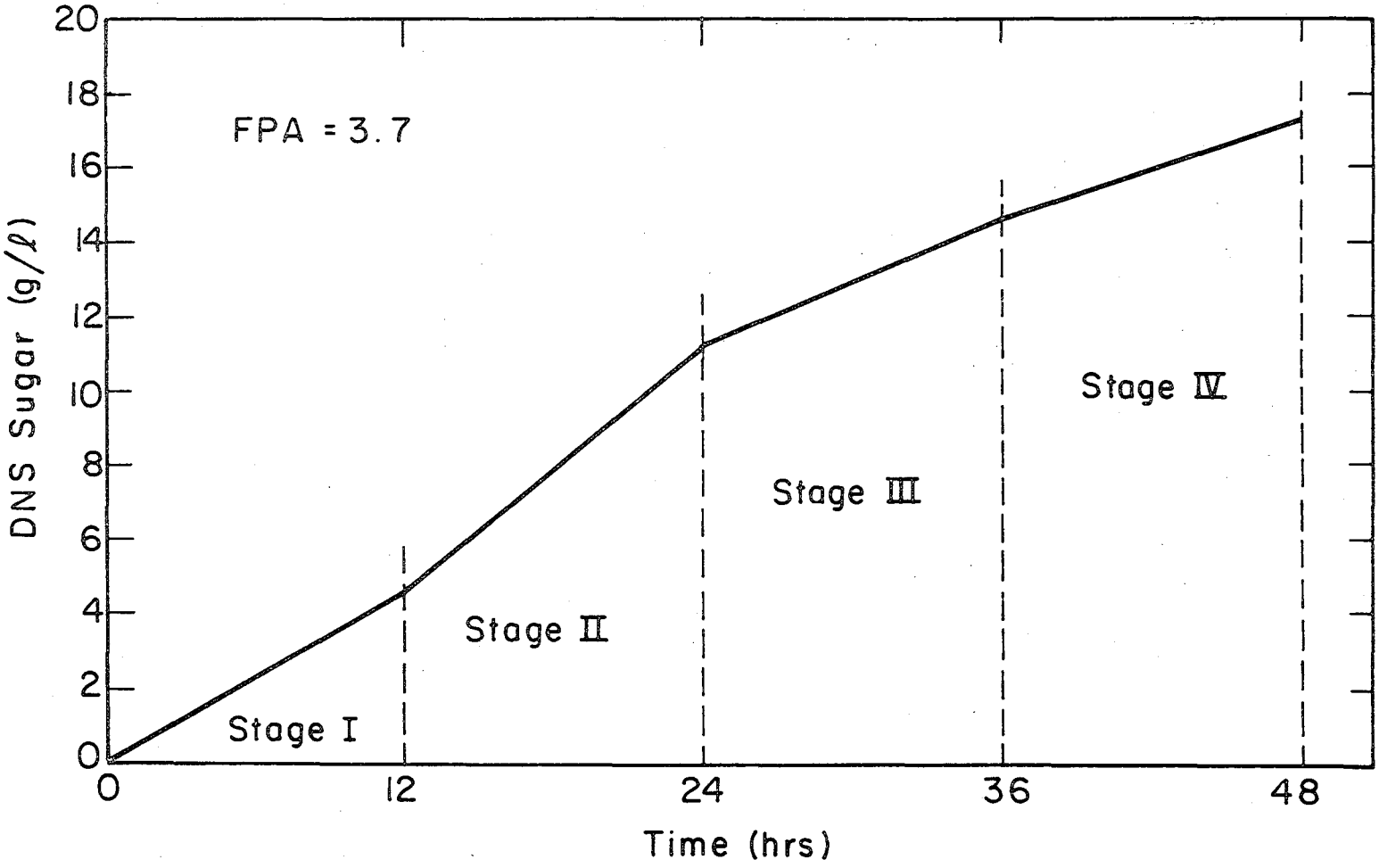

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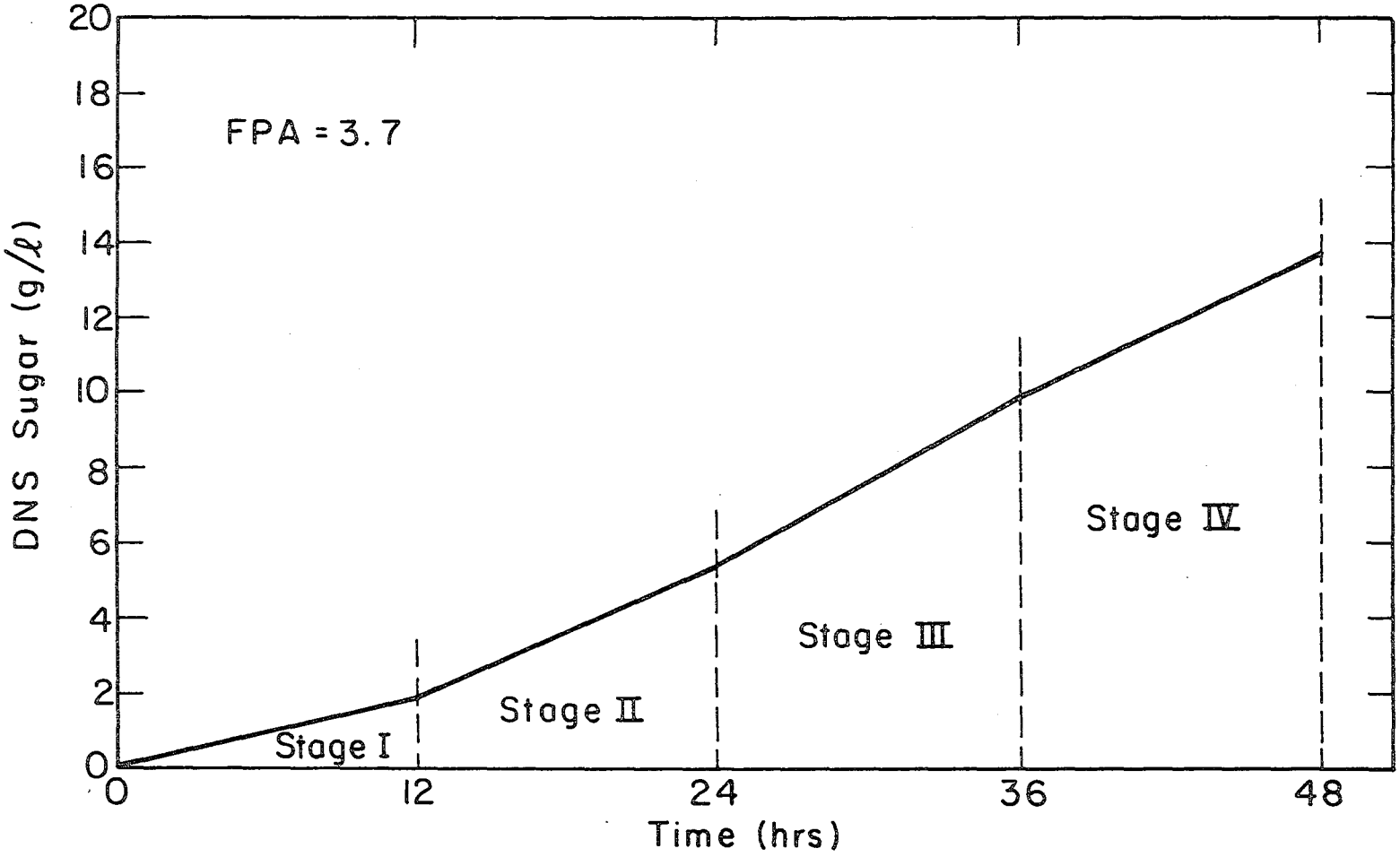
Fig. 5.4. 4-Stage hydrolysis of 24 hr substrate.



XBL 788-10345

Fig. 5.5. 4-Stage hydrolysis of 36 hr substrate.

more stages to adsorb the enzyme; this is expected due to the reduction in the number of accessible sites for adsorption.

Thus, as the hydrolysis reaction proceeds, specific adsorption generally becomes more difficult because the more easily accessible cellulose becomes depleted, and the substrate consists of a solid of increasing crystallinity and resistance to enzymatic hydrolysis. Furthermore, because of the apparent adsorption of enzyme on resistive sites, the activity of the system is decreasing with time; thereby weakening the catalytic strength toward the remaining unhydrolyzed areas of cellulose.

Chapter 6 COUNTER-CURRENT HYDROLYSIS

6.1 Theory

The concept of counter-current hydrolysis arose out of an attempt to solve the problems associated with the complex structure of the cellulosic substrate. It is well known that the amorphous regions of the cellulose complex are much more easily hydrolyzed than the crystalline regions. Therefore, it was hypothesized that by utilizing a counter-current processing scheme, the amorphous regions could be hydrolyzed with a dilute enzyme solution, leaving the crystalline regions open for attack by a more concentrated enzyme solution. Thus, the more reactive parts of the substrate system would come into contact with the less powerful catalytic properties of the dilute enzyme, while the least reactive crystalline regions would be fully exposed to the initial enzymatic attack.

6.2 Experimental Method and Results

Initial attempts to develop a counter-current processing scheme were based on the use of the equipment illustrated (Fig. 6-1). This system consisted of a series of stirred tanks which overflow into settling tanks. Liquid removed from the top of a settling tank was pumped to the next stirred tank, and solids from the bottom of the settling tank were removed via a worm screw and sent to the previous stirred tank.

Equipment was designed and constructed out of stainless steel, with the exception of the worm screws which consisted of wood augers electroplated with chromium. Sigma Motor peristaltic pumps were utilized both as drives for the worm screws and as the pumps for the system.

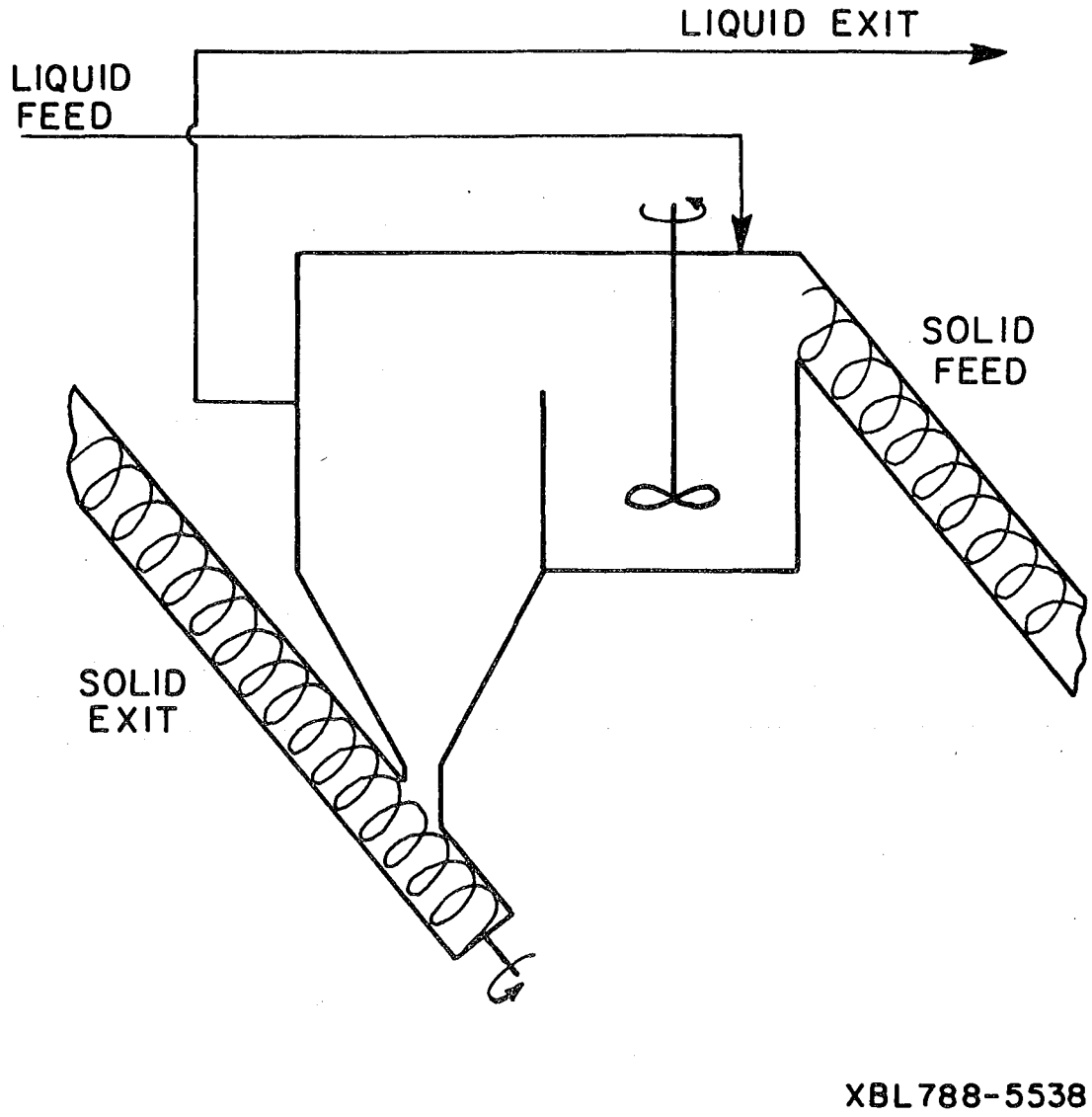


Fig. 6.1. Counter-current process equipment.

When the above system was finally assembled, it was found, unfortunately, that due to the necessarily low rate of solids removal from the settling tanks, the application of worm screws could not effectively be utilized on the laboratory scale.

The inability to develop a continuous flow system led to the necessity of simulating the counter-current hydrolysis system with stirred tank equilibrium stages in which the solid and liquid were filter separated and transported by hand from stage to stage. This processing scheme consisted of four stirred tanks suspended in a 45°C water bath to maintain a constant reaction temperature. Enzyme and substrate were introduced into each of the vessels and allowed to contact for twelve hours. At the end of this contacting period, the liquid and solid were filter separated and the liquid was sent to the next reactor while the solid was sent to the previous reactor. The solid and the liquid each had a residence time of 48 hours in the system.

This process was allowed to proceed through the entire cycle three times (144 hrs) before any samples were taken. The purpose of this was to allow the system to reach steady-state and to minimize any random fluctuations associated with the start of the process. Samples were then taken at each of the twelve hour periods and sugars were measured by the DNS method.

Results are plotted (fig. 6-2) versus a typical batch hydrolysis, and it is found that a four stage counter-current process can equal the conversion obtained by a batch hydrolysis in 48 hours. Work performed by Wei[1] however, indicates that a three stage co-current contacting

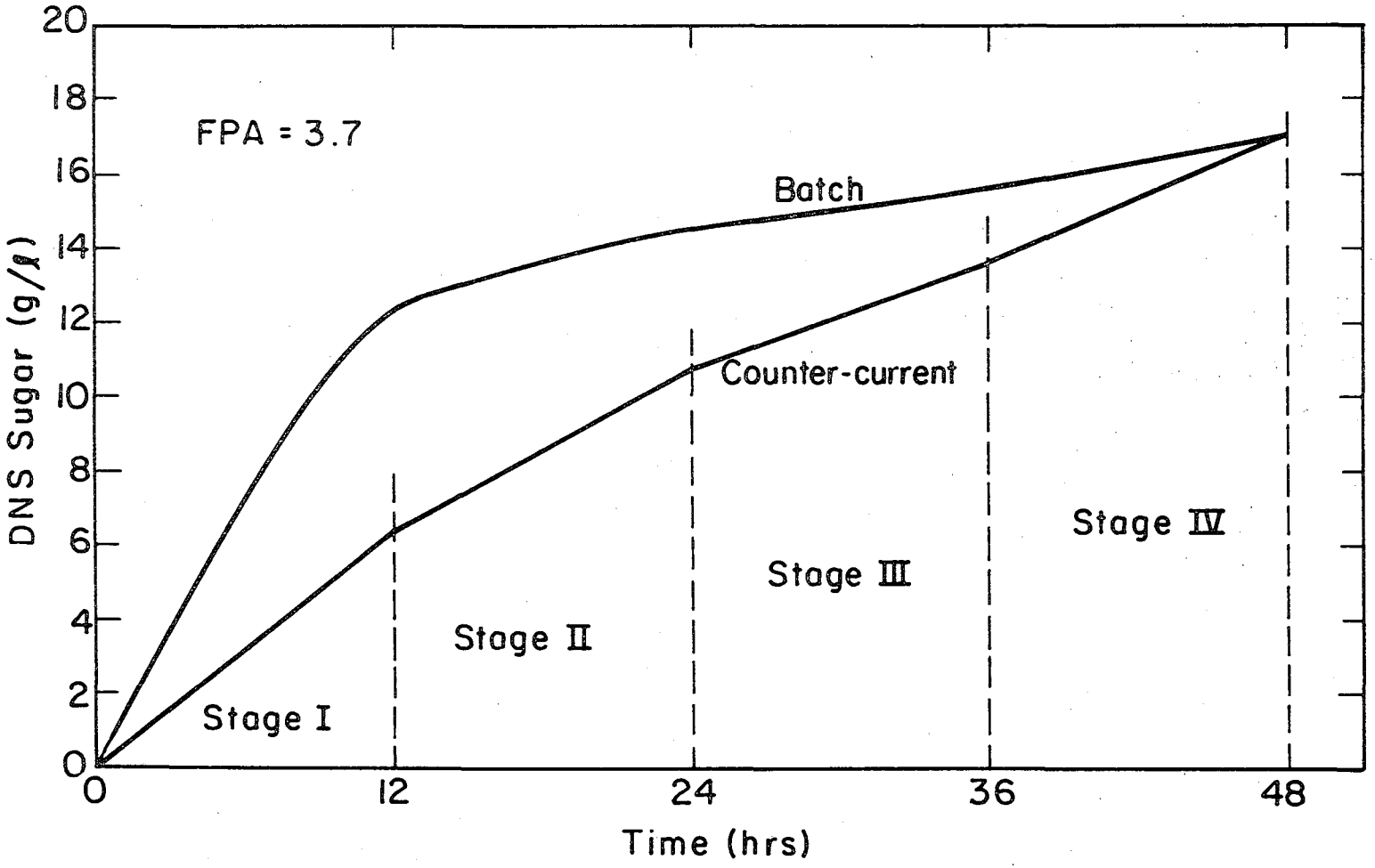


Fig. 6.3. Batch vs 4-stage counter-current hydrolysis.

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system can equal batch conversion. Thus counter-current contacting provides no significant process improvement; in fact, a counter-current system would require more equipment and a more complicated processing scheme -- both of which would tend to raise the cost of the system.

REFERENCES FOR CHAPTER 6

1. Wei, J., M.S. Thesis in Progress, Univ. of Calif.-Berkeley, Dept. of Chemical Eng.

Chapter 7 KINETICS OF HYDROLYSIS

7.1 Derivation of Kinetic Model

To simulate the process for conversion of cellulosic materials to sugars a model for the hydrolysis of cellulose is required. However, the breakdown of cellulose by the action of a cellulase enzyme mixture is a complicated mechanism, which the effects of varying quantities of lignin, amorphous and crystalline cellulose, and possible synergistic enzyme reactions make it very difficult to qualitatively describe this mechanism.

Typically, the enzymatic hydrolysis of cellulose is characterized by a rapid initial rate of conversion followed by a decreasing rate of reaction as time progresses. When product versus time data is plotted, a curve with a hyperbolic shape is obtained. Earlier attempts to quantitatively analyze the shape of this curve based on Langmuir's isothermal adsorption theory have been moderately successful. However, research[1] has indicated that there is inhibition of the rate of reaction by the product sugars.

Therefore, the enzyme reaction can be represented by Michaelis-Menten kinetics relating the enzyme catalyst (E) and the substrate (S), modified for product (P) inhibition:

$$E + S \longrightarrow ES$$

$$ES \longrightarrow E + P$$

$$E + P \rightleftharpoons EP$$

This leads to the familiar rate expression:

$$\frac{dP}{dt} = \frac{V_m S}{K_m(1+P/K_2) + S}$$

To account for the complexity of the substrate system, Yamanaka[2] has suggested a further modification of the rate expression in the form of an accessibility factor (α) to utilize only those regions of substrate accessible to enzymatic attack:

$$\frac{dP}{dt} = \frac{V_m \alpha S}{Km(1+P/K_2) + \alpha S}$$

Work performed by Wei[1] further postulates that a more precise fit of experimental data may be obtained by taking into account the variance in the accessibility of the substrate as more product is formed. Hence:

$$\alpha = \alpha_o e^{-K_1 P}$$

and,

$$\frac{dP}{dt} = \frac{V_m \alpha_o e^{-K_1 P_S}}{K_M(1+P/K_2) + \alpha_o e^{-K_1 P} S}$$

Realizing that the substrate concentration may be expressed as a function of the initial substrate concentration (S_o) and the product concentration:

$$S = S_o - P$$

The rate expression may be written in its final form:

$$\frac{dP}{dt} = \frac{V_m \alpha_o e^{-K_1 P} (S_o - P)}{K_M(1+P/K_2) + \alpha_o e^{-K_1 P} S_o - P)}$$

Where V_m, K_m, α_o, K_1, and K_2 may be found from experiments.

7.2 Initial Rate Studies

7.2.1 Theory

The above rate expression may now be limited to the region when the product concentration is small enough to be considered negligible. This gives the form of the initial rate equation:

$$\left(\frac{dP}{dt}\right)_o = V_o = \frac{V_m \alpha_o S_o}{K_M + \alpha_o S_o}$$

Rewriting and inverting:

$$\frac{1}{V_o} = \left(\frac{K_m/\alpha_o}{V_m}\right)\left(\frac{1}{S_o}\right) + \frac{1}{V_m}$$

which may be utilized according to the Lineweaver-Burk method to determine values for K_m/α_o and V_m.

Because the relationship between FPA and dilution of the enzyme is nonlinear, it is possible to utilize each dilution as an independent enzyme solution. This allows the use of a batch of concentrated enzyme to study the effects of enzyme solutions with varying activities. It is stressed that this application can only be reasonable if the activity -- dilution curve is nonlinear.

7.2.2 Experimental Methods and Results

To apply the Lineweaver-Burk analysis to the kinetic model, it was necessary to obtain initial rate data for varying concentrations of substrate. These concentrations were based on the cellulosic content of the substrate, which for future design considerations was chosen to be corn stover (cellulose content 57.7%). To obtain data that would be relevant for design purposes, solid concentrations were selected as 2.5, 5.0, 7.5, and 10. wt.%. These correspond to cellulose concentrations of 1.44, 2.89, 4.33, and 5.77 wt.%, respectively. Similarly, enzyme activities were selected to produce a scope sufficient to determine the optimal activity -- 2.1, 3.5, 4.4, 5.1, and 5.6 FPA. Due to the large number of initial rate tests required, and the necessity of closely controlling the time, a simple method for conducting the hydrolysis was conceived.

The enzyme complex tends to be adsorbed very rapidly; therefore it is required that the time intervals be kept to a minimum. For this reason, samples were taken at 5, 10, 15, 20, 30, and 45 minutes. To accommodate this rapid sampling, the required amount of stover was placed in a test tube for each of the times that samples were to be taken. Enzyme of the appropriate activity was introduced rapidly to each of the test tubes via a Repipet assembly. Throughout this process, the enzyme and the test tubes of corn stover were kept in a 45^{o}C water bath to prevent any lag in cellulase activity due to temperature difference. The test tubes were then agitated by means of a shaker bath.

At the correct time, a sample was removed from the water bath and injected with 3 drops of 10 N sodium hydroxide to prevent any further catalytic activity. A 1 ml sample of the liquor was then pipeted off and sugars were analyzed by the DNS method. Each activity of enzyme was analyzed twice by this procedure for each of the four substrate concentrations.

A typical curve for this hydrolysis is shown in Figure 7-1, and the data required for the determination of K_m/α_o and V_m are summarized in Table 7-1. Data was analyzed by insertion into a program specifically written to determine the constants by the Lineweaver-Burk method. This program and a short discussion of the approach are included in Appendix 1. Table 7-2 contains the relevant output from the program and Figure 7-2 shows the expected straight line plot of V_m versus the dilution of the enzyme. The fact that this line does not intersect the origin may be attributed to the sensitivity obtained by the DNS analysis (DNS measures all reducing groups).

7.3 Hydrolysis Modeling

7.3.1 Experimental Methods and Results

Based on research performed by Wilke et al,[3] all hydrolyses were run at 5.0 wt.% solids (acid treated corn stover as a substrate) and 3.5 FPA. Hydrolyses were at 45°C in well stirred vessels with a total residence time of 48 hour.

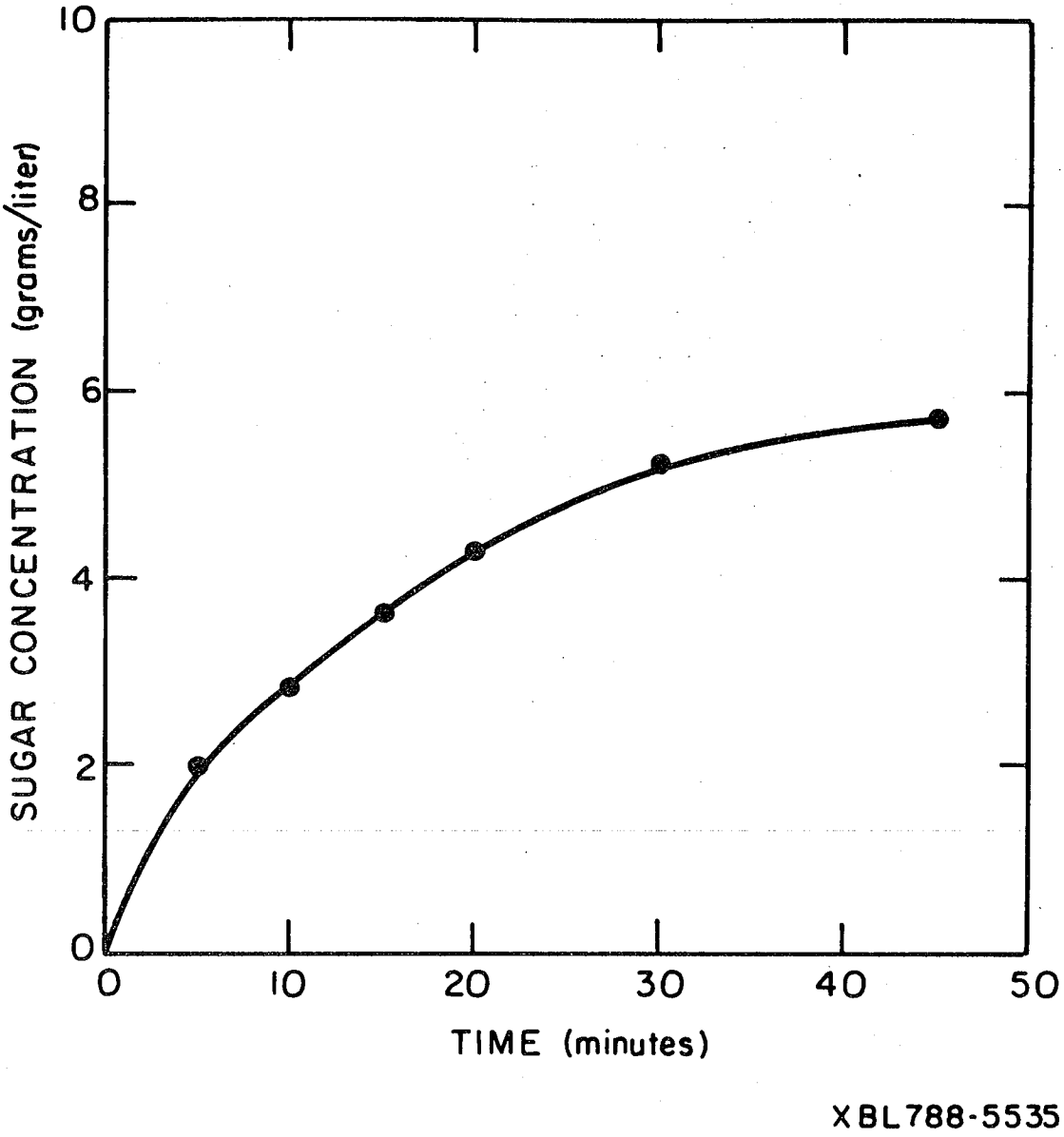

Fig. 7.1. Initial rate hydrolysis.

TABLE 7-1

	$1/V_o$ $(\frac{\ell \cdot min}{g})$				
FPA	2.1	3.5	4.4	5.1	5.6
1/So (ℓ/g)					
0.06932	4.423	3.846	3.333	2.800	2.940
0.03466	3.109	2.564	2.000	1.613	1.613
0.02311	2.753	2.083	1.724	1.500	1.203
0.01733	2.513	1.883	1.563	1.231	1.389

TABLE 7-2

FPA	$\frac{K_m}{\alpha_o}$ (g/l)^q	V_m (g/l)
2.1	19.4404	0.5319
3.5	30.8963	0.8156
4.4	37.8515	1.0982
5.1	41.0660	1.3900
5.6	55.1358	1.6735

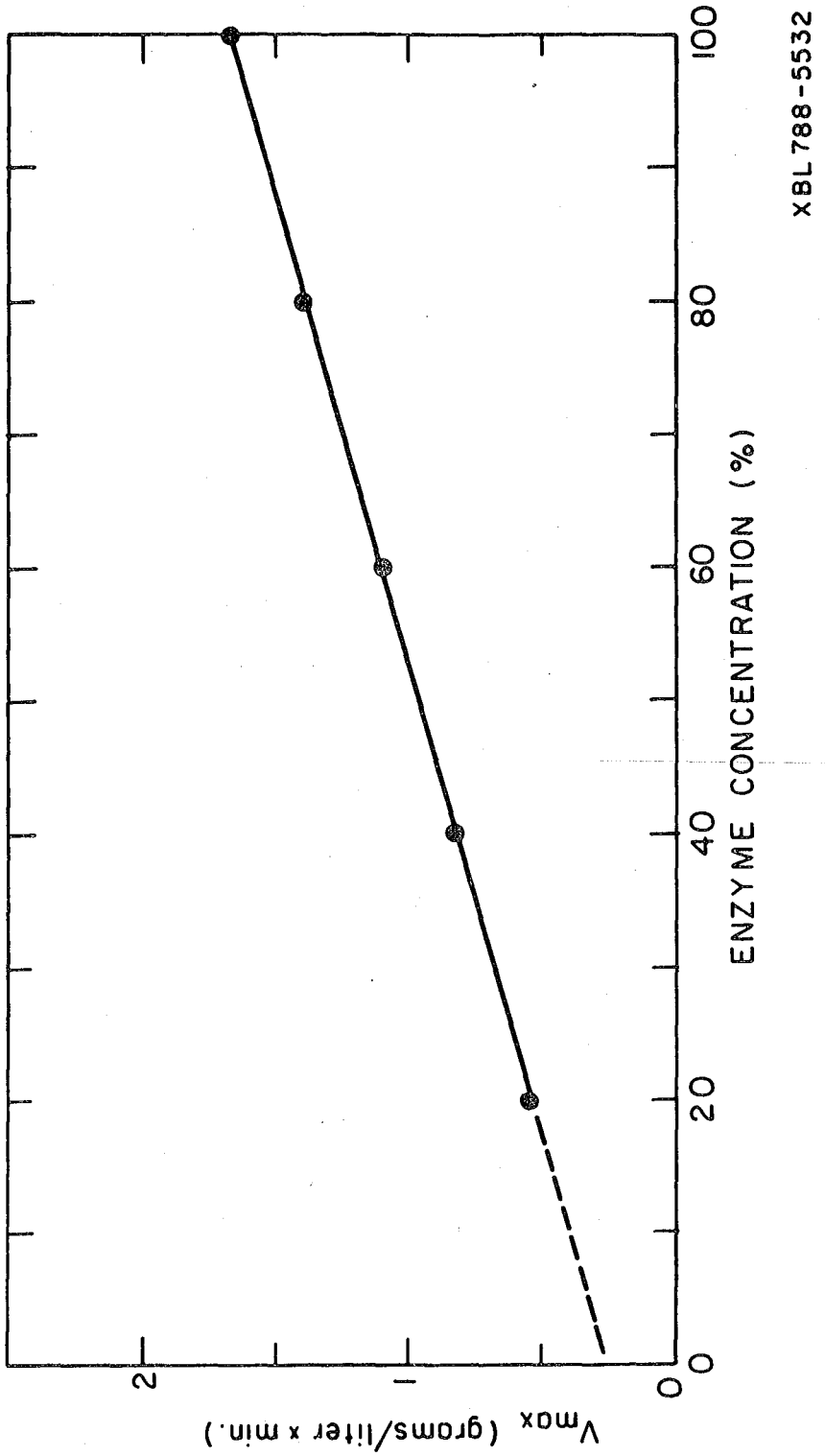

Fig. 7.2. V_{max} vs enzyme dilution.

Previous work had not been concerned with the earlier periods of hydrolysis; however for the purpose of accurate modelling, it was necessary to obtain a well defined curve. For this reason, samples were taken at 1, 2, 4, 8, 12, 36, and 48 hours. Sugars were analyzed by both the DNS method and by gas chromatography. Results were typical of previously reported batch hydrolysis curves, and the average of three batch curves is shown in Figure 7-3.

7.3.2 Computer Fit of Batch Hydrolysis

Having previously determined the kinetic parameters K_m/α_o and V_m, it is now necessary to find the inhibition constant K_2 and the accessibility constant K_1. Utilizing the kinetic model, a relaxation technique may be applied to determine these values for the hydrolysis system of cellulase and corn stover.

The kinetic equation may be written:

$$\frac{dP}{dt} = \frac{V_m e^{-K_1 P} (S_o - P)}{Km/\alpha_o \ (1+P/K_2) + e^{-K_1 P} (S_o - P)}$$

Extending the differential to the change in product concentration with time and measuring all changes from t=0 (P=0) gives:

$$\frac{P}{t} = \frac{V_{me}^{-K_1 P} (S_o - P)}{Km/\alpha_o \ (1+P/K_2) + e^{-K_1 P} (S_o - P)}$$

Where P is the product concentration at time t. Now solving for K_2;

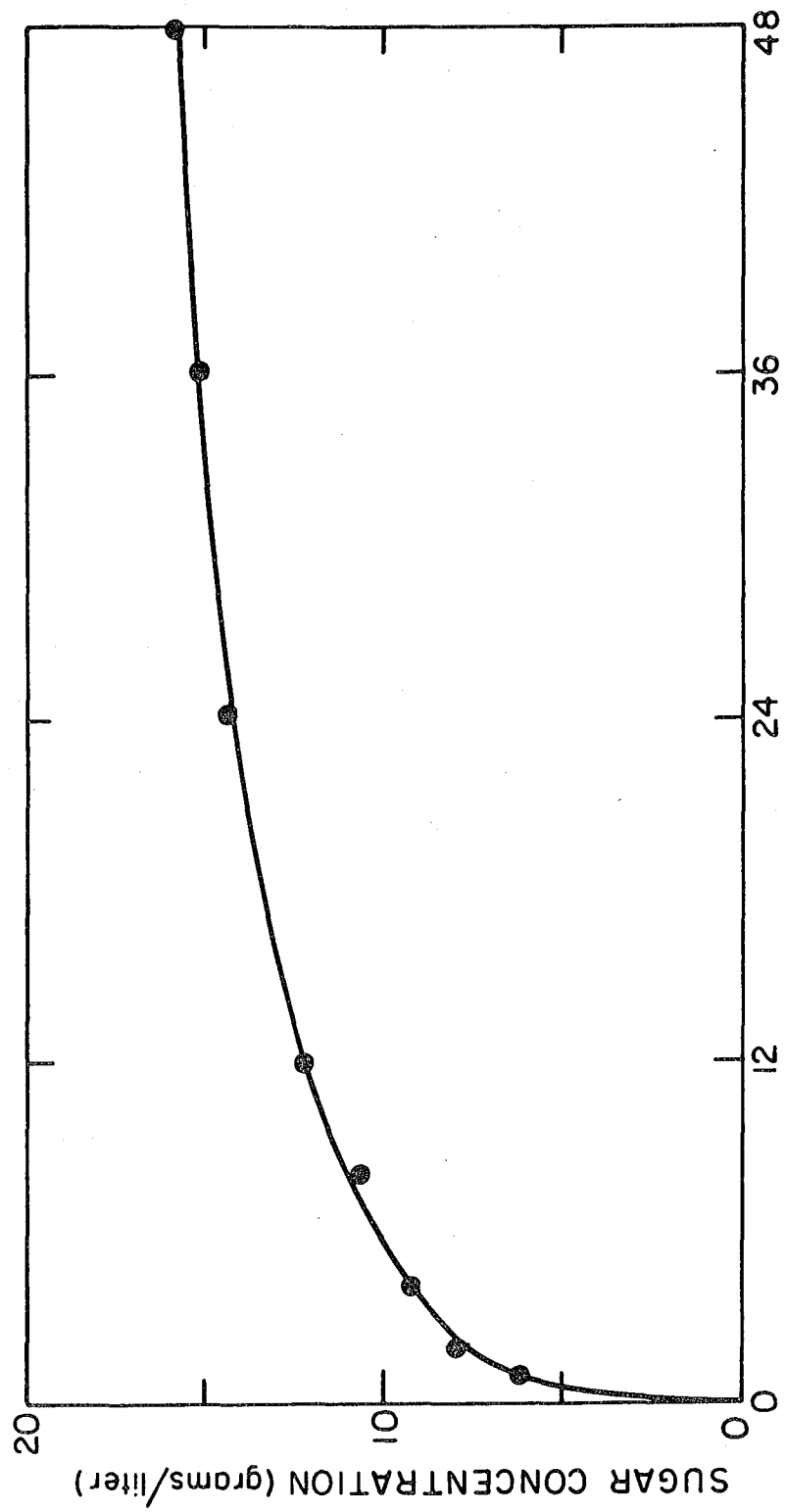

Fig. 7.3. Average batch hydrolysis curve.

it can be shown:

$$K_2 = \frac{P}{\frac{e^{-K_1 P}(S_o - P)}{K_m/\alpha_o}\left(\frac{tV_m}{P} - 1\right) - 1}$$

Applying this equation in a computer program (a listing of this program is included in Appendix 1), the kinetic parameters K_m/α_o and V_m were combined with the P versus t data obtained in the batch hydrolysis experiments. By relaxing the value for K_1 for each of the P and t points, values for the mean K_2 and the standard deviation of K_2 were calculated. When the standard deviation of K_2 versus the value of K_1 reached a minimum, these values were used to determine the constants. The values for K_1 and K_2 in the cellulase -- stover system were found to be 0.19369 and 9.18527647 respectively.

These constants and the kinetic parameters determined earlier were used in the program outlined in 7.3.3 to compare with the experimental data from the batch hydrolysis. Results of this comparison may be seen in Figure 7-4. It is evident that the computer fit thus generated fits the hydrolysis data well enough to fall within experimental error.

7.3.3 Computer Predictions of Batch Hydrolysis

If the kinetic model is rewritten in the following way:

$$P_1 = \frac{tV_m e^{-K_1 P_2}(S_o - P_2)}{Km/\alpha_o\,(1+P_2/K_2) + e^{-K_1 P_2}(S_o - P_2)}$$

it is possible to construct a computer program to iterate over the

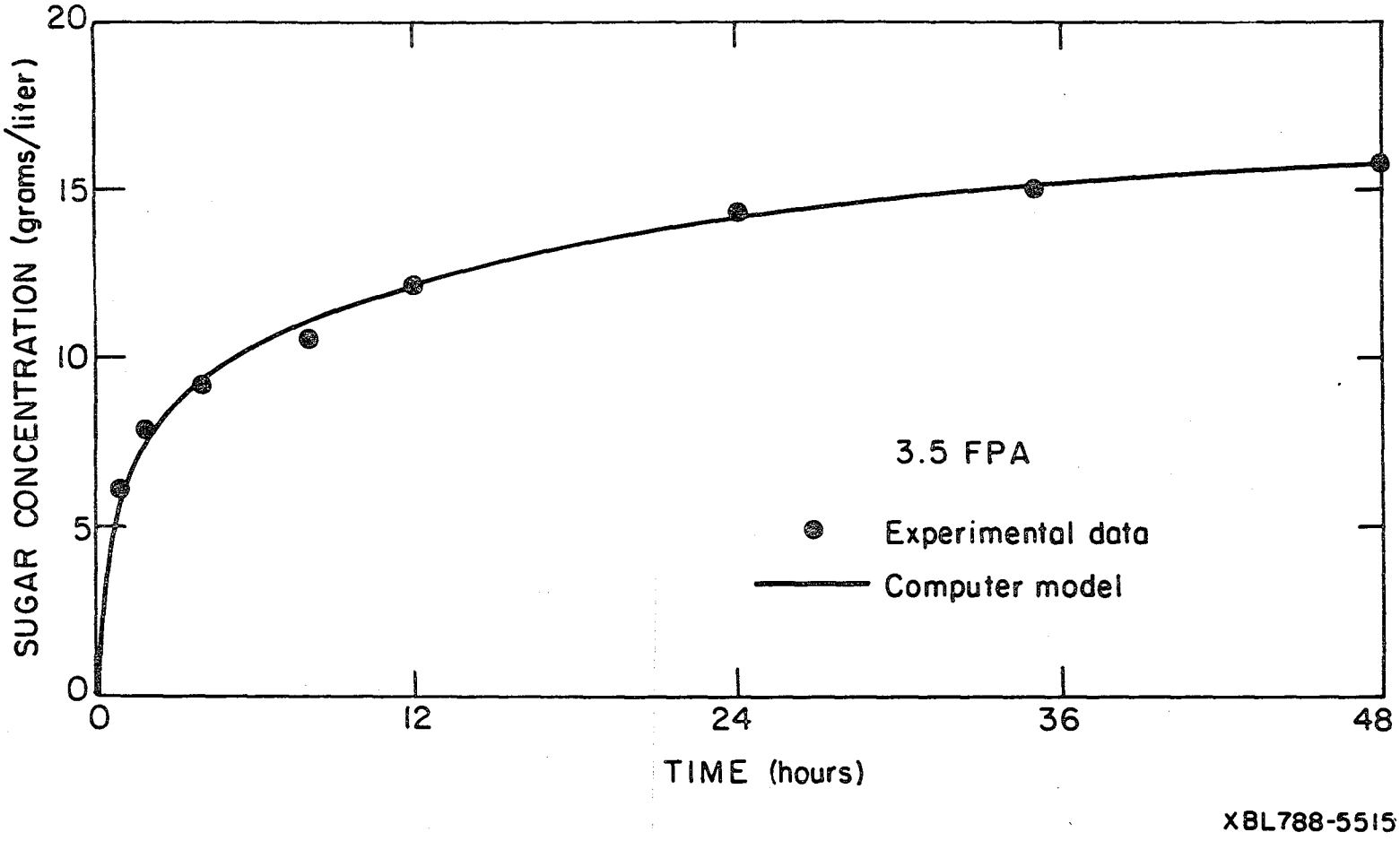

Fig. 7.4. Computer fit of batch hydrolysis.

model, thereby calculating the concentration of sugars at any given time. The listing for this is located in Appendix 1.

The most basic and straightforward approach to this convergence would be to guess a value of P_2, use that value to calculate P_1: and then to use that value of P_1 as a new value for P_2 to calculate a new P_1 -- and so on until the system converged. At best this method tends to be slow, and at worst, it may not converge at all. To overcome the problem of speed, a convergence algorithm known as the Golden Section[4] was utilized. This method effectively decreases the area of consideration by 68% with each iteration. However, when the slope of the curve begins to level off, this technique does not converge very well. This is due to the fact that for a very small Δy there can be a very large Δx, inducing a forced oscillation in the system. This problem can be circumvented by the insertion of a counter within the Golden Section algorithm. When the counter exceeds a predetermined number of iterations, the convergence is then switched to an algorithm which increments the last satisfactory value by a small amount. This method assures that a convergence will be obtained.

Using the kinetic parameters determined in the inital rate experiments and the constants for inhibition and accessibility, it is possible now to predict the product versus time curves for batch hydrolysis. Results of these predicitions may be seen in the accompanying figures (Fig. 7-5 through 7-9). It should be noted that this modeling is under the assumption that the systems are well mixed, so extension of the model to higher substrate concentrations where adequate mixing may or may not be possible is dangerous, and may lead to unreliable predictions.

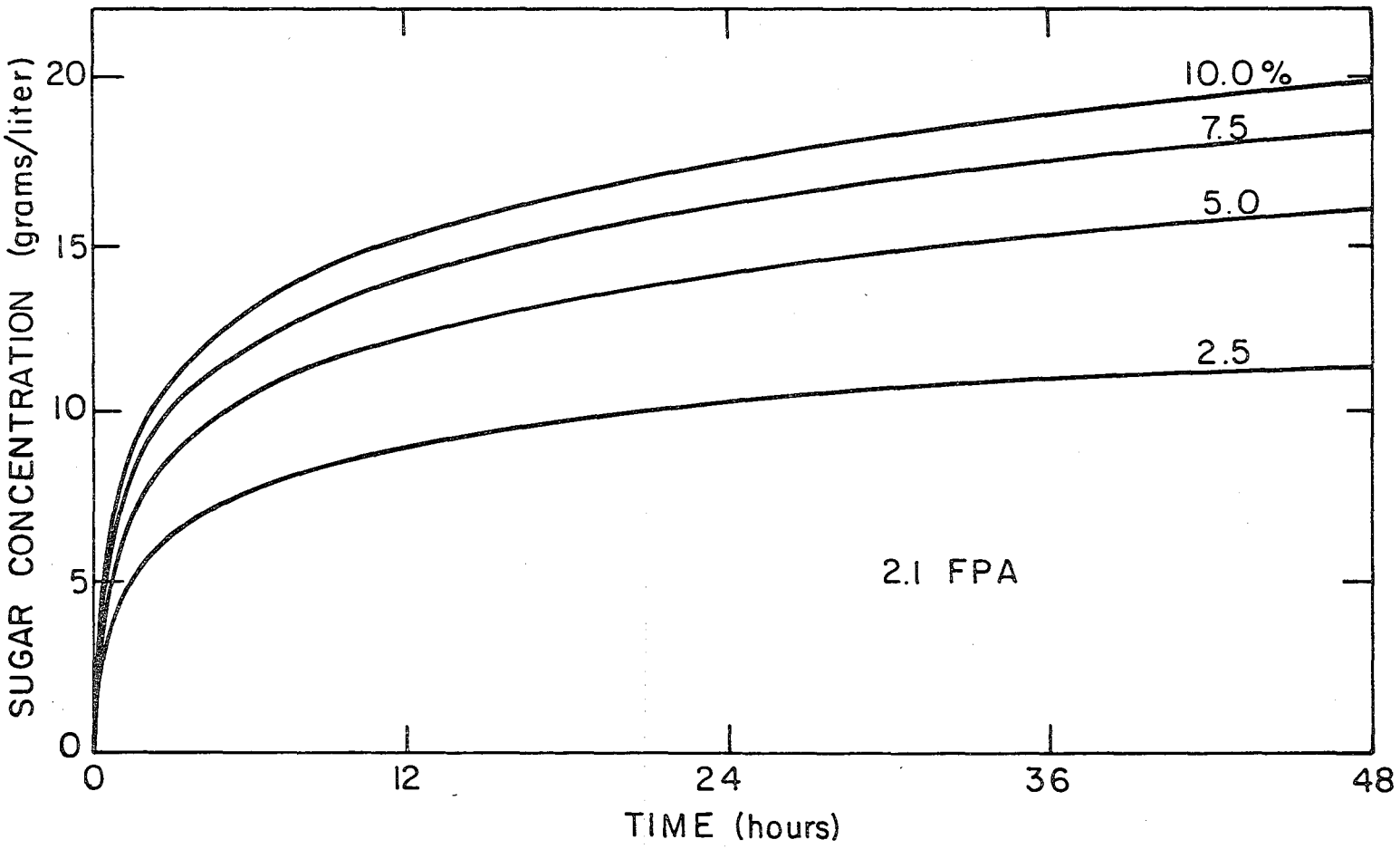

Fig. 7.5. Computer predictions for batch hydrolyses (various substrate concentrations).

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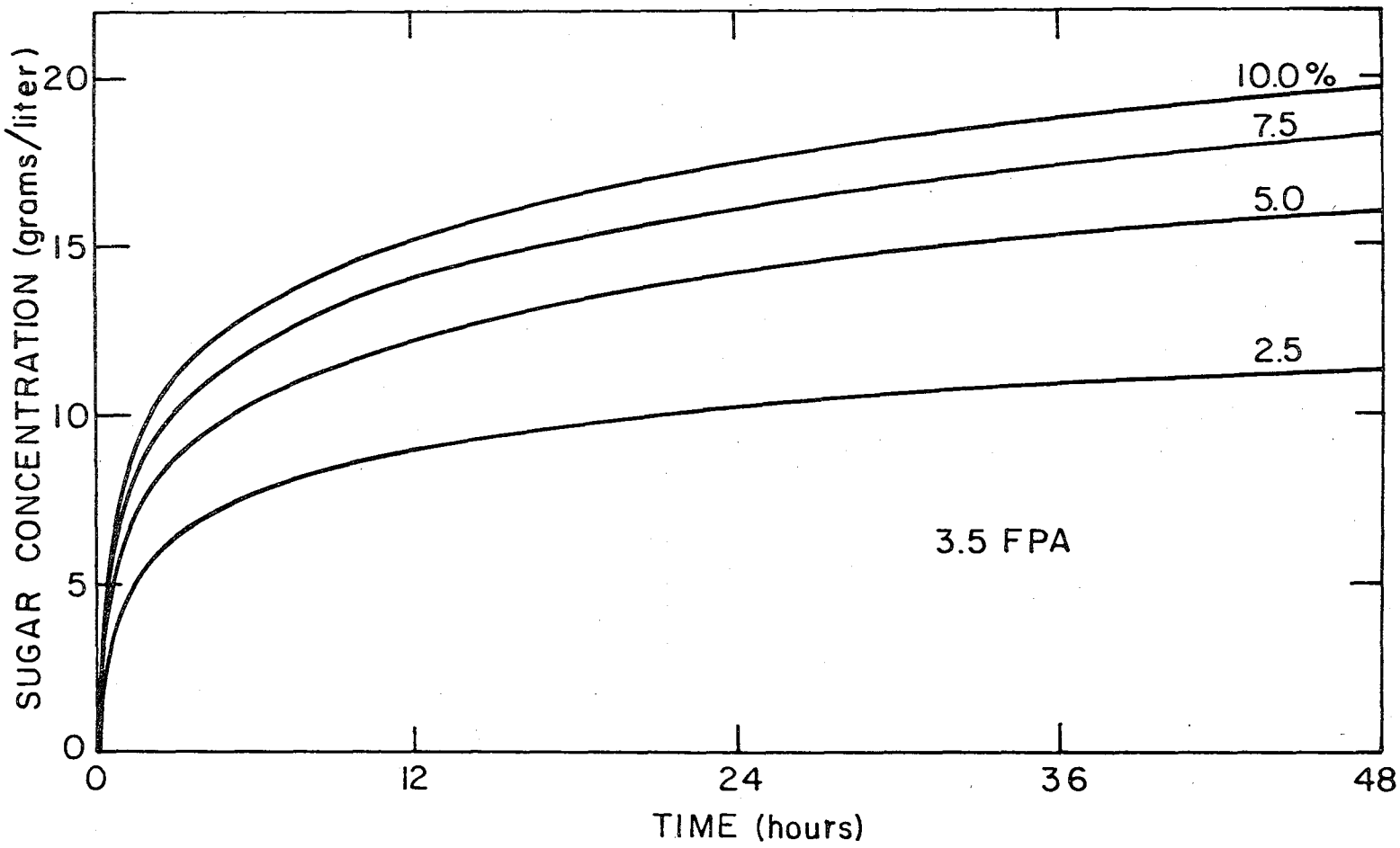

Fig. 7.6. Computer predictions for batch hydrolyses (various substrate concentrations).

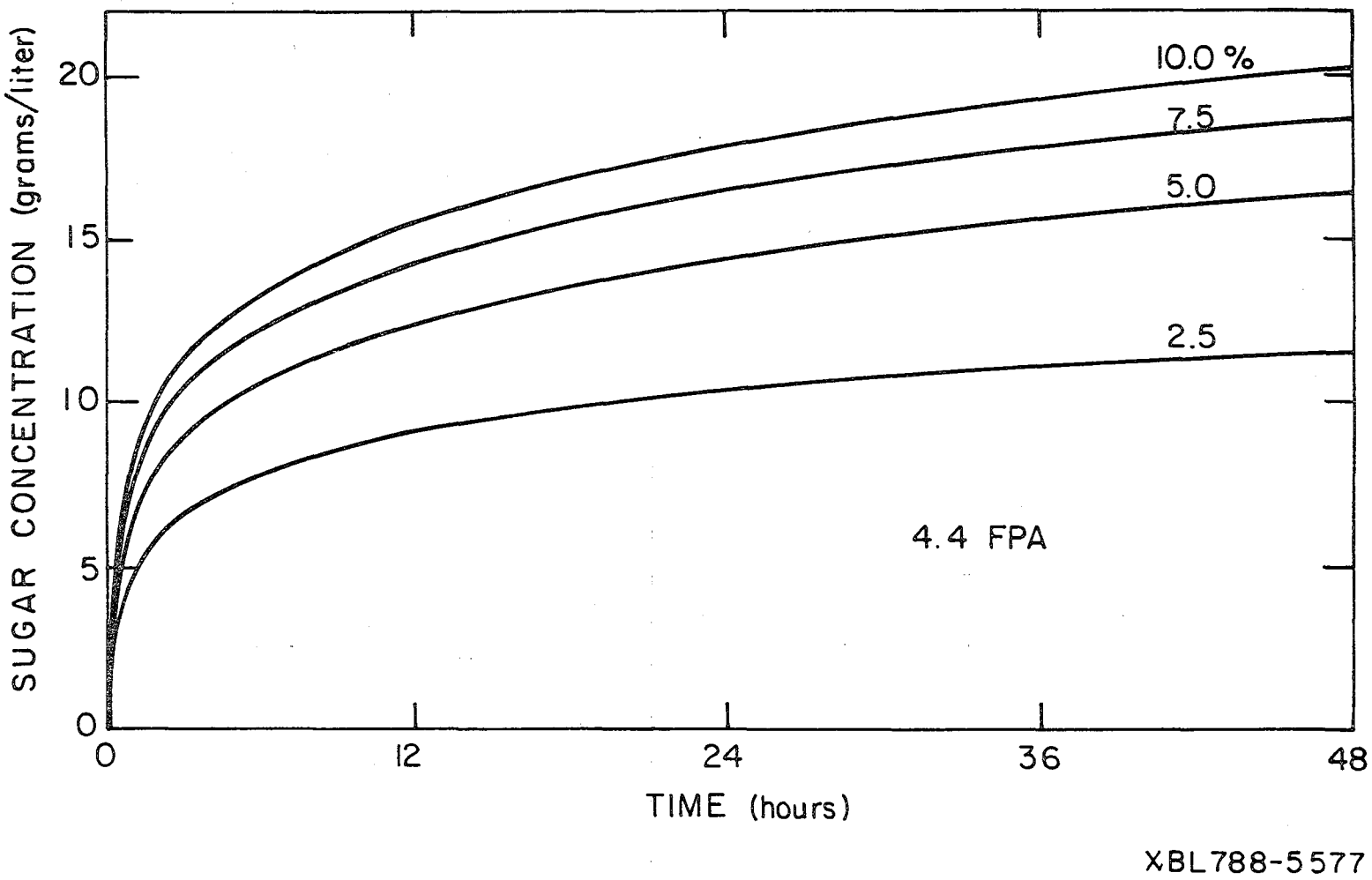

Fig. 7.7. Computer predictions for batch hydrolyses (various substrate concentrations).

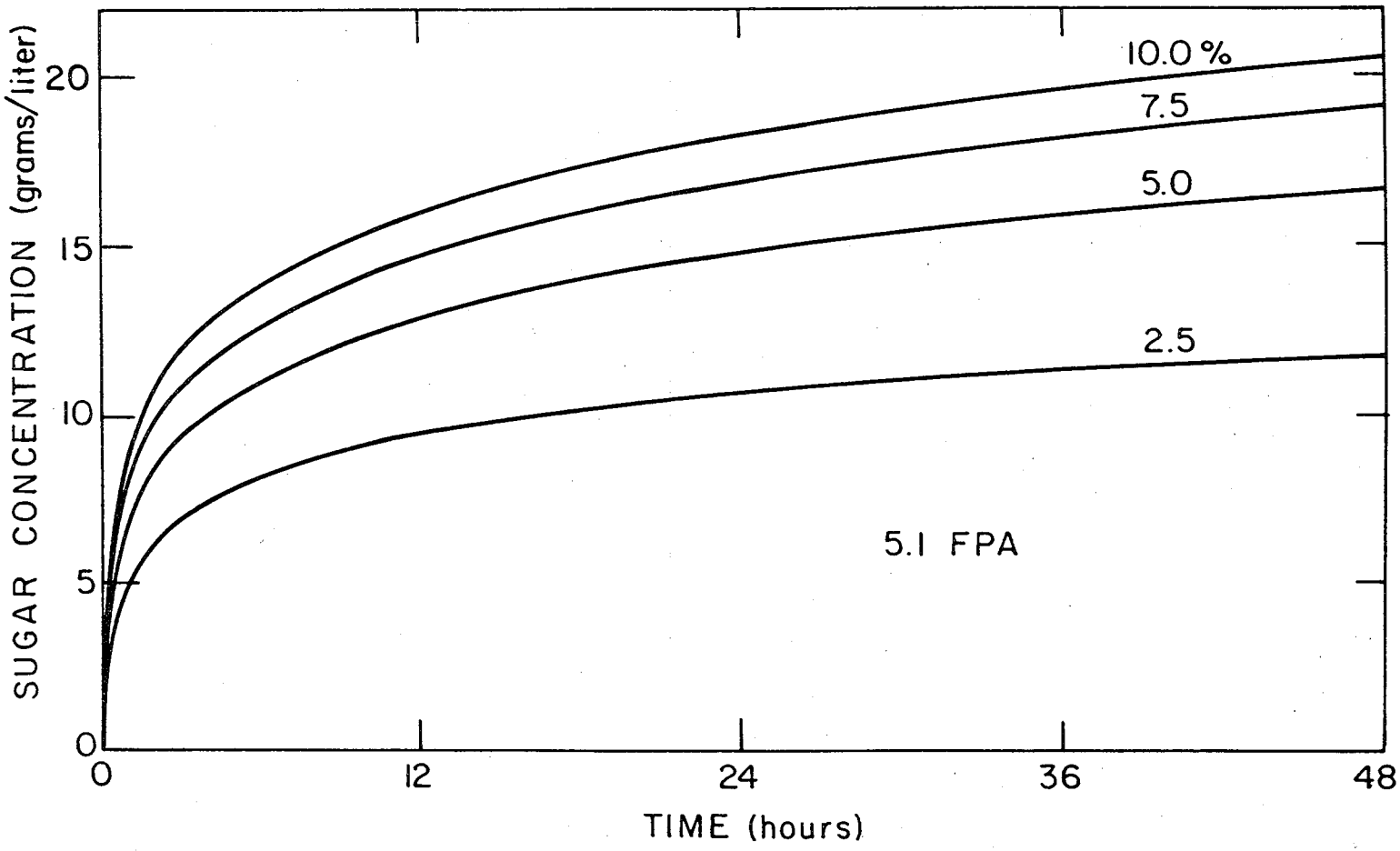

Fig. 7.8. Computer predictions for batch hydrolyses (various substrate concentrations).

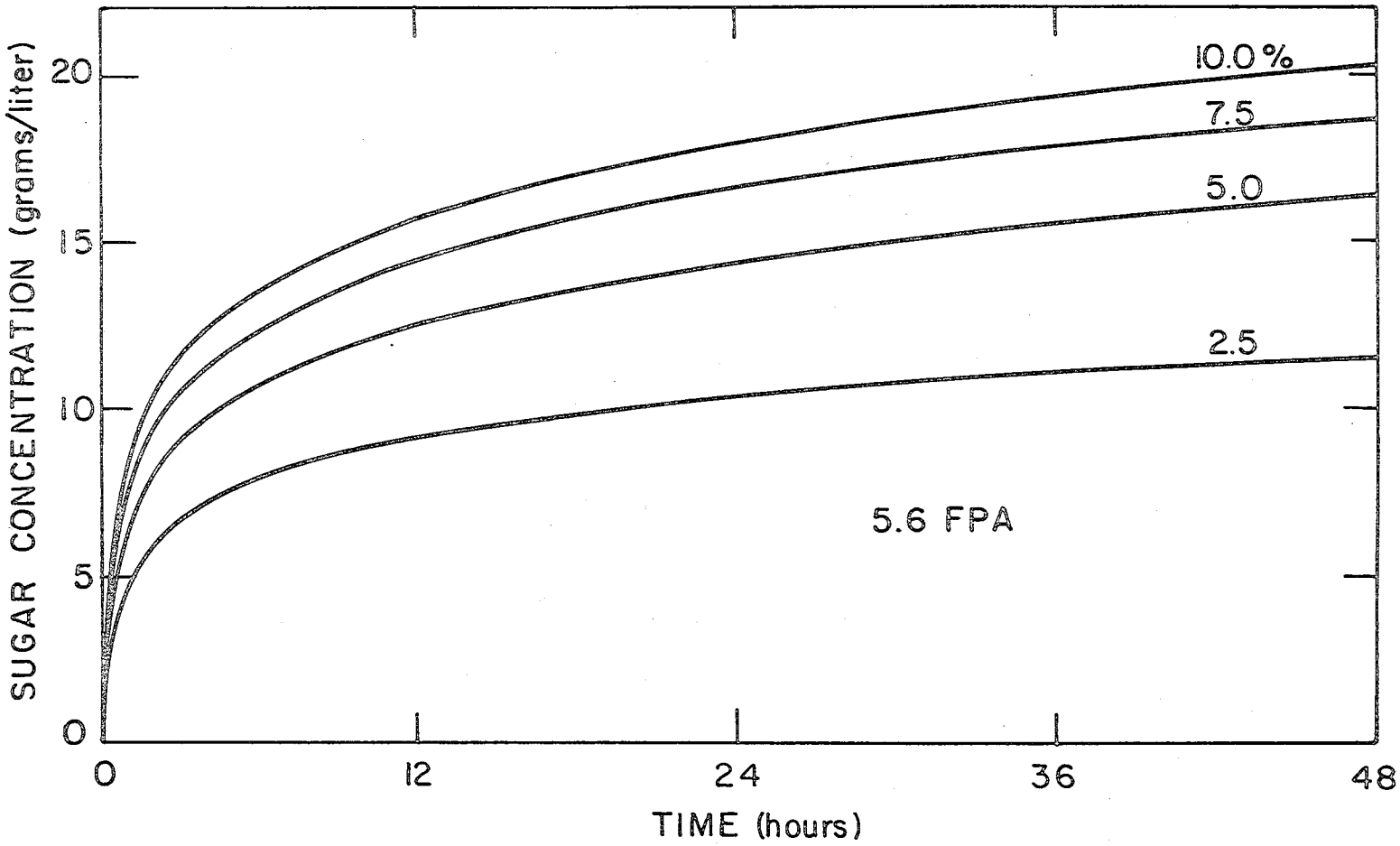

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Fig. 7.9. Computer predictions for batch hydrolyses (various substrate concentrations).

REFERENCES FOR CHAPTER 7

1. Wei, J., M.S. Thesis in Progress, Univ. of Calif.-Berkeley, Dept. of Chemical Eng.

2. Yamanaka, Y. and Wilke, C. R., The Effect of β-Glucosidase on the Enzymatic Hydrolysis of Cellulose, UC-LBL-4413, December 1975.

3. Wilke, C. R., Yang, R., Sciamanna, A. F. and Frietas, R. P., Evaluation and Process Development Studies for Conversion of Biomass to Sugars and Ethanol, UC-LBL-7847, June 1978.

4. Rudd, D. F. and Watson, C. C., Strategy of Process Engineering, John Wiley and Sons, NY, 162, (1968).

Chapter 8 COMPUTER DESIGN

8.1 Design Background

Previous[1,2,3,4] process designs, although useful in their own right, have made no attempt to optimize the design system. Residence time had been set at 40 hours, with a 5.0 wt% solids suspension and a Filter Paper Activity of 3.5. This type of analysis shows that the sugar cost is highly dependent on the cost of stover, the conversion obtained in hydrolysis, and the enzyme recovery and production costs. In the most recent design,[4] cost for production of a 14 wt% sugar solution was found to be about 12¢/pound of sugar. This was assuming 58% enzyme recovery, and 40% cellulose conversion.

8.2 Design Basis

The major processing steps in this design are schematically represented in Figure 8-1. Feed to the process is assumed to be corn stover that has previously been milled and acid pretreated by the process outlined[4] in Table 8-1. Enzyme is assumed to be produced by the two stage continuous fermentation designed by Yang.[4] This is summarized in Table 8-2. Recovery of enzyme from the system is assumed to be 40%.

For purposes of ethanol fermentation, the hydrolysis sugar solution is concentrated to 14 wt% with 70% fermentable sugars. This was found by Cysewski[5] to be optimal for the fermentation process. Waste solids from the hydrolysis section are burned to provide energy for the system. Excess energy from this may further be utilized in the ethanol fermentation system.

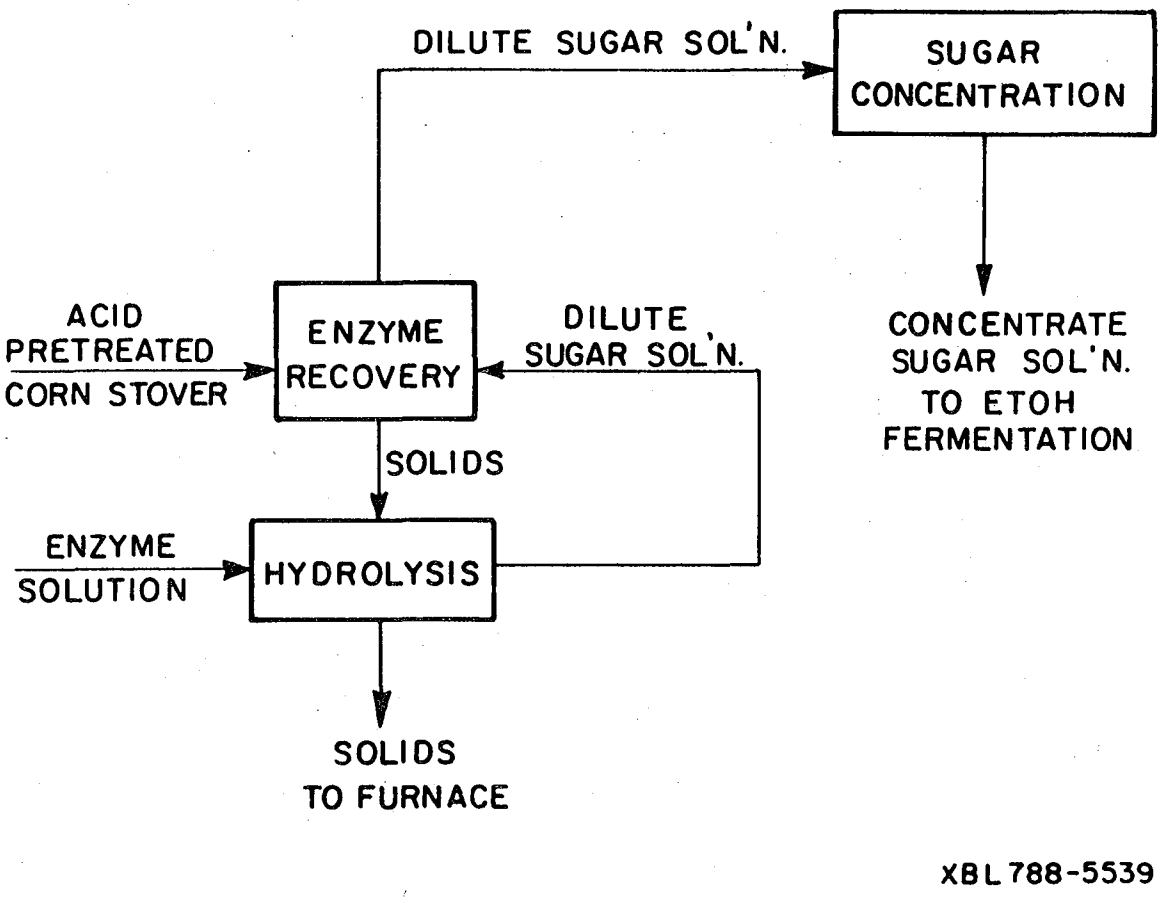

Fig. 8.1. Process schematic.

TABLE 8-1

SOLID PREPARATION

FEED (corn stover)	1376 T/D
MILLING (by hammermills)	-20 mesh
ACID PRETREATMENT	0.09 M H_2SO_4
SUSPENSION	7.5 wt%
TEMPERATURE	100 C
RESIDENCE TIME	5.5 hours
ACID EXTRACTS (70% xylose)	181 T/D, Sugar/acid=2.4
SOLIDS TO SYSTEM	885 T/D

TABLE 8-2

TWO STAGE CONTINUOUS CELLULASE PRODUCTION

INLET CELLULOSE CONCENTRATION	6.5 g/l
TEMPERATURE (both stages)	30 C
pH (both stages)	4.8
SPECIFIC GROWTH RATE	0.06 hr^{-1}
CELL RECYCLE RATIO	0.8
AVERAGE CELL CONCENTRATION	7 g/l
DILUTION RATE	0.027 hr^{-1}
ENZYME PRODUCTIVITY (in International Units)	0.46 U/ml-day

8.3 Cost Estimation

Process equipment costs were estimated by the methods described in Peters[6] and Guthrie.[7] The graphical cost data from these references were fitted to exponential equations relating the F.O.B. equipment cost to the equipment size. These equations were further generalized by dividing by the Marshall Steven cost index for the year of reference. A summary of these equations and their maximum unit capacity is shown in Table 8-3. When the process design dictated a larger total equipment capacity than the listed maximum, an integral number of equally sized units were used.

After the calculation of the F.O.B. equipment costs, a Lang factor[6] of 3.1 was applied to estimated the total fixed capital investment. A breakdown of this factor is shown in Table 8-4. The multiplier was decreased to 1.68 for the concrete hydrolysis vessels because the unit cost already included engineering and construction fees.

Total operating costs are divided into three areas: (1) capital related costs; (2) labor related costs; and (3) utilities costs. A summary of the capital related costs is shown in Table 8-5. Here a 10 year straight line depreciation was assumed and taxes have been omitted on the assumption that the plant would be a municipally operated facility. The effect of possible taxes is considered in a later section. Total capital related costs therefore amount to 24% of the fixed capital investment per year.

Labor costs are based on a rate of $5.99 per hour,[8] with an 8500 hour year. The labor requirement for each section of the process is determined by the number of pieces of equipment in that section.

TABLE 8-3

ITEM	UNIT COST $FOB	SIZE UNIT	MAX SIZE	REFERENCE
MIXING TANKS	MSI $0.654(size)^{0.53}$	gallons	50,000	6
AGITATORS	MSI $3.33(size)^{0.56}$	horsepower	400	6
PUMPS	MSI $(2.64+0.0068(size)^{0.718})$	PSI X GPM	3×10^5	7
SOLID FEEDERS	MSI $0.00462(size)^{0.72}$	pounds/hour	7,400	6
FILTERS	MSI $0.5932(size)^{0.6}$	pounds/hour	7,400	3
HYDROLYSIS TANKS	MSI 0.000783(size)	gallons	------	9
HEATING TUBES	MSI $0.1626(size)^{0.6}$	sq. feet	------	6
EVAPORATORS	MSI $0.938(size)^{0.6}$	sq. feet	------	11

MSI=MARSHALL STEVEN COST INDEX

TABLE 8-4

DETERMINATION OF LANG FACTOR FOR ESTIMATION OF FIXED CAPITAL INVESTMENT FROM MAJOR EQUIPMENT COST

I. DIRECT COSTS (D)	FACTOR
Purchased Equipment (E)	1.0
Installation	0.3
Piping	0.2
Instrumentation	0.1
Insulation	0.06
Electrical	0.1
Building/Facilities	0.3
Land/Yard Improvement	0.1
	2.16
II. INDIRECT COSTS (I)	
Engineering and Construction	0.25D
Contractor's Fee and Contingency	0.15(D+0.25D)
III. FIXED CAPITAL INVESTMENT (D+I)	
(1.15)(1.25)(2.16E)=3.1 E	

TABLE 8-5

CAPITAL RELATED COSTS

ITEM	FACTOR
DEPRECIATION	0.10
INTEREST	0.06
TAXES	0.0
MAINTENANCE	0.06
INSURANCE	0.01
SUPPLIES	0.01
TOTAL	0.24

The total labor cost is then determined by use of a multiplying factor of 1.95 as indicated in Table 8-6. Utilities costs for steam and electric power were set at $\$3/10^6$ BTU's and 3 ¢/KW-hr respectively. The solid hydrolysis residue was burned to provide energy for the system, this could effectively reduce or eliminate the utilities costs, and any excess BTU's can be utilized for ethanol production. No cost for process water was included under the assumption that the water would be reclaimed in the ethanol fermentation system.

Enzyme cost is set at $1.21 per pound based on the design and cost estimation by Yang.[4] Similarly, the corn stove feed cost is set at 0.74 ¢/pound, the costs of milling to -20 mesh and subsequent acid pre-treatment (independent of the original stover cost).[4] Sensitivity of the process with respect to these costs is determined in a later section.

Total product cost ($/yr) is determined by the summation of all of the above costs and credits. The cost per pound of sugar is then calculated by dividing total product cost by the total pounds of sugar produced per year. Product is defined as a 14 wt% solution of hydrolysis sugars.

8.4 Determination of Process Flows

To determine accurately the equipment sizes for application of the cost equations, flows in the system must first be determined. This section is to serve as a generalized outline to the methods used in the process optimization program SUGAR (a listing of this program is included in Appendix 2). The major flow equations are listed, with brief comments indicating their logical order of progression.

TABLE 8-6

LABOR RELATED COSTS

ITEM	FACTOR
DIRECT LABOR COST	1.00
SUPERVISION	0.15
PAYROLL OVERHEAD	0.15
LABORATORY	0.15
PLANT OVERHEAD	0.50
TOTAL	1.95

The pretreated feed stream may be arbitrarily selected, depending on the size of the process desired. SMAX is the solid feed to the system for which this design was set at 73,750 pounds/hour. WSMAX is the weight of liquid that comes in with the solids. This was set at 172,083.3 pounds/hour (corresponding to 30 wt% dry solids).

Knowing the Filter Paper Activity required in the hydrolysis section (FPA), the pounds of enzyme per gallon (ENZ) may be calculated:

ENZ=0.00835*EXP((FPA-3.293)/1.399)

The actual pounds of enzyme per gallon required (RENZ) is based on this number and the assumed actual recovery of enzyme (AR) in the system:

RENZ=(1.-AR)*ENZ

(The actual recovery of enzyme was set at 40%).

Based on the solids concentration desired in the hydrolysis section (SCON) and the solid feed to the hydrolysis section (SMAX), the required volume of hydrolysis liquid (HYDW) may be calculated:

HYDW=SMAX/(SCON*0.00835)-SMAX/8.34

And the total pounds of enzyme required (PENZ) is:

PENZ=HYDW*RENZ

Now the amount of liquid that comes in with the enzyme (WNEZ) may be found using the hydrolysis recycle fraction (RFR):

WENZ=HYDW*(1.-RFR)-WSMAX/8.34

The amount of liquid recycled (RHYD) may also be found:

RHYD=RFR*HYDW

Similarly, the liquid (W) leaving the system is:

W=WENZ+WSMAX/8.34

To design the enzyme recovery system it is necessary to determine an equilibrium coefficient (EQK) and to know the inlet enzyme concentration (YIN) in the liquid stream. It is then possible to iterate through a small program to calculate the number of stages required (NT), and the solid (S) and liquid (W and WS) flows in the system. This is based on a generalized enzyme balance that is successively iterated through a number of stages until the desired enzyme recovery is attained. The reader is referred to the program SUGAR (Appendix 2) for the exact procedure. Based on the flow of solids through the enzyme recovery system (S), the amount of solids that must bypass this system (SBP) can be found by difference:

SBP=SMAX-S

The above flows are fixed, all other flows in the system are residence time dependent. Therefore, by fixing a residence time for hydrolysis (the computer program increments the time, and holds all values in arrays) values for these flows may be calculated. Using the kinetic model the concentration of sugar in the stream leaving the hydrolysis section (P) can be found. This can be used to determine the conversion:

CONV=P/SCON

Now the amount of solids sent to the furnace (SFURN) can be found:

SFURN=SMAX*(1.-CONV)

And the heat from this solid (HEATS) is:

HEATS=SFURN*6000.

The concentration of hydrolyzate sugars (P) is also used to determine the flows in the evaporator section. The flow to the evaporator is

W with P grams/liter of sugar; therefore the pounds of sugar per hour (PSUG) is:

PSUG=P*0.99835*W

To be at 14 wt% solution this amount of sugar requires PRODW gallons of water:

PRODW=(PSUG/0.14-PSUG)/8.34

This means that EVAPW gallons of water must be evaporated:

EVAPW=W-PRODW

This sumarizes the major flows in the design system.

8.5 Sizing of Process Equipment

The worm screw and filter sizes are based on the pounds per hour of solids that they are required to handle. Therefore, no real calculation of size other than the stream flows is required and the cost equations may be directly applied. The size of pumps is based on the flow in gallons per minute, and for the cost equation the size unit is GPM X PSI -- for this purpose a delivery pressure of 1 atm (14.7 psi) is assumed.

The calculation of the total volume of the enzyme recovery system (TVENZR) uses a 0.5 hour contacting time (TENZR), with an 80% working volume based on the liquid volume:

TVENZR=(W+WS)*TENZR/0.8

The volume of each individual vessel (VENZR) is then set by the number of contacting stages required (ENZRN):

VENZR=TVENZR/ENZRN

Similarly, the total volume required for the hydrolysis section (TVHYD) is based on the residence time (HT) in minutes, the required amount

of water (HYDW), and an 80% working volume:

TVHYD=HT*HYDW/48.0

The number of stages (HYDN) is set at three (this was shown by Wei[9] to provide the same conversion as batch hydrolysis), thereby giving the volume of each hydrolysis vessel (VHYDT):

VHYDT=TVHYD/HYDN

These volumes may now be used in the cost relationships.

Agitation for both the enzyme recovery section and the hydrolysis section may now be calculated based on the power required to suspend the solids. The basic eqution for power per unit volume is[10]:

$$\frac{P}{V} = (1-\epsilon_m)^{2/3} \frac{g}{g_c} \rho_m U_t \left(\frac{D_t}{D_a}\right)^{1/2} e^{4.35\beta}$$

where:

$$\beta = \frac{Z_s - E}{D_t} - 0.1$$

(for definition of variables see end of chapter).

In this system standard geometry is assumed,[10] thus:

$$\left(\frac{D_t}{D_a}\right) = 3.0$$

and

$$\beta = 0.567$$

It may be shown that:

$$\rho_m = \frac{\text{Solids \& Liquid}}{\text{Volume}}$$

and

$$(1-\epsilon_m) = \frac{\text{Solids}}{98.4 * \text{Volume}}$$

Using a settling velocity of 0.162 ft/sec calcualted from Stoke's Law, it can be shown that the final equation for the case of the enzyme recovery system (PENZR) becomes:

```
PENZR=0.0081818*(0.162*VENZR*((S+W*62.3)/VENZR)*
     ((S/(98.4*VENZR))**0.666)*1.732*EXP(2.46645))
```

The power requirement for the hydrolysis section may be calculated similarly.

Liquid flowing into the hydrolysis tanks from the enzyme production section (WENZ) is at 30 C, and the desired hydrolysis temperature is 45 C. To determine the heat transfer area (HHTA) required to bring this liquid up to temperature, it is necessary to first calculate the number of BTU's required (BTUR):

$$BTUR=WENZ* C_p *\Delta T$$

Using the heat capacity and density of water the equation becomes:

```
BTUR=WENZ*225.18
```

Now assuming an overall heat transfer coefficient of 250 BTU's/(hr-F-ft^2)[6] and heating water available at 100 C the heat transfer area may be

found:

HHTA=BTUR/24750.

To complete the sizing of the equipment an evaporative sugar concentrator must be designed. Assuming the heat of vaporization of water to be 1000 BTU's/pound, the heat required (EVBTU) to evaporate EVAPW gallons of water is:

EVPBTU=EVAPW/8340.

If an overall heat transfer coefficient of 560 BTU's/(ft^2-hr-F) and a temperature driving force of 50 F are assumed,[11] the total evaporator area (AEVAP) is calcualted:

AEVAP=EVPBTU/28000.

8.6 Results and Discussion of Computer Optimization

Using the approach and equations outlined in the previous sections, a program for the economic optimization of this process was written. This program (SUGAR) is included in Appendix 2 with definitions of all the process variable and examples of both the input and the output. A brief discussion of the general results of this optimization is now presented, with a detailed process design of the economic minimum case being presented in the following chapter.

Figures 8-2 through 8-5 show the general shape of the curves generated. Each figure contains the cost data for a given substrate concentration and varying Filter Paper Activities plotted against time. At low residence times the cost tends to rise abruptly, leveling out at longer times, until it slowly begins to turn up again. It can be seen (Fig. 8-3 to 8-5) that as the initial substrate concentration is increased, there is very little difference with higher Filter Paper

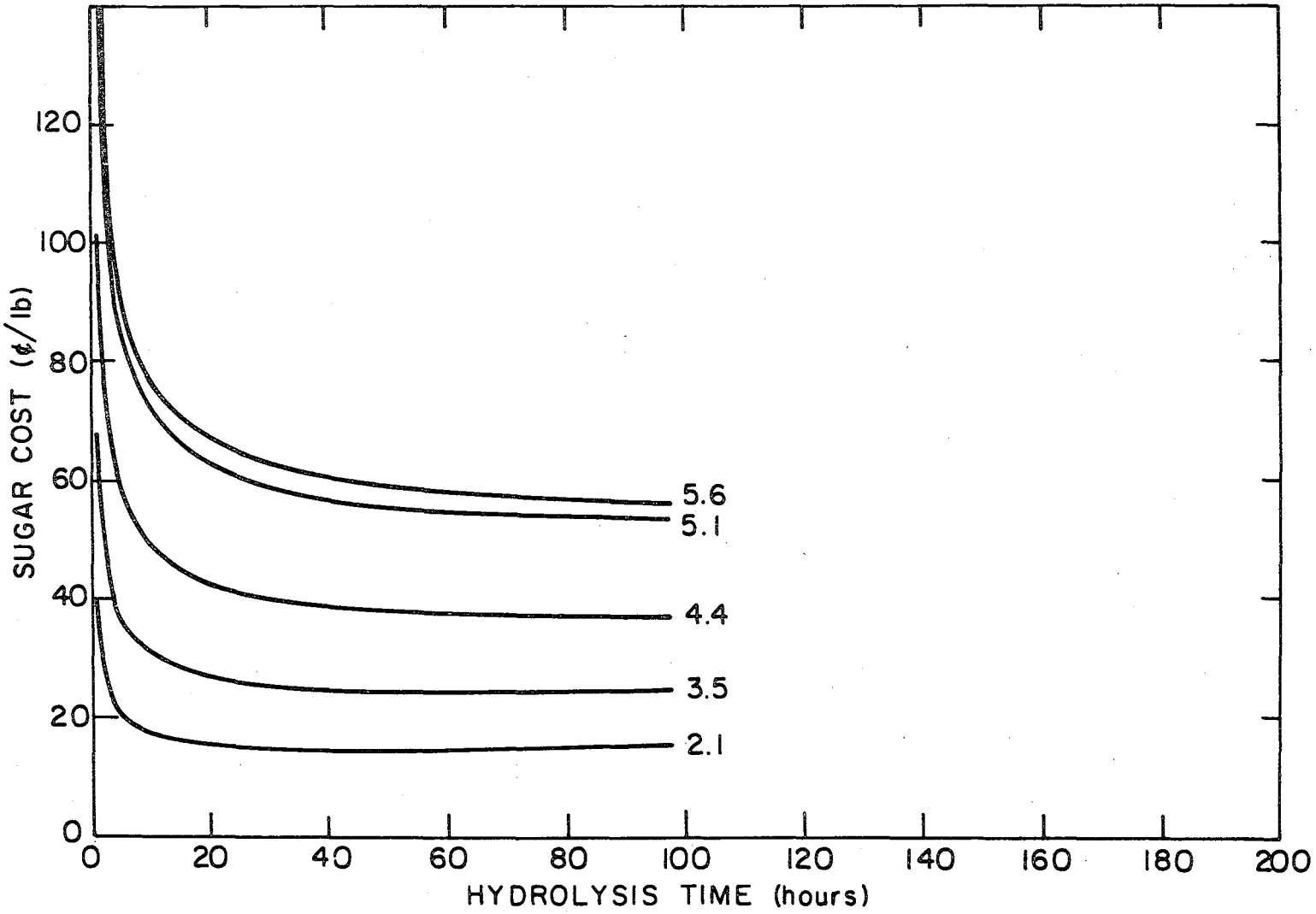

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Fig. 8.2. 2.5% substrate at various FPA's.

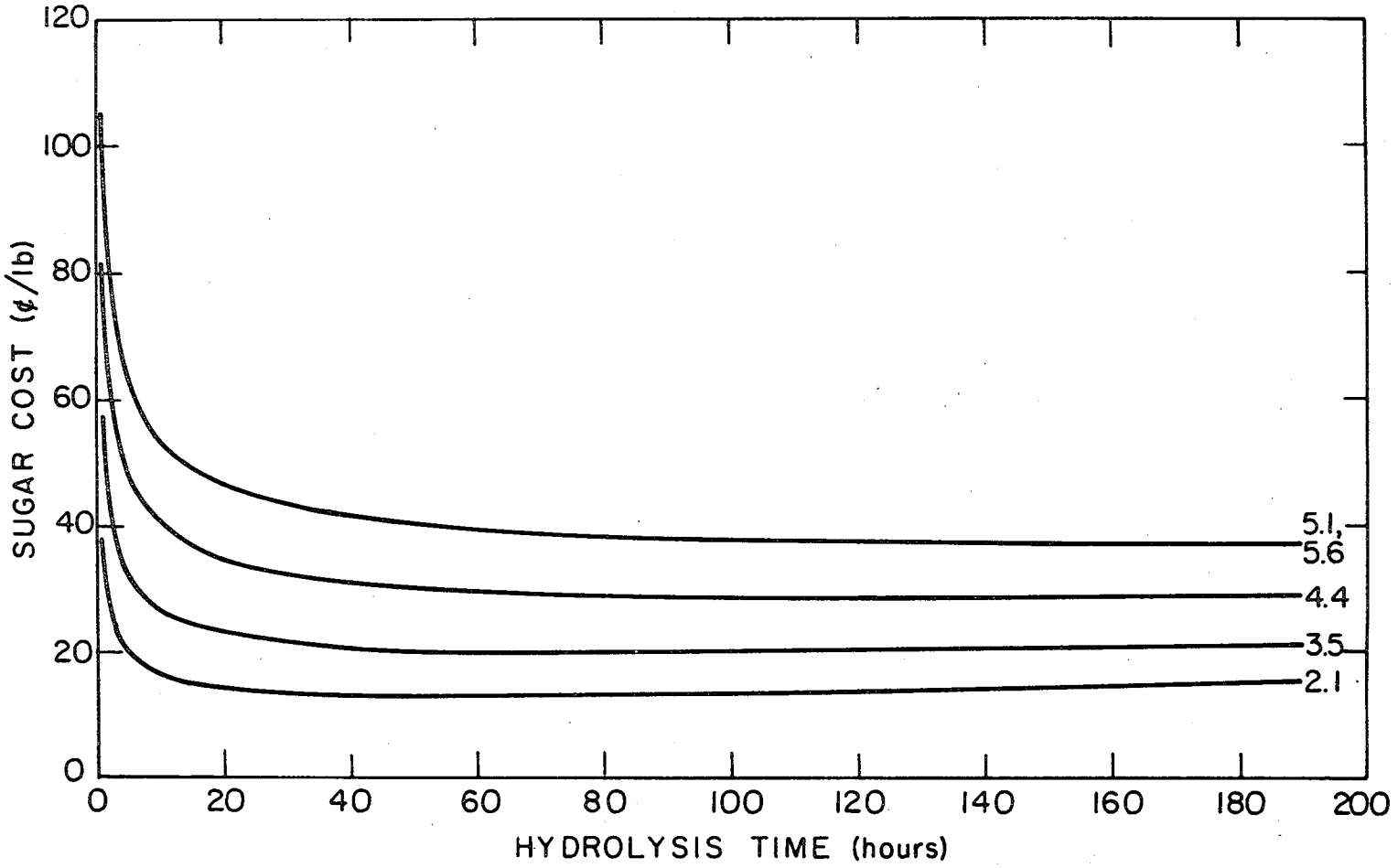


Fig. 8.3. 5.0% substrate at various FPA's.

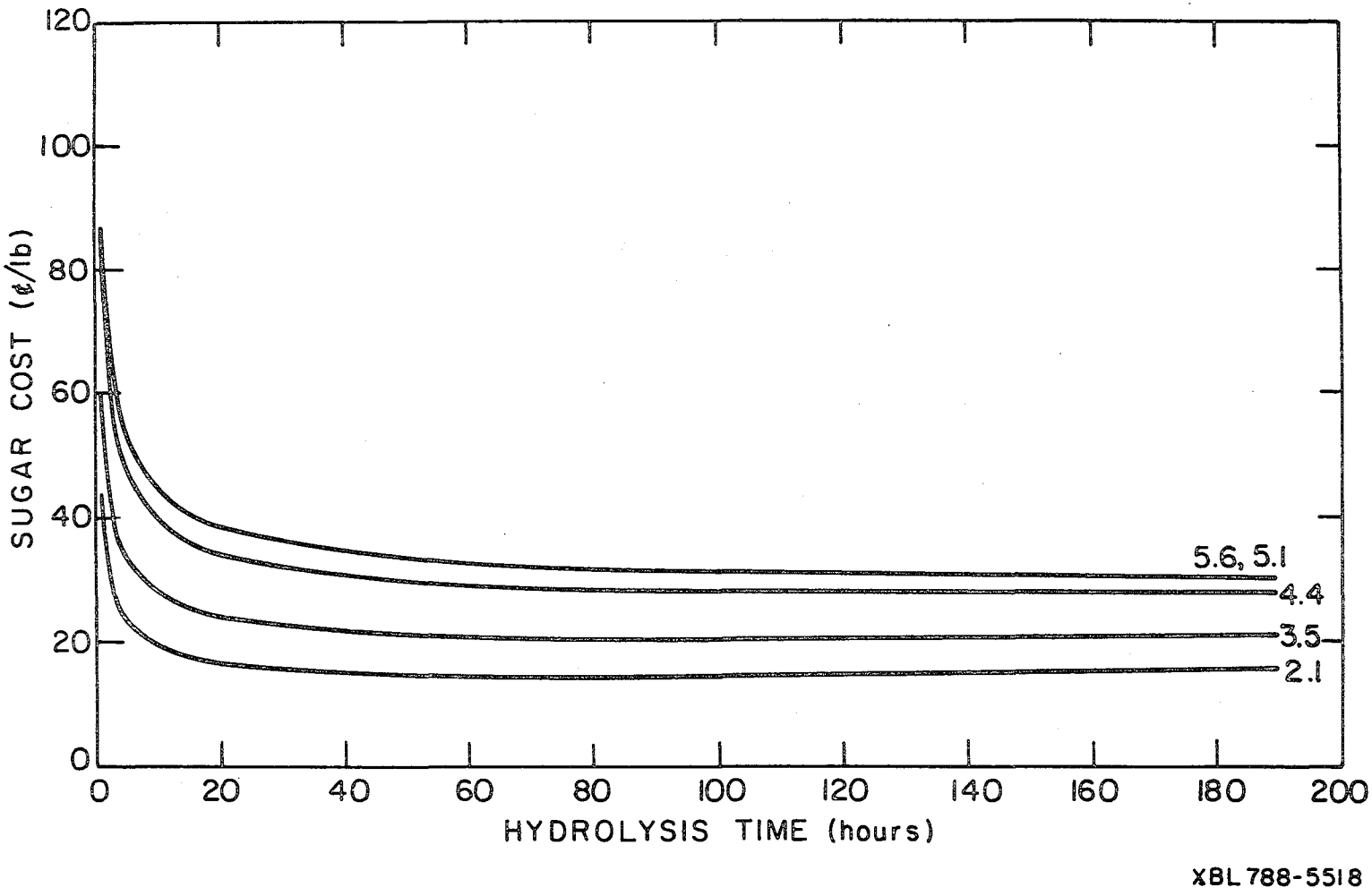


Fig. 8.4. 7.5% substrate at various FPA's.

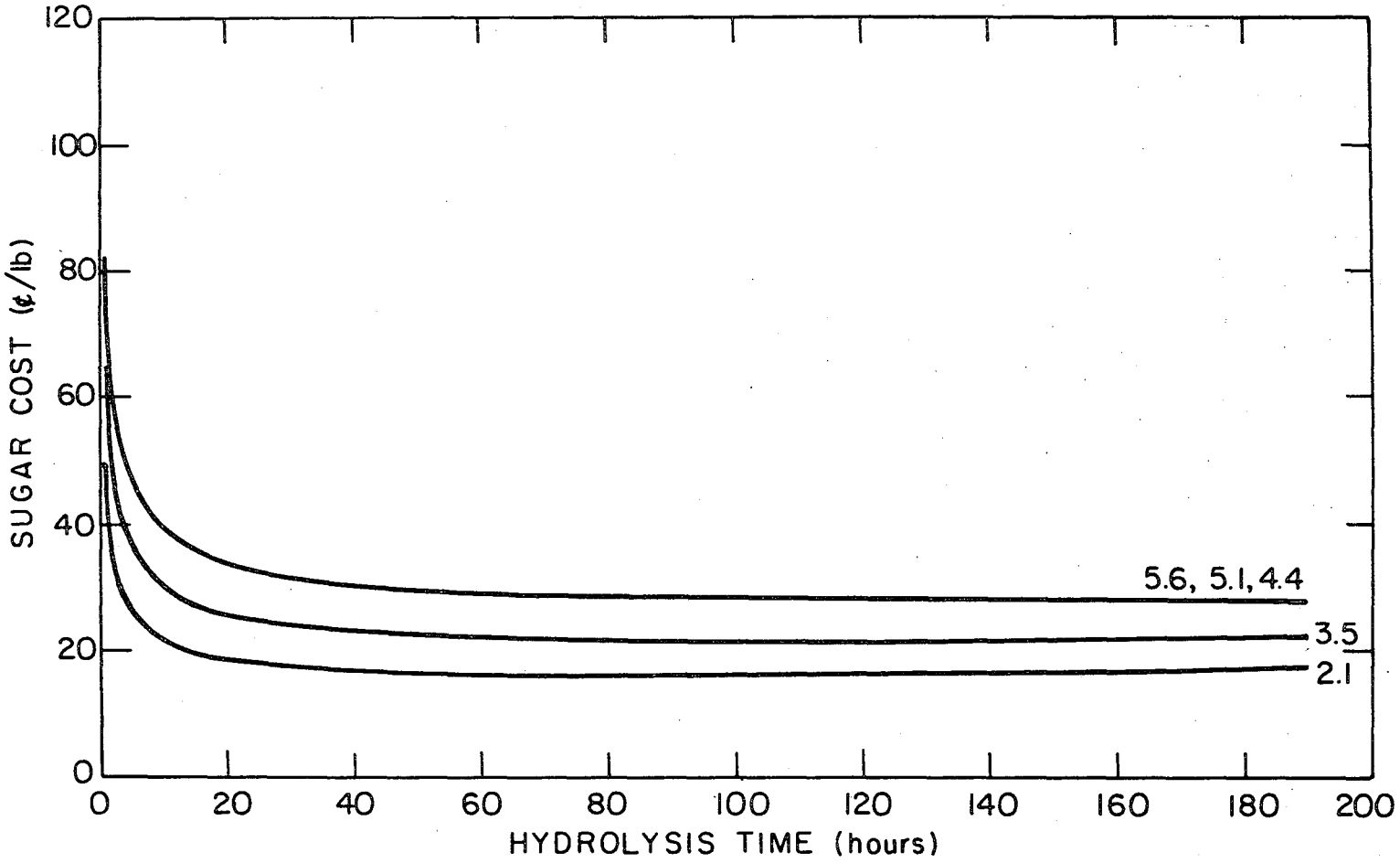


Fig. 8.5. 10% substrate at various FPA's.

Activiites. In Figure 8-6 it is shown that, with the exception of a 2.5% suspension (this shall be discussed later), at lower Filter Paper Activities the lower substrate concentrations tend to be more cost effective. This shifts as the Filter Paper Activities rise, and the higher concentrations tend to be more favorable. However, this shift is still not sufficient to offset the much lower costs obtained at the lower Filter Paper Activities. This shows the optimal Filter Paper Activity to be 2.1 (optimal, that is within the range of this study).

By plotting the sugar cost versus the initial substrate concentration (Fig. 8-7), it is possible to determine the optimal solids suspension for the hydrolysis section. This is found to be 5.0 wt%. It should be kept in mind, that although good results are predicted with each of these substrate concentrations, actual results may not compare very well. On the high end (10%) this could be due to poor mixing or mass transfer, and on the low end (2.5%) it could be due to a rapid blocking of accessible sites due to the low substrate concentration. Figures 8-8 and 8-9 are included for completeness. They show the expected yield curves of sugar per pound of enzyme at various substrate concentrations and enzyme activities.

It should be noted that the above analysis was based on a recycle of 50% in the hydrolysis section. The effects of changing recycle on the sugar cost are detailed in the following chapter.

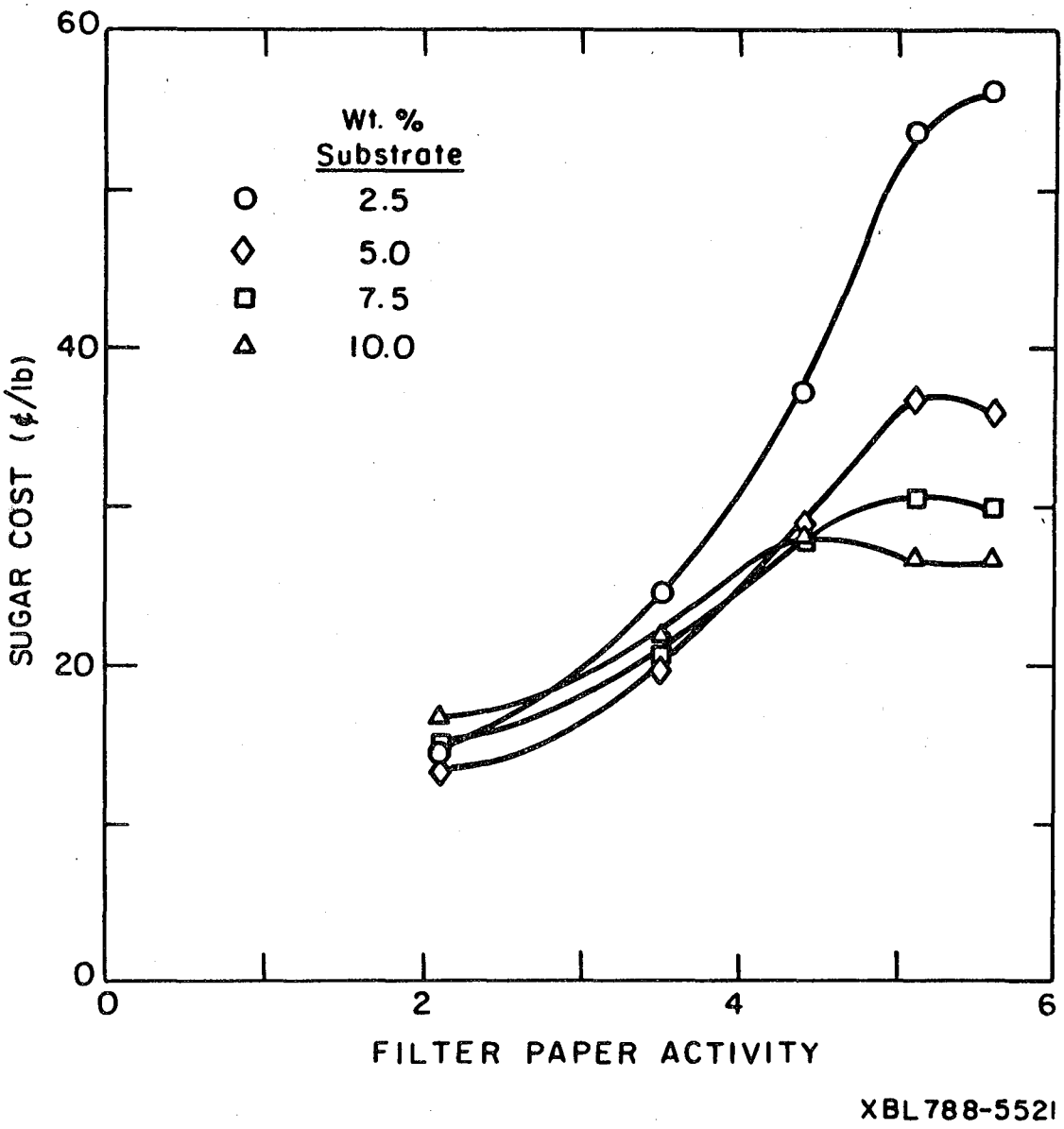


Fig. 8.6.

Sugar cost as function of filter paper activity at various substrate concentrations.

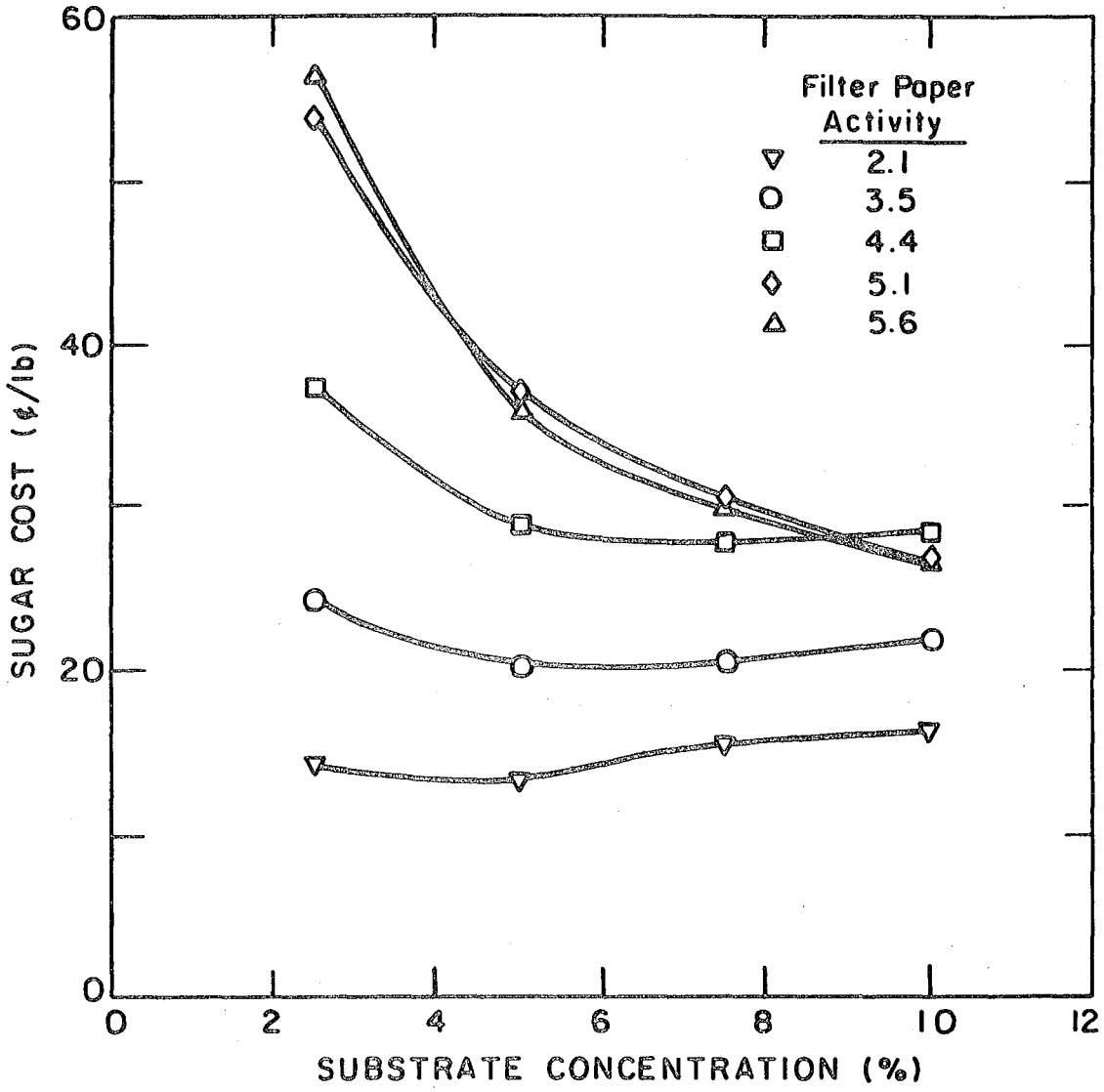


Fig. 8.7.

Sugar cost as function of initial substrate concentration at various filter paper activities.

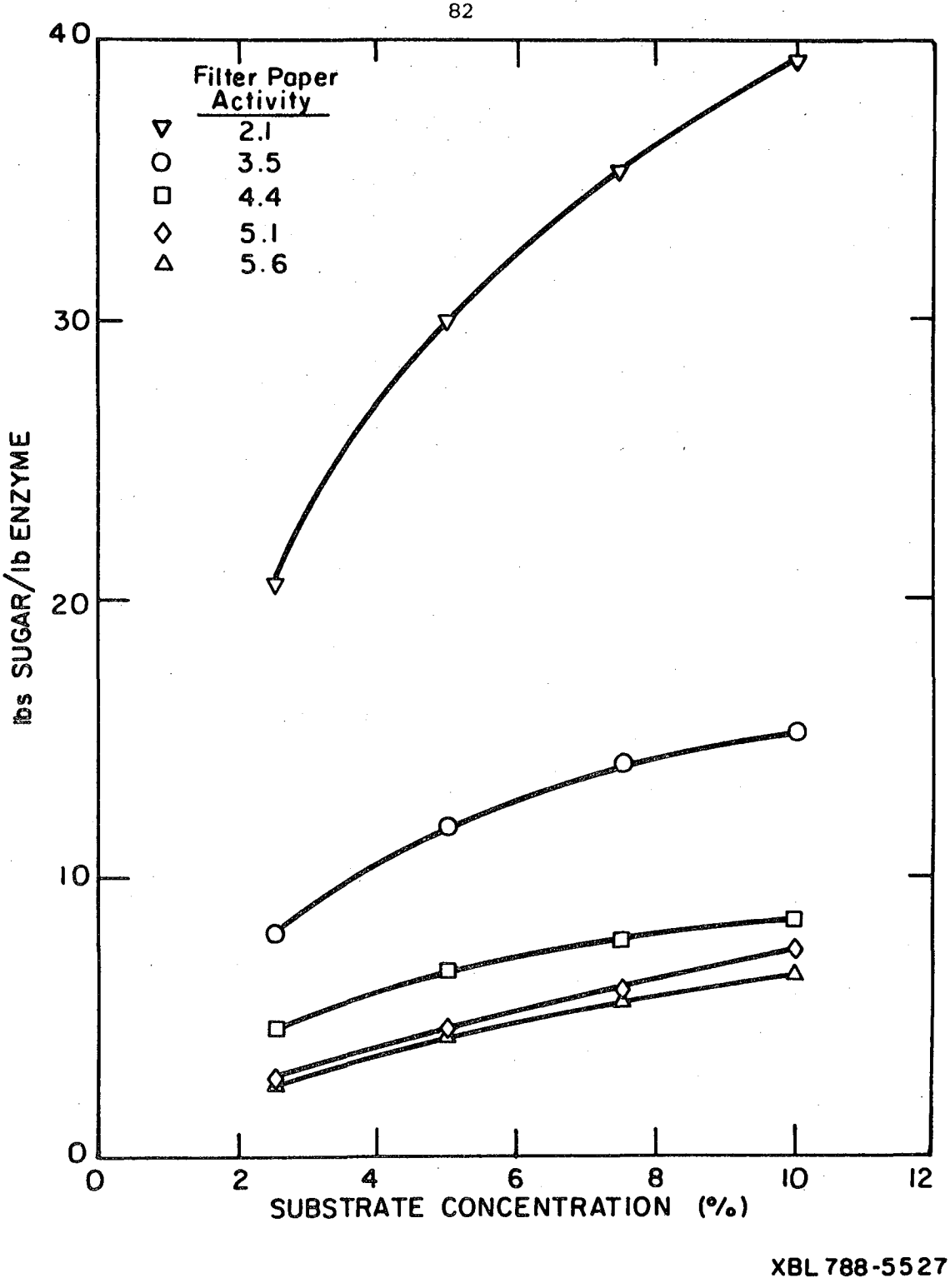


Fig. 8.8.

Expected sugar per pound of enzyme as function of concentration at various filter paper activities.

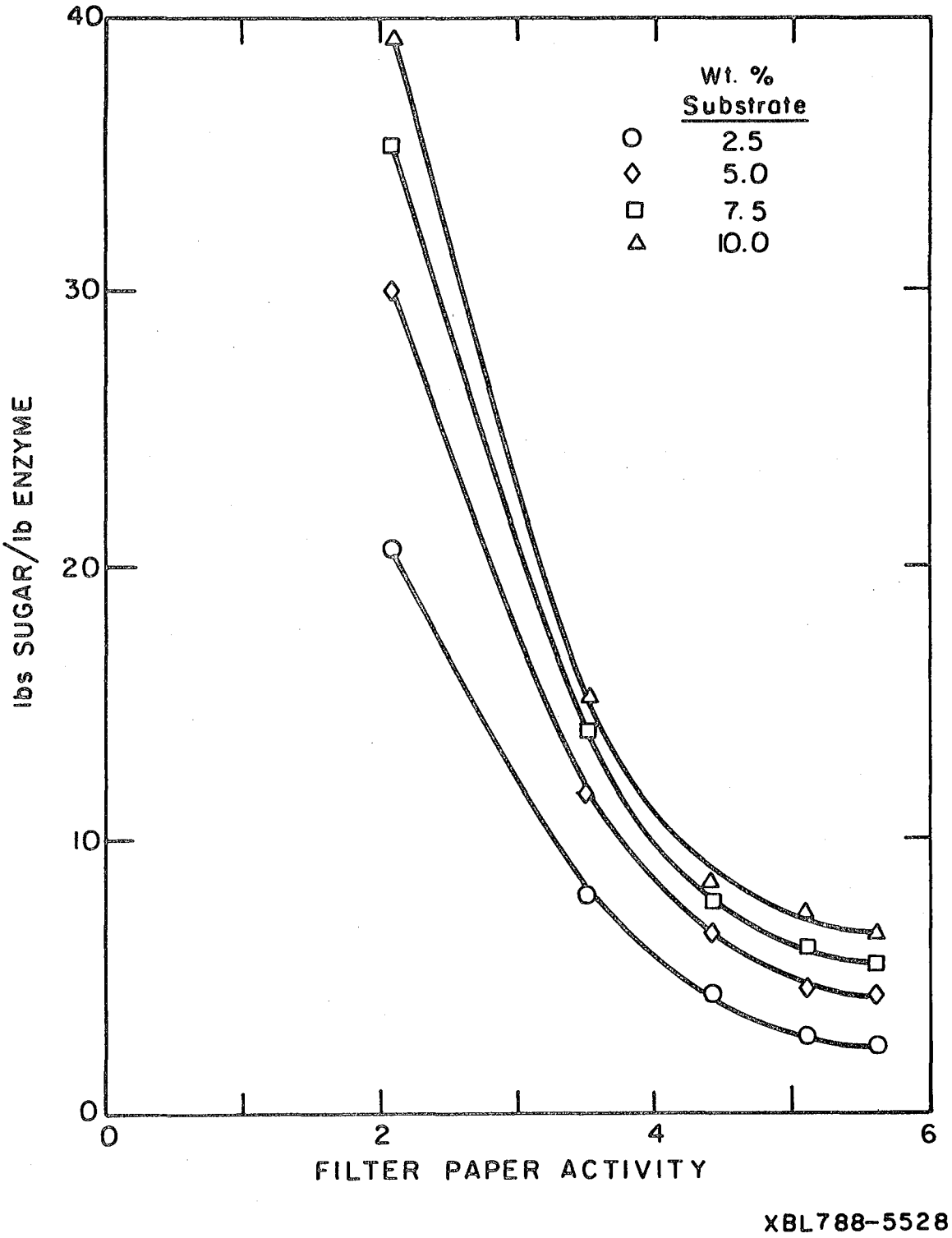


Fig. 8.9.

Expected sugar per pound of enzyme as function of paper activity at various filter substrate concentrations.

REFERENCES FOR CHAPTER 8

1. Mitra, G. and Wilke, C. R., Biotech. and Bioeng. Symp. No. 5, 253, (1975).
2. Cysewski, G. R. and Wilke, C. R., Biotech. and Bioeng., 18, 1297, (1976).
3. Wilke, C. R., vonStockar, U., Yang, R., Cysewski, G. R., Biotech. and Bioeng., 18, 1315, (1976).
4. Wilke, C. R., Yang, R., Sciamanna, A. F. and Freitas, R. P., Evaluation and Process Development Studies for Conversion of Biomass to Sugars and Ethanol, UC-LBL-7847, June 1978.
5. Cysewski, G. R. and Wilke, C.R., Fermentation Kinetics and Process Economics for the Production of Ethanol, UC-LBL-4480, March 1976.
6. Peters, M. S. and Timmerhaus, K. D., Plant Design and Economics for Chemical Engineers, McGraw-Hill, NY, (1968).
7. Guthrie, K. M., Process Plant Estimating Evaluation and Control, Craftsman Book Co., CA, (1974).
8. Wall Street Journal, June 5, 1978.
9. De Renzo, D. J. (ed.), Energy from Bioconversion of Waste Materials, Noyes Data Corp. NJ (1977).
10. McCabe, W. L. and Smith, J. C., Unit Operations of Chemical Engineering, McGraw-Hill, NY, 267, (1967).
11. Spencer, G. L. and Meade, G. P., Cane Sugar Handbook, John Wiley and Sons, NY, (1945).

Chapter 9 OPTIMAL PROCESS DESIGN AND ECONOMIC EVALUATION

Based on the hydrolysis modeling in Chapter 7 and the design equations from Chapter 8, a process for the hydrolysis of corn stover has been designed and evaluated with regard to economics. From the results as presented in Chapter 8 it is known that the optimal Filter Paper Activity is 2.1, and the optimal substrate concentration is 5.0 wt%. This was determined based on a 0.5 recycle fraction.

In this chapter, it is first determined what the recycle ratio is to be for the optimal economic design. This design is then detailed as to major processing equipment and annual processing costs. Finally, sensitivity of the cost is determined to taxes and interest, stover cost, enzyme recovery, and enzyme cost.

9.1 Determination of Optimal Recycle Fraction

One of the input variables to the program SUGAR is the recycle fraction in the hydrolysis section (RFR); this allows the possibility of studying the effect of recycle on the process design. It should be noted that the program fixes the highest possible recycle fraction based on the maximum solubility of enzyme in solution.

Figure 9-1 dramatically indicates how recycle affects sugar cost. The results may best be explained by the fact that as the recycle fraction is increased, the concentration of sugar in the hydrolysis section rises. This rise in concentration causes a higher inhibitory effect on the hydrolysis reaction; thereby lowering the pounds of sugar produced for every pound of enzyme (Fig. 9-2). Since it is expected that enzyme is one of the major cost factors,[1] it is reasonable

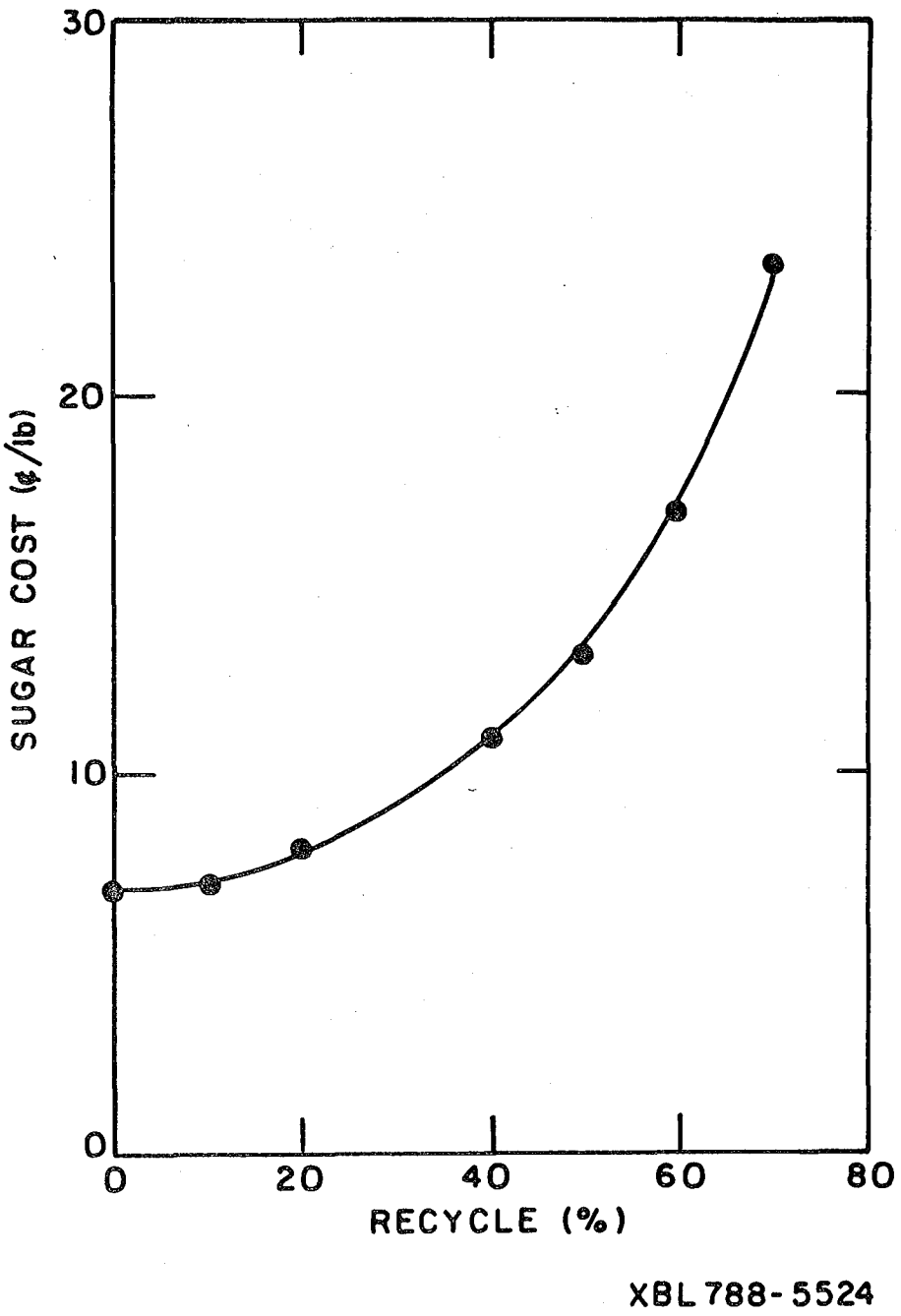


Fig. 9.1.

Sugar cost as function of hydrolyzate recycle fraction.

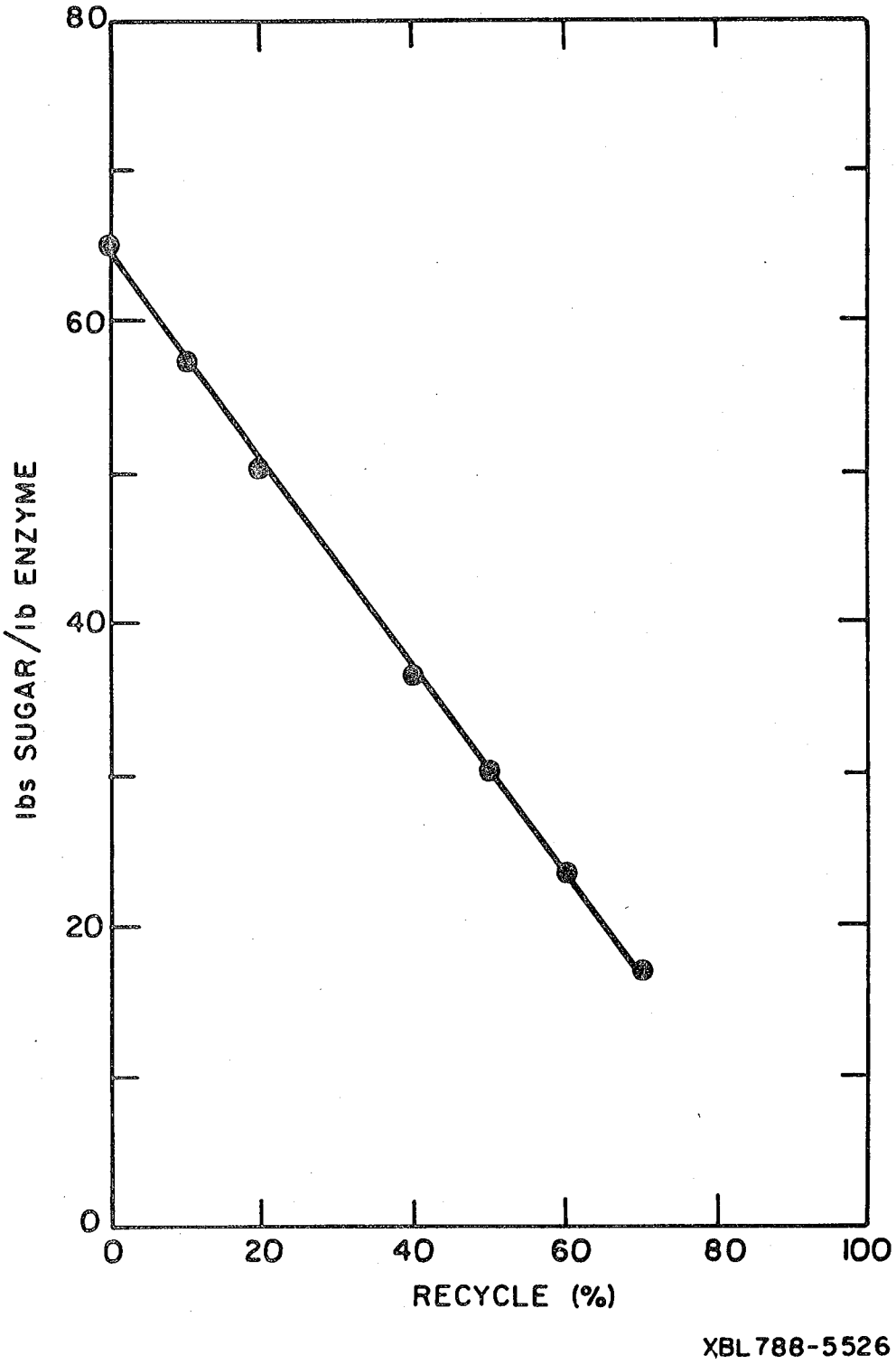


Fig. 9.2.

Sugar produced per pound of enzyme as function of hydrolyzate recycle fraction.

that the cost of sugar would rise. Therefore, the optimal recycle fraction is found to be 0.0, no recycle at all.

9.2 Process Design

The design basis of this process is shown in Table 9-1. Figure 9-3 shows a schematic process flow diagram of the process that produces 17,231 gallons per hour of a 14% sugar solution. The principal items of equipment corresponding to the flow sheet are listed in Table 9-2.

After the corn stover has been milled and acid pretreated, the washed solids (at a 30% consistency) are contacted counter-currently in four mixer-filter stages with the sugar stream from the hydrolysis section for enzyme recovery. Each vessel is well mixed, and solid-liquid separation is achieved by use of horizontal belt filters. An enzyme recovery of close to 100% is predicted based on an adsorption coefficient of $6.93X10^{-5}$(FPA/gal of soln)/(FPA/lb of stover) obtained for a 7.5 wt% suspension.

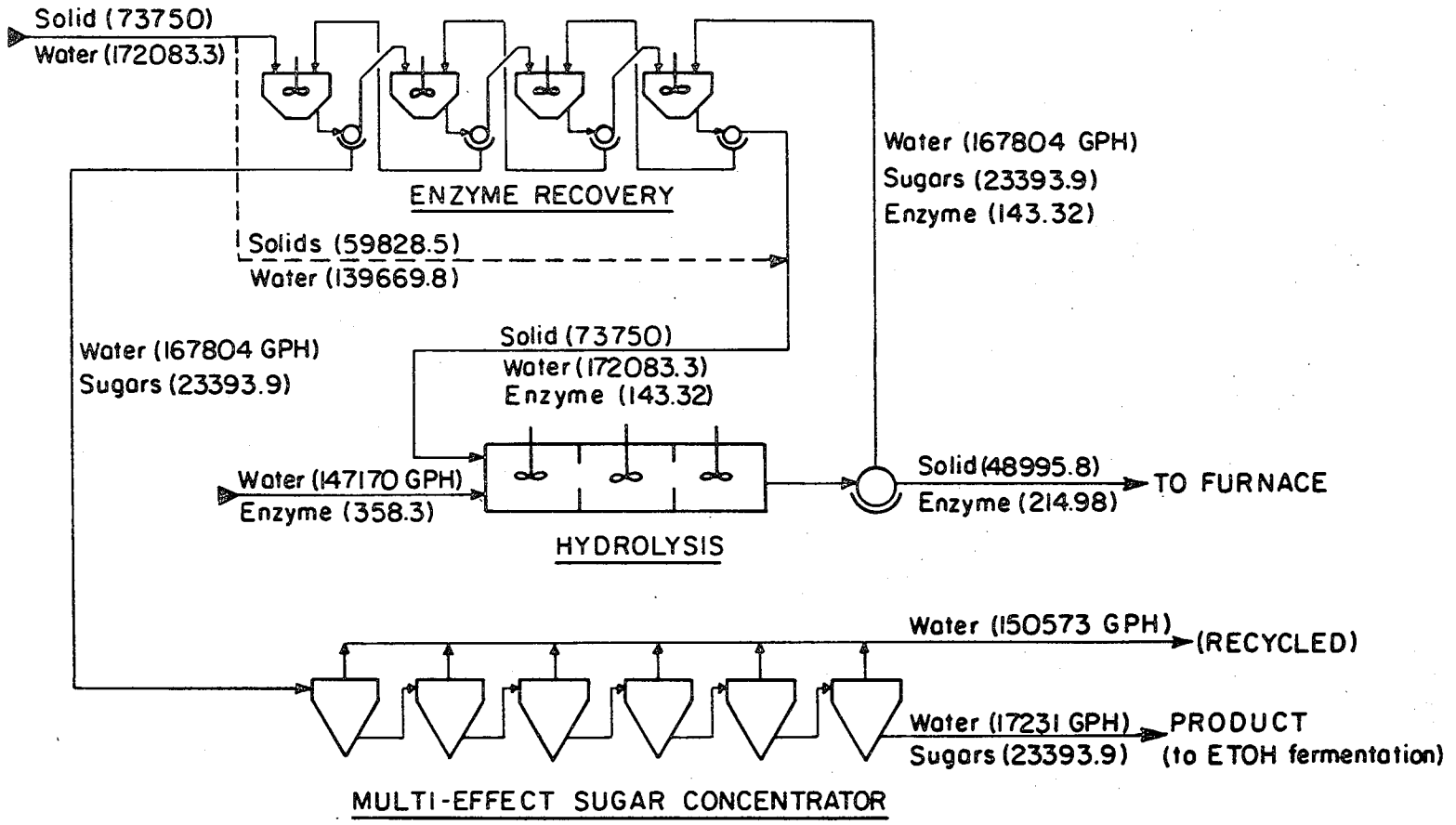
Hydrolysis is conducted at 45 C, 2.1 FPA, and at 5.0 wt% suspension. Residence time is 62 hours, resulting in a 34% conversion of the raw material to sugars. Sugar is produced at the rate of 23,393.9 pounds/hour with an input of 358.3 pounds/hour of enzyme, amounting to 65.28 pounds of sugar per pound of enzyme. Waste solids from the hydrolysis section amount to 48,995.8 pounds/hour, and these are sent to a furnace to be burned. After supplying process utility requirements, there are $1.88X10^{8}$ excess BTU's/hour.

Sugar solution leaves the hydrolysis section at a 1.675 wt% solution. This is concentrated in a six effect evaporator to 14 wt% (70% fermentable). In this step, 150,573 gallons/hour of water are evaporated, which is

TABLE 9-1

DESIGN BASIS FOR CELLULOSE HYDROLYSIS

FEED (pretreated corn stover)	885 T/D
CARBOHYDRATE CONTENT	57.7%
ENZYME STRENGTH	2.1 FPA
SOLIDS CONCENTRATION (in hydrolysis)	5.0%
ENZYME RECOVERY	40%
HYDROLYSIS RECYCLE FRACTION	0.0
SUGAR SOLUTION	14% (70% fermentable)
FEED COST	0.74 ¢/pound
ENZYME COST	$1.21/pound



Note: all flows in lbs/hr unless otherwise indicated

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Fig. 9.3. Process flow scheme.

assumed to be recycled through the system. Product sugar solution amounts to 17,231 gallons/hour.

Total fixed capital investment for the process is estimated to be $\$17.13 \times 10^6$. A breakdown of this into major processing sections is presented in Table 9-3. Total product cost is estimated at $\$1.36 \times 10^7$ per year, amounting to a sugar cost of 6.84¢/pound. A summary of the major cost factors is presented in Table 9-4.

Based on this cost of 6.84 ¢/pound of hydrolyzate sugars in a 14% solution, a projected cost of ethanol may be found. The most recent[1] process design shows sugar cost and concentration amounting to 78.6% of the ethanol cost of $1.79 per gallon. Sugar cost (and evaporation) in this design amounts to about 12 ¢/pound. Using these figures, the cost of ethanol produced from the utilization of sugars from this process is found to be $1.19/gallon. This amounts to about 34% reduction in the cost of ethanol.

TABLE 9-2

ITEM	UNIT SPECIFICATION	NUMBER OF UNITS	COST/UNIT ($)
ENZYME RECOVERY	TOTAL 1.93×10^6		
Tanks	Volume 26,828 gallons, stainless steel construction	4	76,596
Agitators	239 Hp, stainless steel construction	32	37,661
Solid Feeders	Screw conveyor, 13,922 lb/hr	6	2,341
Pumps	16,7804 GPM X PSI	2	8,749
Filters	Horizontal belt, 13,922 lb/hr	4	95,696
HYDROLYSIS	TOTAL 5.75×10^6		
Tanks	Concrete digesters, 4.33×10^6 gal	3	1.79×10^6
Agitators	197.5 Hp, stainless steel construction	3	33,839
Solid Feeder	Screw conveyor, 48,996 lb/hr	1	5,795
Pumps	41112 GPM X PSI	4	19,428
Filter	Horizontal belt, 48,996 lb/hr	1	203,600
Bypass Feeder	Worm screw, 59,829 lb/hr	1	6,691
Heating Tubes	Stainless steel, 44,849 total sq. feet		6,437
SUGAR CONCENTRATOR	TOTAL 305,307		
Evaporator	6 effects, 44,849 total sq. feet		305,307

TABLE 9-3

CAPITAL INVESTMENT SUMMARY

	$ X 10^{-6}	Percent
ENZYME RECOVERY	5.97	34.85
HYDROLYSIS	10.21	59.60
EVAPORATION	0.95	5.55
TOTAL	17.13	100.00

TABLE 9-4

SUGAR PRODUCTION COSTS

	¢/pound	Percent
FIXED CHARGES	2.07	30.24
LABOR RELATED CHARGES	0.59	8.55
STOVER COST	2.33	34.11
ENZYME COST	1.85	27.10
TOTAL	6.84	100.00

9.3 Sensitivity Analysis

By the breakdown of costs shown in Table 9-4, it is obvious that both stover and enzyme cost have a strong effect on the cost of sugar production. In a like manner, the amount of enzyme recovered has an effect on sugar cost through its relationship with the enzyme cost.

Figure 9-4 shows the relationship between enzyme cost and the resulting sugar cost. As expected, when the cost of enzyme goes up, sugar cost rises in a linear fashion, with the minimum cost of 4.98 ¢/pound at zero enzyme cost. In Figure 9-5 the effect of substrate cost is also shown to be a linear function. By relating the slopes of the lines in Figures 9-4 and 9-5, it can be seen that the cost of sugar is much more sensitive to enzyme cost than to stover cost. As the enzyme recovery rises, it is expected that the sugar cost would fall. This is demonstrated in Figure 9-6. For purposes of design, this process was assumed to be a municipally operated facility. Based on this, interest was assumed to be 6% and there were no taxes. Sensitivity of the cost of sugar to these criteria was tested by raising the interest rate to 12% and the taxes to 6%. Cost was found to rise from the 6.84¢/pound to 8.31 ¢/pound.

9.4 Comments and Recommendations

It is strongly stressed that the exact numerical results of this program are dependent on the kinetic model employed. The model as presented is not meant to describe the true mode of cellulase action, it is only used as a simple method to fit and describe the hydrolysis curve. However, this analysis does show the relative importance of each of the sections in the processing scheme. And its strength lies

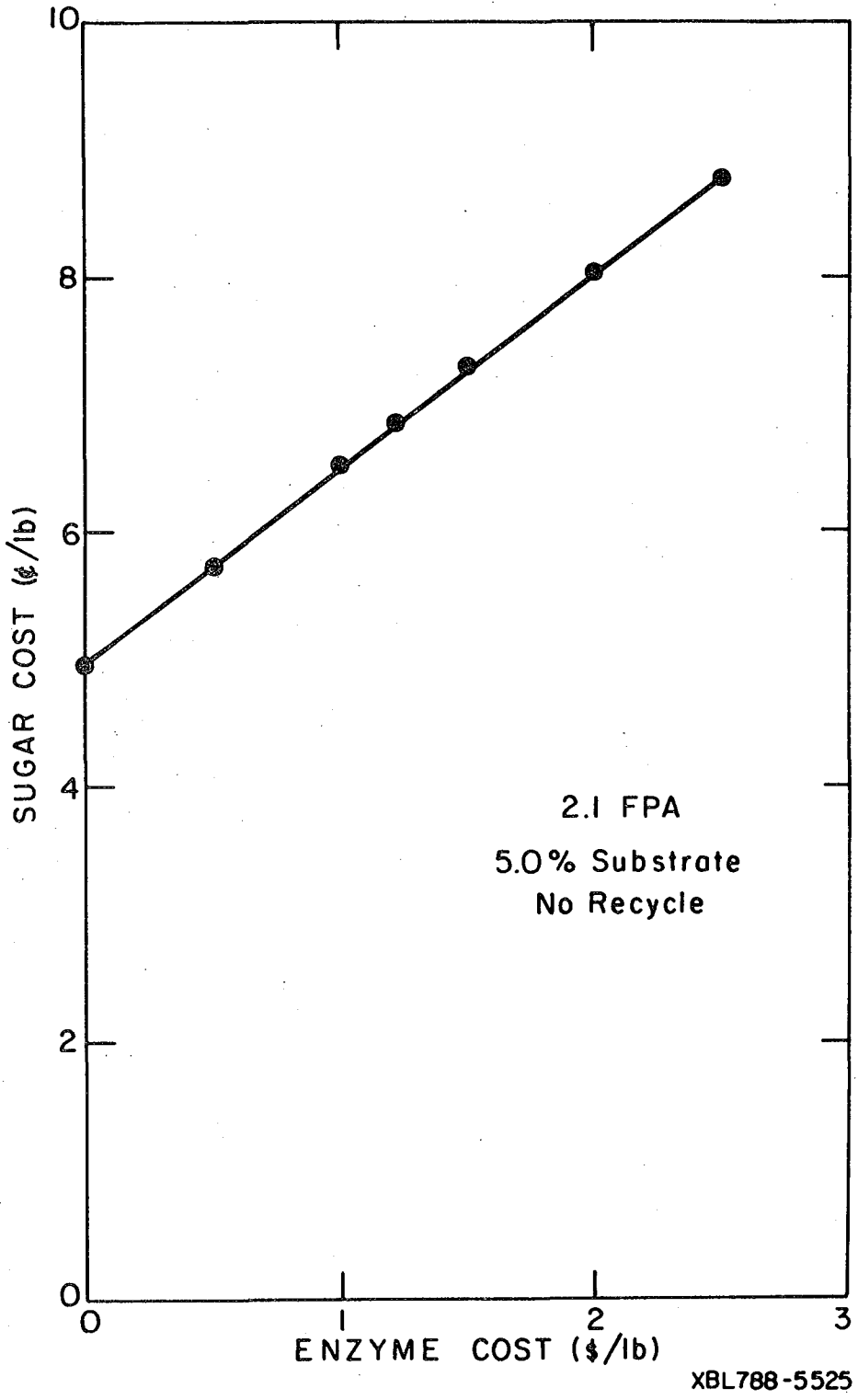

Fig. 9.4.

Sugar cost as a function of enzyme cost.

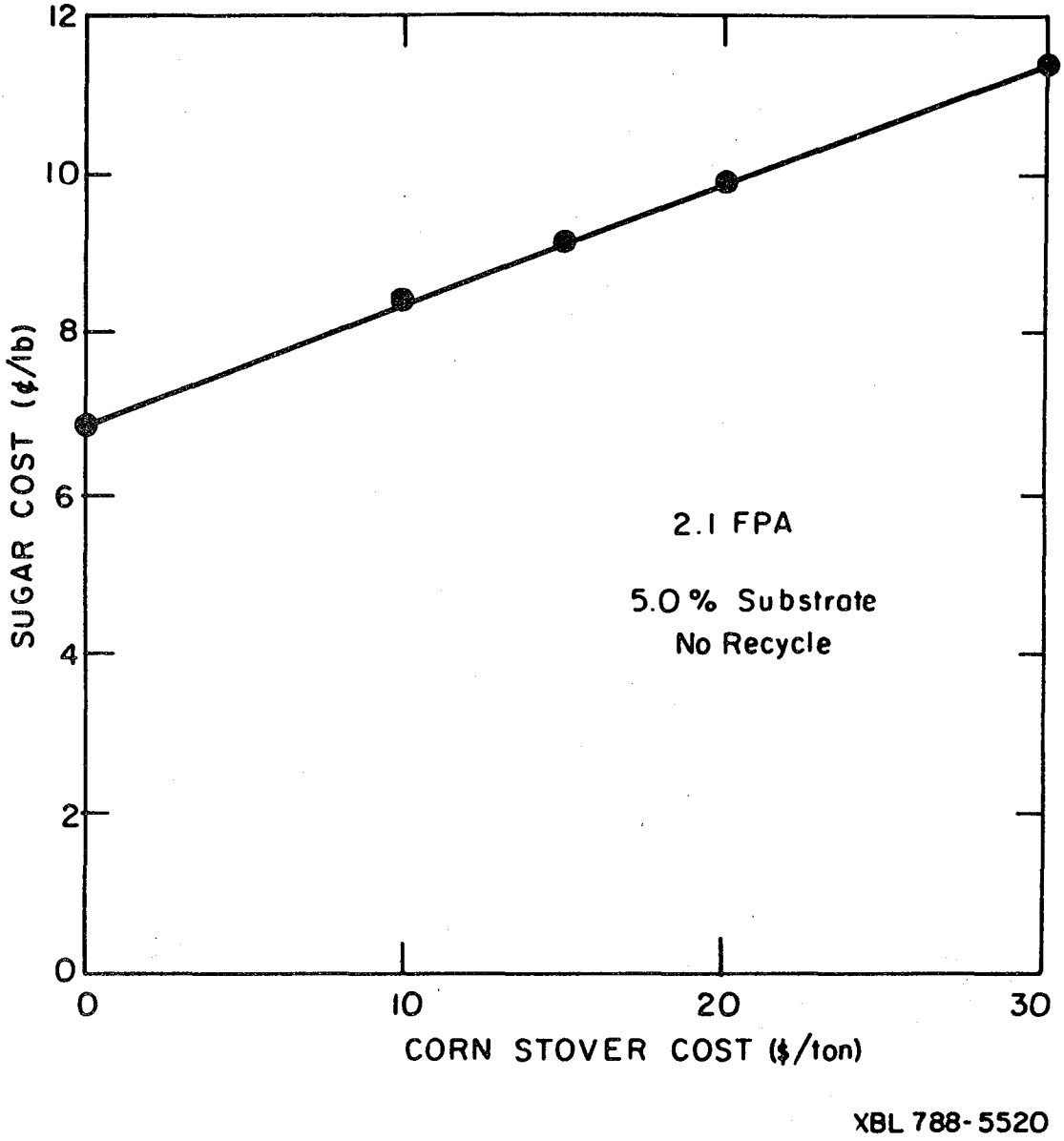

Fig. 9.5.

Sugar cost as a function of substrate cost.

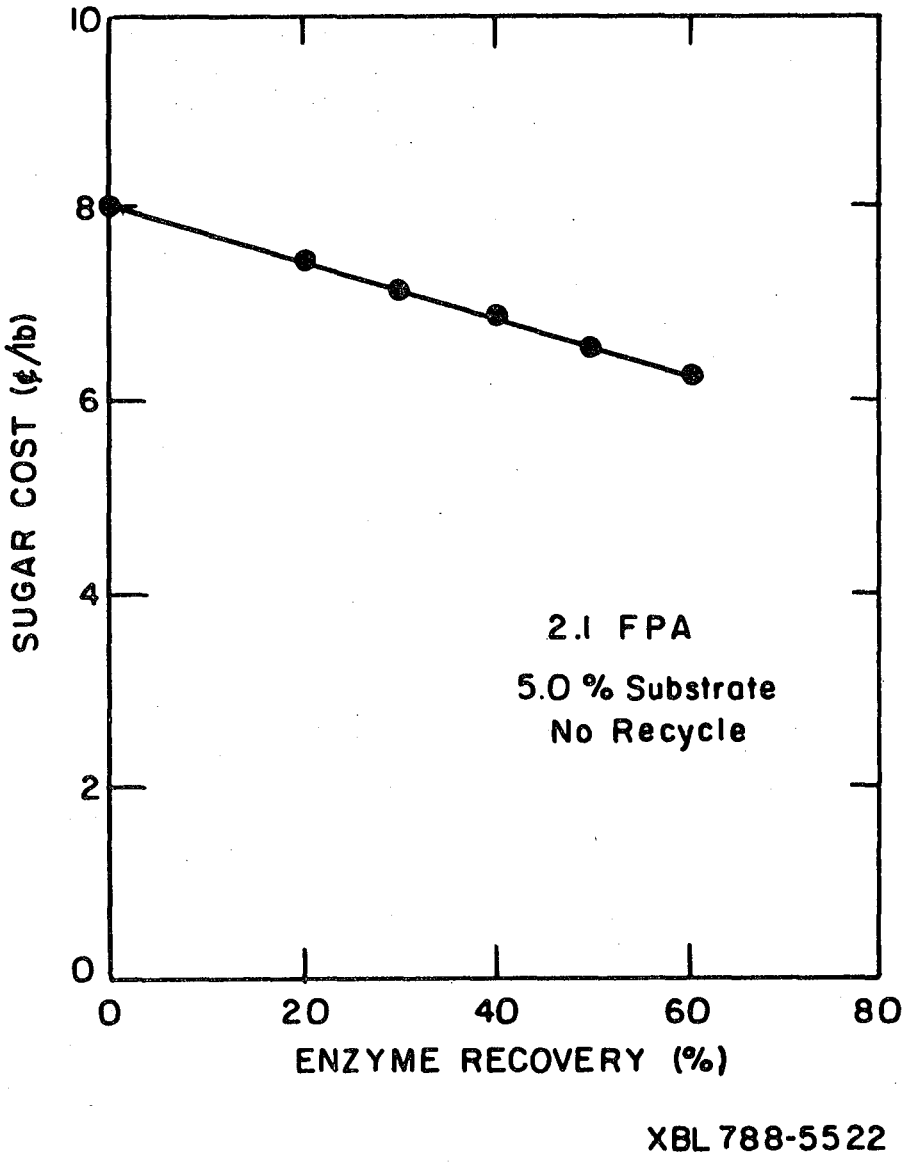

Fig. 9.6.

Sugar cost as a function of enzyme recovery.

in the fact that no simple assumptions concerning conversion and inhibition are necessary.

It is believed that future work should be directed to specific areas that are amenable to basic engineering research. This would include: (1) studies on the shearing and grinding of cellulosic materials to enhance accessibility of the substrate to enzyme attack; (2) improved enzyme production costs through the use of inducers or less expensive raw materials; and (3) studies on economic methods of recovering the enzyme from the spent hydrolysis solids. The true test of the strengths and weaknesses of the process would be to move the process from isolated laboratory runs to a small scale pilot plant, thereby allowing practical engineering applications.

REFERENCES FOR CHAPTER 9

1. Wilke, C. R., Yang, R., Sciamanna, A. F. and Frietas, R. P., Evaluation and Process Development Studies for Conversion of Biomass to Sugars and Ethanol, UC-LBL-7847, June 1978.

Appendix 1

A.1.1. Determination of Kinetic Parameters

As shown in Chapter 7, the initial rate expression can be written:

$$V_o = \frac{V_m S_o}{Km/do + S_o}$$

Applying Lineweaver-Burk analysis and rewriting:

$$\frac{1}{V_o} = \frac{K_m/\alpha_o}{V_m}\frac{1}{S_o} + \frac{1}{V_m}$$

Let:

$$Y = 1/V_o$$

and:

$$X = 1/S_o$$

$$Al = \frac{K_m/\alpha_o}{V_m}$$

$$A0 = 1/V_m$$

Then:

$$Y = Al(X) + AD$$

Data may be fit by linear regression in the following program with output:

$$VM = V_m$$

and

$$KM = K_m/\alpha_o$$

```
DIMENSION X(100), Y(100)
N= enter number of data points
I=1
1 READ,X(I),YI)
I=I+1
IF(I.LE.N) GO TO 1
J=1
SUMXY=0
SUMX=0
SUMY=0
SUMXX=0
2 SUMXY=SUMXY+X(J)*Y(J)
SUMX=SUMX+X(J)
SUMY=SUMY+Y(J)
SUMXX=SUMXX+X(J)**2
J=J+1
IF(J.LE.N) GO TO 2
A1=(SUMXY-((SUMC*SUMY)/N))/(SUMX**2)/N))
AD=(SUMY/N)-(A1*(SUMX/N))
KM=A1/A0
VM=1.0/A0
PRINT,KM,VM,N,J,I
READ,AGAIN
I=1
IF(AGAIN.LE.0) GO TO 1
```

```
STOP
END
```

A.1.2. Determination of Kinetic Constants

The accessibility constant (K_1) and the inhibition constant (K_2) may be determined through the use of a relaxation technique and experimental data:

```
DIMENSION T(10),P(10),K2(10)
5 READ,VM,KM,SO,K1,S
I=1
6 READ,T(I),P(I)
I=I+1
IF(I.LE.N) GO TO 6
D=0
C=0
MK2=0
DSDV=0
SDV=0
10 J=1
SUMK=0
SUMKK=0
7 C=(VM*T(J))/(P(J)*KM)*(SO-P(J))
D=(SO-P(J))/KM
K2(J)=P(J)/((C-D)*EXP(K1*P(J))-1)
SUMK=SUMK+K2(J)
SUMKK=SUMKK+K2(J)**2
```

```
J=J+1
IF(J.LE.N) GO TO 7
MK2=SUMK/N
SDV=SQRT((N+SUMKK-SUMK**2)/(N*(N-1)))
DSDV=(SDV/MK2)*100
PRINT,K1,SDV,MK2,DSDV
K1=K1-X
IF(K1.GE.-1) GO TO 10
READ,AGAIN
IF(AGAIN.GT.O) GO TO 5
STOP
END
```

A.1.3. Determination of Sugar Concentration with Time

For a discussion of this method, the reader is referred to Chapter 7.

```
      PROGRAM PROD1 (INPUT,OUTPUT,TAPE5=INPUT,TAPE6=OUTPUT)
    5 READ (5,400) ENZC
      IF(ENZC.LT.1.) GO TO 40
  400 FORMAT (F3.0)
      READ (5,500) AKM,VM,SO
  500 FORMAT (3F8.5)
      WRITE (6,550) ENZC,SO
  550 FORMAT (3X,*ENZ. CONC. =*,F4.0,3X,* SUB. CONC. =*,F7.3)
      AK1=-0.19369
      AK2=9.18527647
      T=0.0
```

```
      P1=0.0
      P2=0.0
      N=0
   10 P2=P1-(P1-P2)*(SQRT(5.)-1.)/2.
      N=N+1
   11 CONTINUE
      D=AKM*(1.+P2/AK2)+SO-P2)*EXP(AK1*P2)
      E=T*VM*(SO-P2)*EXP(AK1*P2)
      P1=E/D
      IF(N.GE.40) GO TO 20
      IF(ABS(P1-P2).GT.0.1) GO TO 10
      PAV=(P1+P2)/2.
      WRITE (6,600) T,PAV
      T=T+60.
      AP2=P2
      N=0
      GO TO 10
   20 IF(ABS(P1-P2).GT.0.1) GO TO 30
      PAV=(P1+P2)/2.
      WRITE (6,600) T,PAV
  600 FORMAT (3X,*TIME =*,F6.0,3X,*PRODUCT =*,F5.1)
      T=T+60.
      IF(T.GT.2880.0) GO TO 5
   30 P2=AP2
      P2=P2+0.01
      AP2=P2
```

```
      GO TO 11
   40 STOP
      END
```

Appendix 2

A.2.1.

```
      **PROGRAM SUGAR (INPUT,OUTPUT,TAPE5=INPUT,TAPE6=OUTPUT)**

      PROGRAM SUGAR (INPUT,OUTPUT,TAPE5=INPUT,TAPE6=OUTPUT)
      DIMENSION P(100),SFORM(100),CONV(100),S2(100),HFILM(100),
     1HSCRN(100),HEATS(100),HAGN(100),HT(100),TVHYD(100),VHYDT(100),
     2CHYDT(100),PHYD(100),CHYDA(100),PSUG(100),SPE(100),
     3TOTALH(100),TFCIH(100),XLH(100),FIXH(100),XLABOH(100),POWERH
     1(100),STILH(100),TOTOPH(100),EVAPW(100),PRODW(100),EVPBTU
     2(100),ALVAP(100),STEAM(100),CEVAP(100),ELVAP(100),
     3OTIEVP(100),XLEVAP(100),XLABEV(100),TFCIEV(100),
     4FIXEVP(100),TOTOPV(100),PRODC(100),SUGAFC(100),CHYDF
     5(100),CHYDS(100),TOTOTI(100),XSBTU(100),CP(100),X(15),Y(15)
C
C
    1 WRITE(6,1000)
 1000 FORMAT(1H1)
      WRITE(6,1001)
 1001 FORMAT(10X,*THIS PROGRAM DETERMINES MINIMUM SUGAR COST*)
      WRITE(6,1061)
 1061 FORMAT(/)
      WRITE(6,1002)
      WRITE(6,1002)
 1002 FORMAT(1X,100(1H*))
      READ(5,1003) FPA
 1003 FORMAT(F3.1)
      IF(FPA.LE.0.0)GO TO 74
      READ(5,1004) VM,AKM,ENZR
 1004 FORMAT(3F11.2)
      READ(5,1005) SCON,SMAX,WSMAX
 1005 FORMAT(3F10.1)
      READ(5,1006) AMSI,PCOST,SCOST
 1006 FORMAT(3F8.4)
      READ(5,1111) AR,REP
 1111 FORMAT(2F6.4)
      WRITE(6,1061)
      WRITE(6,1007) FPA
 1007 FORMAT(5X,*THE FILTER PAPER ACTIVITY IS *,F3.1)
      WRITE(6,1008) SCON
 1008 FORMAT(5X,*THE SUBSTRATE CONCENTRATION IS *,F5.1,
     1* G/L IN THE HYDROLYSIS SECTION*)
      WRITE(6,1009) SMAX
 1009 FORMAT(5X,*THE FEED IS PRETREATED SUBSTRATE AT *,
     1F7.1,* #/HR*)
      WRITE(6,1061)
      WRITE(6,1002)
      WRITE(6,1002)
      WRITE(6,1002)
      YIN=0.4*FPA*3787.88
      ENZ=0.00835*EXP((FPA-3.193)/1.399)
      RENZ=(1.-AR)*ENZ
      WRITE(6,1061)
      WRITE(6,1010)
 1010 FORMAT(5X,*ENZYME RECOVERY SYSTEM*)
      WRITE(6,1061)
      WRITE(6,1112) AR
 1112 FORMAT(5X,*ACTUAL TOTAL ENZYME RECOVERY =*,F6.4)
      SU=0.577*SCON
      HYDW=SMAX/(SCON*0.00835)-SMAX/8.34
      PENZ=HYDW*RENZ
```

```
      **PROGRAM SUGAR (INPUT,OUTPUT,TAPE5=INPUT,TAPE6=OUTPUT)**

      WENZ=HYDW*(1.-RFR)-WSMAX/8.34
      RHYD=RFR*HYDW
      W=WENZ+WSMAX/8.34
      IF((PENZ/WENZ).GT.0.044873) GO TO 650
      IF(WENZ.LE.0.0) GO TO 650
  651 WSR=WSMAX/(SMAX*8.34)
      EQK=0.0000693
      S=(0.075*W)/(1.-0.075*(1.+WSR))
      WS=WSR*S
      IF(S.GT.SMAX) GO TO 60
      GO TO 11
  650 WRITE(6,1011)
      WRITE(6,1090) RFR
 1090 FORMAT(5X,F6.4,* IS TOO HIGH A RECYCLE RATIO*,
     1* THE PROGRAM NOW CHANGES THE RECYCLE RATIO*)
      WENZ=PENZ/0.044873
      W=WENZ+WSMAX/8.34
      RHYD=HYDW-W
      RFR=RHYD/HYDW
      GO TO 651
   11 X(1)=0.0
      Y(1)=0.0
      R=ENZR
      NT=1
   12 NT=NT+1
      Y(2)=(1.-ENZR)*YIN
      X(NT)=Y(NT)/EQK
      Y(NT+1)=(Y(NT)*(W+WS)+W*(X(NT)-X(NT-1))-WS*Y(NT-1))/W
      X(NT+1)=Y(NT+1)/EQK
      ENZR=(Y(NT+1)-Y(2))/Y(NT+1)
      IF(ENZR.GT.R) GO TO 50
      IF(ABS(ENZR-R).GT.0.0001) GO TO 12
      GO TO 50
   60 WRITE(6,1011)
 1011 FORMAT(5X,*WARNING WARNING WARNING WARNING*)
      WRITE(6,1012) SMAX,ENZR
 1012 FORMAT(5X,F7.1,* #/HR OF SUBSTRATE WILL NOT GIVE *,
     1*AN ENZYME RECOVERY OF *,F4.2)
      WRITE(6,1013) S
 1013 FORMAT(5X,F10.1,* #/HR OF SUBSTRATE WOULD BE REQUIRED*)
      WRITE(6,1014) S
 1014 FORMAT(5X,*THE PROGRAM NOW PROCEEDS USING*,F7.1,* #/HR*)
      WRITE(6,1002)
      SMAX=S
      WSMAX=WS
      WRITE(6,1061)
   50 WRITE(6,1015) W
 1015 FORMAT(5X,F12.1,* GPH OF SUGAR SOLUTION ARE COUNTER-*,
     1*CURRENTLY*)
      WRITE(6,1016) S
 1016 FORMAT(5X,*CONTACTED WITH *,F7.1,* #/HR OF SUBSTRATE *)
      WRITE(6,1017) ENZR
 1017 FORMAT(5X,*TO PROVIDE AN ENZYME RECOVERY OF *,F4.2,* OF THE*,
     1* FREE ENZYME IN SOLUTION*)
      WRITE(6,1061)
      WRITE(6,1018) WS
 1018 FORMAT(5X,F7.1,* GPH OF LIQUID ARE CARRIED OVER WITH*,
     1* THE SOLIDS*)
```

```
      **PROGRAM SUGAR (INPUT,OUTPUT,TAPE5=INPUT,TAPE6=OUTPUT)**

      WRITE(6,1002)
      WRITE(6,1001)
      WRITE(6,1019)
 1019 FORMAT(5X,*DESIGN OF SYSTEM *)
      WRITE(6,2001)
      ENZRN=FLOAT(NT)
      AGN=ENZRN
      SCRN=ENZRN+1.
      PUPN=ENZRN
      FILN=ENZRN
      S1=S
      TENZR=0.5
      TVENZR=(W+WS)*TENZR/0.8
      VENZR=TVENZR/ENZRN
  100 IF(VENZR.GT.50000.) GO TO 200
      CENZRT=XMSI*0.654*VENZR**0.53
      PENZR=0.001818*(0.162*VENZR*((S+W*62.3)/VENZR)
     1*((S/198.4*VENZR))**0.666)*1.732*EXP(2.46645))
  101 IF(PENZR.GT.400.) GO TO 201
      CENZRA=XMSI*3.33*PENZR**0.56
  102 IF(S1.GT.74000.) GO TO 202
      CENZRF=XMSI*0.5932*S1**0.6
      CSCREW=XMSI*0.00462*S1**0.72
      PUMP=W*0.245
  103 IF(PUMP.GT.300000.) GO TO 203
      CENZRP=XMSI*(2.64+0.0068*PUMP**0.786)
      WRITE(6,1020)
 1020 FORMAT(5X,*ITEM*,15X,*SIZE*,15X,*NUMBER*,15X,
     1*COST/UNIT*)
      WRITE(6,1021) VENZR,ENZRN,CENZRT
 1021 FORMAT(5X,*TANKS*,5X,F15.0,*GAL*,10X,F4.0,
     1,5X,*$*,F15.2)
      WRITE(6,1022) PENZR,AGN,CENZRA
 1022 FORMAT(5X,*AGITATOR*,7X,F7.1,*HP*,14X,F4.0,
     1,5X,*$*,F15.2)
      WRITE(6,1023) S1,SCRN,CSCREW
 1023 FORMAT(5X,*SOLID FEEDER*,7X,F7.1,**/HR*,12X,
     1F4.0,15X,*$*,F15.2)
      WRITE(6,1024) W,PUPN,CENZRP
 1024 FORMAT(5X,*PUMPS*,10X,F12.1,*GPM X PSI*,10X,
     1F4.0,15X,*$*,F15.2)
      WRITE(6,1025) S1,FILN,CENZRF
 1025 FORMAT(5X,*FILTERS*,11X,F7.1,**/HR*,12X,F4.0,
     115X,*$*,F15.2)
      WRITE(6,1002)
      TOTALE=ENZRN*CENZRT+AGN*CENZRA+SCRN*CSCREW+PUPN
     1*CENZRP+FILN*CENZRF
      XLE=(ENZRN+AGN+SCRN+PUPN+FILN)/10.
      WRITE(6,1026) TOTALE
 1026 FORMAT(5X,*TOTAL PURCHASED EQUIPMENT COST = *,
     11PE15.7)
      TFCIE=3.1*TOTALE
      WRITE(6,1027)
 1027 FORMAT(5X,*  MULTIPLYING FACTOR 3.1 *)
      WRITE(6,1028) TFCIE
 1028 FORMAT(5X,*TOTAL FIXED CAPITAL INVESTMENT = *,
     11PE15.7)
      FIXE=0.24*TFCIE
```

```
      **PROGRAM SUGAR (INPUT,OUTPUT,TAPE5=INPUT,TAPE6=OUTPUT)**

      XLABOE=99264.25*XLE
      POWERE=AGN*PENZR*7923.1
      UTILE=POWERE*0.03
      TOTOPE=FIXE+XLABOE
      WRITE(6,1001)
      WRITE(6,1001)
      WRITE(6,1029)
 1029 FORMAT(5X,*========OPERATING COSTS $/YR==================*)
      WRITE(6,1030) FIXE
 1030 FORMAT(5X,*FIXED CHARGES====*,F11.2)
      WRITE(6,1031) XLABOE
 1031 FORMAT(5X,*LABOR RELATED CHARGES====*,F11.2)
      WRITE(6,1002)
      WRITE(6,1001)
      WRITE(6,1033) TOTOPE
 1033 FORMAT(5X,*=====TOTAL OPERATING COST ($/YR)===*,
     1F15.7)
      WRITE(6,1032)
 1032 FORMAT(5X,*OPERATING COSTS DO NOT INCLUDE UTILITIES*)
      WRITE(6,1002)
      WRITE(6,1002)
      WRITE(6,1002)
      WRITE(6,1034)
 1034 FORMAT(5X,*HYDROLYSIS SECTION*)
      WRITE(6,1002)
      GO TO 35
  200 VENZR=VENZR/2.
      ENZRN=2.*ENZRN
      AGN=2.*AGN
      SCRN=2.*SCRN
      FILN=2.*FILN
      GO TO 100
  201 PENZR=PENZR/2.
      AGN=2.*AGN
      GO TO 202
  202 S1=S1/2.
      FILN=2.*FILN
      SCRN=SCRN*2.
      GO TO 102
  103 PUMP=PUMP/2.
      PUPN=2.*PUPN
      GO TO 103
   35 BPN=0.0
      CBPSCR=0.0
      IF(S.EQ.SMAX) GO TO 36
      BPN=1.0
      SBP=SMAX-S
   36 IF(SBP.GT.74000.) GO TO 37
      CBPSCR=AMSI*0.00462*SBP**0.72
      GO TO 38
   37 SBP=SBP/2.
      BPN=2.*BPN
      GO TO 36
   38 I=0
      M=0
      AK1=-0.19369
      AK2=9.1052764?
      T=60.
```

```
      **PROGRAM SUGAR (INPUT,OUTPUT,TAPE5=INPUT,TAPE6=OUTPUT)**

      P1=0.0
      P2=P1
      AP2=P2
      P3=P2
      N=0
   39 I=I+1
      M=M+1
   40 P2=P1-(P1-P2)*(SQRT(5.)-1.)/2.
      N=N+1
   41 CONV(I)=P3/SCON
      P3=CONV(I)*SMAX/(W*0.00835)
      D=AK1*(1.+P3/AK2)+(S0-P2)*EXP(AK1*P2)
      E=T*VM*(S0-P2)*EXP(AK1*P2)
      P1=E/D
      IF(N.GT.40) GO TO 42
      IF(ABS(P1-P2).GT.0.1) GO TO 40
      P(I)=(P1+P2)/2.
      AP2=P2
      GO TO 44
   42 IF(ABS(P1-P2).GT.0.1) GO TO 43
      P(I)=(P1+P2)/2.
      GO TO 44
   43 P2=AP2
      IF(P2.GT.P1) GO TO 600
      P2=P2+0.01
      AP2=P2
      GO TO 41
  600 P2=AP2
      P2=P2-0.01
      AP2=P2
      GO TO 41
   44 SFURN(I)=SMAX*(1.-CONV(I))
      S2(I)=SFURN(I)
      HT(I)=T
      HYDN=3.
      HFILN(I)=1.
      HSCRN(I)=1.
      HEATS(I)=SFURN(I)*6000.
      HAGN(I)=3.
      BTUR=WENZ*225.18
      HPUPN=3.
      RPUPN=1.
      PPUPN=PUPN/3.0
      TVHYD(I)=HT(I)*HYDW/48.0
      VHYDT(I)=TVHYD(I)/HYDN
      CHYDT(I)=XMSI*0.000783*VHYDT(I)
      PHYD(I)=0.001818*(0.162*VHYDT(I)*((SMAX+HYDW
     1*62.3)/VHYDT(I))*((SMAX/(98.4*VHYDT(I)))**
     10.666)*1.732*EXP(2.46645))
  500 IF(PHYD(I).GT.400.) GO TO 501
      CHYDA(I)=XMSI*3.33*PHYD(I)**0.56
      HPUMP=HYDW*0.245
  510 IF(HPUMP.GT.300000.) GO TO 511
      CHYDP=XMSI*(2.64*0.0068*PUMP**0.718)
      HHTA=BTUR/24750.
      CHHTA=XMSI*0.1626*HHTA**0.6
  520 IF(S2(I).GT.74000.) GO TO 521
      CHYDF(I)=XMSI*0.5932*S2(I)**0.6
```

```
      **PROGRAM SUGAR (INPUT,OUTPUT,TAPE5=INPUT,TAPE6=OUTPUT)**

      CHYDS(I)=XMSI*0.00462*S2(I)**0.72
  530 IF(PUMP.GT.300000.) GO TO 531
      PPUMPC=XMSI*(2.64+0.0068*PUMP**0.718)
      PUMP2=RHYD*0.245
  540 IF(PUMP2.GT.300000.) GO TO 541
      RPUMPC=XMSI*(2.64+0.0068*PUMP2**0.718)
      GO TO 45
  501 PHYD(I)=PHYD(I)/2.
      HAGN(I)=2.*HAGN(I)
      GO TO 500
  511 HPUMP=HPUMP/2.
      HPUPN=2.*HPUPN
      GO TO 510
  521 S2(I)=S2(I)/2.
      HSCRN(I)=2.*HSCRN(I)
      HFILN(I)=2.*HFILN(I)
      GO TO 520
  531 PUMP=PUMP/2.
      PPUPN=2.*PPUPN
      GO TO 530
  541 PUMP2=PUMP2/2.
      RPUPN=2.*RPUPN
      GO TO 540
   45 PSUG(I)=P(I)*0.00895*W
      SPE(I)=PSUG(I)/PENZ
      TOTALH(I)=HYDN*CHYDT(I)+HFILN(I)*CHYDF(I)+HSCRN(I)*
     1CHYDS(I)+HAGN(I)*CHYDA(I)+HPUPN*CHYDP+RPUPN*RPUMPC
     1+PPUPN*PPUMPC+CHHTA+BPN*CBPSCR
      TFCIH(I)=0.1*(TOTALH(I)-HYDN*CHYDT(I))*1.68*
     1HYDN*CHYDT(I)
      XLH(I)=(HYDN+HFILN(I)+HSCRN(I)+HAGN(I)+HPUPN+
     1RPUPN+PPUPN+BPN)/2.
      FIXH(I)=0.24*TFCIH(I)
      XLABOH(I)=99234.25*XLH(I)
      POWERH(I)=HAGN(I)*PHYD(I)*7923.1
      UTILH(I)=POWERH(I)*0.03+(BTUR-HEATS(I))*0.0255
      TOTOPH(I)=FIXH(I)+XLABOH(I)
      PRODW(I)=(PSUG(I)/0.50-PSUG(I))/0.34
      EVAPW(I)=W-PRODW(I)
      EVPBTU(I)=EVAPW(I)*6340.
      AEVAP(I)=EVPBTU(I)/28000.
      STEAM(I)=EVAPW(I)*1.668
      CEVAP(I)=XMSI*0.938*AEVAP(I)**0.6
      XSBTU(I)=0.0
      SEVAP(I)=AEVAP(I)/8000.
      UTIEVP(I)=STEAM(I)*3./7000.
      XLEVAP(I)=SEVAP(I)/7.
      XLABEV(I)=9928.25*XLEVAP(I)
      TOTUTI(I)=UTILH(I)+UTIEVP(I)+UTILE
      IF(TOTUTI(I).LT.0.0) GO TO 800
  801 TFCIEV(I)=0.1*CEVAP(I)
      FIXEVP(I)=0.2**TFCIEV(I)
      STOVC=SOCST*SVAX*9500.
      ENZC=PSCST*PENZ*9500.
      TOTOPV(I)=FIXEVP(I)+XLABEV(I)
      PRODC(I)=TOTOPV(I)+TOTOPH(I)+TOTOPE+ENZC+STOVC+TOTUTI(I)
      SUGAPC(I)=PRODC(I)*100./(PSUG(I)*3500.)
      T=T+60.
```

```
      **PROGRAM SUGAR (INPUT,OUTPUT,TAPE5=INPUT,TAPE6=OUTPUT)**

      IF(T.LE.5760.) GO TO 39
      CMIN=1000.
      K=1
      GO TO 900
  800 XSUTU(I)=ABS(TOTUTI(I))/0.025
      TOTUTI(I)=0.0
      GO TO 801
  900 DO 46 I=1,M
      IF(CMIN.LT.SUGARC(I)) GO TO 46
      IF(CMIN.EQ.SUGARC(I)) GO TO 47
      K=I
      CMIN=SUGARC(I)
      GO TO 46
   47 WRITE(6,1011)
      WRITE(6,1035)
 1035 FORMAT(5X,*THERE MAY BE MORE THAN ONE MINIMUM COST*)
   46 CONTINUE
      I=K
      WRITE(6,1002)
      WRITE(6,1036) HT(I),CONV(I),P(I)
 1036 FORMAT(5X,*HYDROLYSIS TIME =*,F6.0,*MIN*,*  CONVERSION =*
     1,F4.2,* SUGAR CONCENTRATION =*,F10.5,*G/L*)
      WRITE(6,1002)
      WRITE(6,1037) PSUG(I)
 1037 FORMAT(5X,**/HR SUGAR PRODUCED = *,F7.1)
      WRITE(6,1038) PENZ,SPE(I)
 1038 FORMAT(5X,**/HR ENZYME USED = *,F6.1,5X,* *SUGAR/*ENZ*,
     1* = *,F5.2)
      WPITE(6,1039) WENZ
 1039 FORMAT(5X,*GPH OF WATER IN ENZYME = *,F8.0)
      WRITE(6,1040) W,RHYD,RFR
 1040 FORMAT(5X,*GPH OF SUGAR SOLN. = *,F12.0,5X,*GPH RECYCLE *,
     1**=*,F12.0,* RECYCLE RATIO =*,F5.3)
      WRITE(6,1041) SMAX,SBP
 1041 FORMAT(5X,**/HR FEED = *,F7.1,5X,* FEED THROUGH BYPASS = *
     1,F7.1)
      WPITE(6,1042) SFURN(I)
 1042 FORMAT(5X,**/HR SOLID TO FURNACE = *,F7.1)
      WRITE(6,1002)
      WRITE(6,1019)
      WRITE(6,1020)
      WRITE(6,1021) VHYDT(I),HYDN,CHYDT(I)
      WRITE(6,1022) PHYD(I),HAGN(I),CHYDA(I)
      WRITE(6,1023) S2(I),HSCRN(I),CHYDS(I)
      WRITE(6,1024) HPUMP,HPUPN,CHYDP
      WRITE(6,1025) S2(I),HFILN(I),CHYDF(I)
      WRITE(6,1043) PUMP,PPUPN,PPUMPC
 1043 FORMAT(5X,*SUGAR PUMP*,5X,F12.1,*GPM X PSI*,10X,
     2F4.0,15X,*$*,F15.2)
      WRITE(6,1044) PUMP2,RPUPN,RPUMPC
 1044 FORMAT(5X,*RECYCLE PUMP*,3X,F15.1,*GPM X PSI*,10X,
     2F4.0,15X,*$*,F15.2)
      WRITE(6,1045) SBP,BPN,CBPSCR
 1045 FORMAT(5X,*BYPASS FEEDER*,3X,F7.1,**/HR*,12X,
     2F4.0,15X,*$*,F15.2)
      WRITE(6,1046) HHTA,CHHTA
 1046 FORMAT(5X,*HEATING TUBES*,3X,F15.0,*SQ. FT.*,
     135X,*$*,F15.2)
```

```
      **PROGRAM SUGAR (INPUT,OUTPUT,TAPE5=INPUT,TAPE6=OUTPUT)**

      WRITE(6,1002)
      WRITE(6,1026) TOTALH(I)
      WRITE(6,1027)
      WRITE(6,1028) TFCIH(I)
      WRITE(6,1029)
      WRITE(6,1030) FIXH(I)
      WRITE(6,1031) XLABOH(I)
      WRITE(6,1002)
      WRITE(6,1035) TOTOPH(I)
      WRITE(6,1032)
      WRITE(6,1002)
      WRITE(6,1002)
      WRITE(6,1002)
      WRITE(6,1048)
 1048 FORMAT(5X,*EVAPORATION SECTION*)
      WRITE(6,1002)
      WRITE(6,1049) W
 1049 FORMAT(5X,*GPH FEED TO EVAPORATOR = *,F12.0)
      WRITE(6,1050) EVAPW(I)
 1050 FORMAT(5X,*GPH WATER EVAPORTED = *,F12.0)
      WRITE(6,1051) PRODW(I)
 1051 FORMAT(5X,*GPH OF PRODUCT = *,F6.0)
      WRITE(6,1002)
      WRITE(6,1019)
      WRITE(6,1052) AEVAP(I),EEVAP(I),CEVAP(I)
 1052 FORMAT(5X,* EVAPORATOR*,5X,F7.0,
     1* TOTAL SQ. FT.*,5X,F4.0,*EFFECTS*,3X,*$*,F15.0)
      WRITE(6,1002)
      WRITE(6,1026) CEVAP(I)
      WRITE(6,1027)
      WRITE(6,1028) TFCIEV(I)
      WRITE(6,1029)
      WRITE(6,1030) FIXEVP(I)
      WRITE(6,1031) XLABEV(I)
      WRITE(6,1002)
      WRITE(6,1033) TOTOPV(I)
      WRITE(6,1052)
      WRITE(6,1002)
      WRITE(6,1002)
      WRITE(6,1002)
      WRITE(6,1002)
      WRITE(6,1053) STOVC
 1053 FORMAT(5X,*SUBSTRATE COST $/YR = *,1PE15.7)
      WRITE(6,1054) ENZC
 1054 FORMAT(5X,*ENZYME COST $/YR = *,1PE15.7)
      WRITE(6,1055) PRODC(I)
 1055 FORMAT(5X,*PRODUCT COST $/YR = *,1PE15.7)
      WRITE(6,1056) SUGARC(I)
 1056 FORMAT(5X,*SUGAR COST CENTS/# = *,F7.2)
      WRITE(6,1061)
      WRITE(6,1002)
      WRITE(6,1061)
      WRITE(6,1062) XSBTU(I)
 1062 FORMAT(5X,*THERE ARE *,1PE15.7,
     1* EXCESS BTU'S/HR IN THIS SYSTEM*)
      WRITE(6,1002)
```

```
      **PROGRAM SUGAR (INPUT,OUTPUT,TAPE5=INPUT,TAPE6=OUTPUT)**

      WRITE(6,1002)
      WRITE(6,1060)
1060  FORMAT(8X,*TIME*,7X,*CONC.*,6X,*COST*)
      DO 72 I=1,M
      WRITE(6,1057) HT(I),P(I),SUGARC(I)
1057  FORMAT(5X,F6.0,5X,F6.2,5X,F7.2)
   72 CONTINUE
      WRITE(6,1002)
      WRITE(6,1002)
      WRITE(6,1002)
      WRITE(6,1002)
      GO TO 1
   74 STOP
      END
```

Appendix 2

A.2.2. Input for Program SUGAR

Input for the program takes the form shown in Table A.2.1 (for definitions of the variables see section A.2.4.). Care must be taken to insure that input follows the spacing as indicated in the program format statements; an example for one of the base case input data is shown in Table A.2-2.

TABLE A.2-1

INPUT VARIABLES AS READ BY SUGAR

FPA
VM AKM ENZR
SCON SMAX WSMAX
XMSI PCOST SCOST
AR RFR

TABLE A.2-2

INPUT FORMATING FOR SUGAR

```
2.1
0.5319    19.4404    0.98
25.0    73750.0    172083.3
526.6    1.21    0.0074
0.40  0.50
```

A.2.3. Output from Program SUGAR

```
      THIS PROGRAM DETERMINES MINIMUM SUGAR COST

**********************************************************************************************
**********************************************************************************************

   THE FILTER PAPER ACTIVITY IS 2.1
   THE SUBSTRATE CONCENTRATION IS  50.0 G/L IN THE HYDROLYSIS SECTION
   THE FEED IS PRETREATED SUBSTRATE AT 73750.0 #/HR

**********************************************************************************************
**********************************************************************************************
**********************************************************************************************

   ENZYME RECOVERY SYSTEM

   ACTUAL TOTAL ENZYME RECOVERY = .4000
     167803.8 GPH OF SUGAR SOLUTION ARE COUNTER-CURRENTLY
   CONTACTED WITH 13921.5 #/HR OF SUBSTRATE
   TO PROVIDE AN ENZYME RECOVERY OF 1.00 OF THE FREE ENZYME IN SOLUTION

    3894.9 GPH OF LIQUID ARE CARRIED OVER WITH THE SOLIDS
**********************************************************************************************

   DESIGN OF SYSTEM

   ITEM              SIZE                NUMBER              COST/UNIT
   TANKS          26828.GAL               4.              $      76596.64
   AGITATOR       259.1HP                 32.             $      37661.47
   SOLID FEEDER     13921.5#/HR               6.                    2341.95
   PUMPS          167803.0GPM X PSI             2.            $       8749.22
   FILTERS        13921.5#/HR             4.              $      95696.03
**********************************************************************************************
   TOTAL PURCHASED EQUIPMENT COST =   1.9258877E+06
     MULTIPLYING FACTOR 3.3
   TOTAL FIXED CAPITAL INVESTMENT =   6.3702520E+06


   =======OPERATING COSTS $/YR==================
   FIXED CHARGES==== 1432860.48
   LABOR RELATED CHARGES====  476564.40
**********************************************************************************************

   ====TOTAL OPERATING COST ($/YR)===  1.9094249E+06
   OPERATING COSTS DO NOT INCLUDE UTILITIES
**********************************************************************************************
**********************************************************************************************
**********************************************************************************************
   HYDROLYSIS SECTION
**********************************************************************************************
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   HYDROLYSIS TIME = 3720.MIN  CONVERSION = .34 SUGAR CONCENTRATION =  16.696056/L
**********************************************************************************************
   #/HR SUGAR PRODUCED = 23593.7
   #/HR ENZYME USED =  358.3      #SUGAR/#ENZ = 65.28
   GPH OF WATER IN ENZYME =  1471.70.
   GPH OF SUGAR SOLN. =      16760.      GPH RECYCLE =          0. RECYCLE RATIO =0.000
   #/HR FEED = 73750.0      FEED THROUGH BYPASS = 59828.5
   #/HR SOLID TO FURNACE = 48995.8
**********************************************************************************************
   DESIGN OF SYSTEM
   ITEM              SIZE                NUMBER              COST/UNIT
   TANKS          4334931.GAL              3.            $      1787412.57
   AGITATOR         197.5HP                3.            $        33839.33
   SOLID FEEDER      48995.8#/HR                1.                 $         5794.79
   PUMPS              4211.9GPM X PSI            3.                 $        19427.75
   FILTERS           48995.3#/HR                1.                 $       203599.87
   SUGAR PUMP         4111.9GPM X PSI            1.                 $         8749.22
   RECYCLE PUMP            0.0GPM X PSI            1.                 $         1390.22
   BYPASS FEEDER   59828.5#/HR                1.                 $         6691.09
   HEATING TUBES          7139.5Q. FT.                                          $         6436.74
**********************************************************************************************
   TOTAL PURCHASED EQUIPMENT COST =   5.7917845E+06
     MULTIPLYING FACTOR 3.2
   HYDROLYSIS TANKS MULTIPLYING FACTOR 1.68
   TOTAL FIXED CAPITAL INVESTMENT =   1.0216154E+07
   =======OPERATING COSTS $/YR=================
   FIXED CHARGES==== 2451877.05
   LABOR RELATED CHARGES====  678442.38
**********************************************************************************************
   ====TOTAL OPERATING COST ($/YR)===  3.1303194E+06
   OPERATING COSTS DO NOT INCLUDE UTILITIES
**********************************************************************************************
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**********************************************************************************************
   EVAPORATION SECTION
**********************************************************************************************
   GPH FEED TO EVAPORATOR =      16760.
   GPH WATER EVAPORTED =      14959.
   GPH OF PRODUCT =  2805.
**********************************************************************************************
   DESIGN OF SYSTEM
    EVAPORATOR      49146. TOTAL SQ. FT.        6.EFFECTS    $         322535.
**********************************************************************************************
   TOTAL PURCHASED EQUIPMENT COST =   3.2253505E+05
     MULTIPLYING FACTOR 3.1
   TOTAL FIXED CAPITAL INVESTMENT =   9.9985865E+05
   =======OPERATING COSTS $/YR=================
   FIXED CHARGES====  239966.08
   LABOR RELATED CHARGES====    8713.11
**********************************************************************************************
   ====TOTAL OPERATING COST ($/YR)===  2.4867919E+05
   OPERATING COSTS DO NOT INCLUDE UTILITIES
**********************************************************************************************
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**********************************************************************************************


   SUBSTRATE COST $/YR =   4.638875DE+06
   ENZYME COST $/YR =   3.6855159E+06
   PRODUCT COST $/YR -   1.3612814E+07
   SUGAR COST CENTS/# =    6.85
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THERE ARE 1.d765026E+08 EXCESS BTU'S/HR IN THIS SYSTEM

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TIME	CONC.	COST
60.	5.90	19.03
120.	7.56	14.66
180.	8.62	12.06
240.	9.36	11.10
300.	9.94	10.45
360.	10.42	9.98
420.	10.83	9.61
480.	11.18	9.04
540.	11.50	8.82
600.	11.78	8.62
660.	12.03	8.45
720.	12.27	8.31
780.	12.48	8.19
840.	12.68	8.08
900.	12.87	7.98
960.	13.04	7.90
1020.	13.20	7.82
1080.	13.36	7.75
1140.	13.50	7.68
1200.	13.64	7.62
1260.	13.77	7.57
1320.	13.90	7.51
1380.	14.02	7.46
1440.	14.13	7.42
1500.	14.24	7.29
1560.	14.35	7.25
1620.	14.45	7.22
1680.	14.55	7.19
1740.	14.65	7.16
1800.	14.74	7.14
1860.	14.83	7.11
1920.	14.91	7.09
1980.	15.00	7.07
2040.	15.08	7.05
2100.	15.15	7.03
2160.	15.23	7.02
2220.	15.30	7.00
2280.	15.38	6.99
2340.	15.45	6.97
2400.	15.52	6.96
2460.	15.58	6.95
2520.	15.65	6.94
2580.	15.71	6.93
2640.	15.77	6.92
2700.	15.83	6.91
2760.	15.89	6.90
2820.	15.95	6.90
2880.	16.01	6.89
2940.	16.06	6.88
3000.	16.12	6.88
3060.	16.17	6.87
3120.	16.22	6.87
3180.	16.27	6.86
3240.	16.33	6.86

3300.	16.38	6.86
3360.	16.42	6.85
3420.	16.47	6.85
3480.	16.52	6.85
3540.	16.56	6.85
3600.	16.61	6.85
3660.	16.65	6.85
3720.	16.70	6.85
3780.	16.74	6.85
3840.	16.78	6.85
3900.	16.82	6.85
3960.	16.86	6.85
4020.	16.90	6.85
4080.	16.94	6.85
4140.	16.98	6.85
4200.	17.02	6.85
4260.	17.06	6.85
4320.	17.09	6.86
4380.	17.14	6.86
4440.	17.16	6.86
4500.	17.20	6.86
4560.	17.24	6.86
4620.	17.27	6.87
4680.	17.31	6.87
4740.	17.34	6.88
4800.	17.37	6.88
4860.	17.41	6.88
4920.	17.43	6.89
4980.	17.47	6.89
5040.	17.51	6.89
5100.	17.54	6.89
5160.	17.57	6.90
5220.	17.60	6.91
5280.	17.64	6.91
5340.	17.67	6.91
5400.	17.70	6.91
5460.	17.72	6.92
5520.	17.75	6.93
5580.	17.78	6.93
5640.	17.80	6.94
5700.	17.83	6.94
5760.	17.86	6.95

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A.2.4. Definitions of Variables in Program SUGAR

AEVAP: Total heat transfer area of evaporator system (square feet)

AGN: Number of agitators in the enzyme recovery system (dimensionless)

AKM: The K_m of the enzyme (grams/liter)

AK1: Accessibility factor constant (liters/gram)

Ak2: End product inhibition constant (grams/liter)

AP2: Stored value of P2 (grams/liter)

AR: Actual percent recovery of the enzyme expressed as a fraction (dimensionless)

BPN: Number of bypass screws required (dimensionless)

BTUR: Number of BTU's required to treat the hydrolysis vessels (BTU's/hour)

CBPSCR: Cost of bypass screw (dollars)

CENZRA: Cost of enzyme recovery agitator (dollars)

CENZRF: Cost of enzyme recovery filter (dollars)

CENZRP: Cost of enzyme recovery pump (dollars)

CENZRT: Cost of enzyme recovery tank (dollars)

CEVAP: Cost of evaporator system (dollars)

CHHTA: Cost of hydrolysis heat transfer area (dollars)

CHYDA: Cost of hydrolysis agitator (dollars)

CHYDF: Cost of hydrolysis filter (dollars)

CHYDP: Cost of hydrolysis pump (dollars)

CHYDS: Cost of hydrolysis screw (dollars)

CHYDT: Cost of hydrolysis tanks (dollars)

CMIN: The minimum sugar cost (cents/pound)

CONV: Percent conversion of the substrate expressed as a fraction (dimensionless)

CSCREW: Cost of enzyme recovery screw (dollars)

D: Denominator of the hydrolysis rate expression

E: Numerator of the hydrolysis rate expression

EEVAP: Number of effects in the evaporation system (dimensionless)

ENZ: Weight of enzyme required for specified FPA (pounds/gallon)

ENZC: Total yearly cost of enzyme utilized (dollars)

ENZR: Recovery of enzyme in the enzyme recovery system percent expressed as a fraction (dimensionless)

ENZRN: Number of units in the enzyme recovery system (dimensionless)

EQK: Absorption equilibrium constant for enzyme on corn stover (FPA/gal/FPA/pound)

EVAPW: Amount of water evaporated (gallons/hour)

EVPBTU: Number of BTU's required to vaporize EVAPW (BTU's/hour)

FILN: Number of filters in the enzyme recovery system (dimensionless)

FIXE: Fixed costs in the enzyme recovery system (dollars/year)

FPA: Filter paper activity desired (FPA)

HAGN: Number of agitators in the hydrolysis system (dimensionless)

HEATS: Number of BTU's produced from combustion of hydrolysis solids (BTU's/hour)

HFILN: Number of filters in the hydrolysis section (dimensionless)

HHTA: Hydrolysis heat transfer area (square feet)

HPUMP: Capacity of hydrolysis pump (GPMxPSI)

HPUPN: Number of hydrolysis screws (dimensionless)

HT: Hydrolysis residence time (minutes)

HYDN: Number of hydrolysis tanks (dimensionless)

HYDW: Amount of water flowing in the hydrolysis system (gallons/hour)

I,K,M,N: Counters for loops (integers)

NT: Number of units required for the enzyme recovery system (dimensionless, integer)

P: Sugar concentration based on conversion (grams/liter)

PCOST: Total yearly cost of protein (dollars)

PENZ: Pounds of enzyme in hydrolysis (pounds)

PENZR: Amount of enzyme make-up required (pounds)

PHYD: Power required in the hydrolysis tanks (Hp)

POWERE: Power required in the enzyme recovery system (hp)

POWERH: Power required in the hydrolysis system (Hp)

PPUMPC: Hydrolysis product pump cost (dollars)

SFURN: Amount of hydrolysis solids to furnace (pounds/hour)

SMAX: Solid feed to the system (pounds/hour)

SO: Substrate concentration for the kinetic equation (grams/liter)

SPE: Sugar produced per unit of enzyme (pounds sugar/pounds enzyme)

STEAM: Amount of steam required for the evaporation section (pounds/hour)

STOVC: Yearly cost of corn stover (dollars)

SUGARC: Cost of the sugar (cents/pound)

S1: Amount of solids fed through equipment in the enzyme recovery system (pounds/hour)

S2: Amount of solids fed through the hydrolysis system equipment (pounds/hour)

T: Time of hydrolysis (minutes)

TENZR: Contact time for enzyme recovery system (hours)

TFCIE: Total fixed capital investment for the enzyme recovery system (dollars)

TFCIEV: Total fixed capital investment for the hydrolysis section (dollars)

TOTALE: Total purchased equipment cost in the enzyme recovery system (dollars)

TOTALH: Total purchased equipment cost for the hydrolysis system (dollars)

PPUPN: Number of hydrolysis product pumps (dimensionless)

PRODC: Total yearly cost of product (dollars)

PRODW: Amount of water in the product (gallons/hour)

PSUG: Amount of sugar produced (pounds/hour)

PUMP: Capacity of the enzyme recovery pump (GPMxPSI)

PUMP2: Capacity of the hydrolysis product pump (GPMxPSI)

PUPN: Number of pumps in the enzyme recovery system (dimensionless)

P1: Concentration of sugar from corn stover (grams/liter)

P2: Concentration of sugar from corn stover (grams/liter)

P3: Concentration of the recycle (grams/liter)

R: Recovery of enzyme in the enzyme recovery system percent expressed as a fraction (dimensionless)

RENZ: Required amount of enzyme make-up (pounds/gallon)

RFR: Percent recycle expressed as a fraction (dimensionless)

RHYD: Amount of recycle liquid (gallons/hour)

RPUMPC: Cost of the recycle pump (dollars)

RPUPN: Number of recycle pumps (dimensionless)

S: Amount of solids moved through the enzyme recovery by system (pounds/hour)

SBP: Amount of solids moved through the bypass screw (pounds/hour)

SCON: Initial substrate concentration (grams/liter)

SCOST: Cost of the pretreated substrate (dollars/pound)

SCRW: Number of screws in the enzyme recovery system (dimensionless)

TOTOPE: Total operating costs for enzyme recovery system (dollars/year)

TOTPH: Total operating costs for the hydrolysis system (dollars/year)

TOTOPV: Total operating costs for the evaporation system (dollars/year)

TOTUTI: Total cost of utilities (dollars/year)

TVENZR: Total volume of the enzyme recovery system (gallons)

TVHYD: Total volume of the hydrolysis section (gallons)

UTIEVP: Cost of utilities for the evaporation section (dollars/year)

UTILE: Cost of utilities for the enzyme recovery system (dollars/year)

UTILH: Cost of utilities for the hydrolysis section (dollars/year)

VENZR: Volume of enzyme recovery tank (gallons)

VHYDT: Volume of hydrolysis tank (gallons)

VM: The V_{max} of the enzyme (grams/liter'sec)

W: The water flow through the enzyme recovery system (gallons/hour)

WENZ: Liquid in the enzyme stream (gallons/hour)

WS: Liquid carried over with the solids in the enzyme recovery system (gallons/hour)

WSMAX: Liquid carried in with solid feed (gallons/hour)

WSR: Fraction of liquid with the solids (gallons/pound)

X: Enzyme absorbed on the solids (pounds/hour)

XLABEV: Cost of labor for the evaporator (dollars/year)

XLABOE: Cost of labor for the enzyme recovery system (dollars/year)

XLABOH: Cost of labor for the hydrolysis section (dollars/year)

XLE: Number of men required for the enzyme recovery system (dimensionless)

XLEVAP: Number of men required for the evaporation system (dimensionless)

XLH: Number of men required for the hydrolysis section (dimensionless)

XMSI: Marshal-Stevens Cost Index (dimensionless)

XSBTU: Number of BTU's produced in the system (BTU's/hour)

Y: Enzyme in the liquid (pounds/hour)

YIN: Enzyme inlet concentration to the enzyme recovery system (pounds/gallon)

This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

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