KINETIC, ENGINEERING AND ECONOMIC STUDY OF THE PRODUCTION OF ETHANOL FROM WASTE PULP

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by

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ABSTRACT

An attempt was made to determine the economic viability of converting cellulose, present in waste pulp, into industrial ethanol by a two-stage process: acidic hydrolysis followed by alcoholic fermentation.

For this purpose, cellulose in the waste pulp was determined in terms of potential sugar and the change in this potential sugar was investigated in an acid solution. It was found that this reaction followed first order kinetics. The decomposition of glucose in acidic solution at the same conditions was then studied as the hydrolyzate of cellulose contains predominantly glucose. This reaction too was found to be of first order. In both cases the rate constants were found to depend on acid concentration as well as on temperature and the relevant functional relations were established. The overall hydrolysis reaction was thus taken to be represented by a first order consecutive reaction mechanism. On this assumption the process was analysed for different types of reactors and the yield predicted theoretically. The process was then operated batchwise in a bench scale reactor and yields were determined experimentally. Good agreement was found between predicted and determined values.

The fermentability of the resultant sugar solution into ethanol and the B.O.D. of the effluent were also determined.

The process engineering and economic analysis of the process was studied with previously established data both for continuous and batchwise operations. It was found that the

capacity of the plant and the potential sugar content of the waste play important roles in the economic viability of the process in both cases and the minimum economic plant size was determined for the waste in question. In addition, it was established that the number of acid batches per solids batch influences the yield and the batch plant was optimized accordingly.

ACKNOWLEDGEMENTS

I would like to express my sincere gratitude to Dr. H. Sawistowski, who gave me constant help and advice during all stages of this work.

I would also like to thank my wife for all her help and understanding.

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LIST OF SYMBOLS

Symbol	Meaning
A	Constant in equation (3.4)
A	Cellulose in waste pulp in terms of potential sugar in equation (5.1)
A'	Constant in equation (4.4)
B	Constant in equation (3.3)
B	Sugar in equation (5.1)
B'	Constant in equation (4.3)
B_1	Constant in equation (3.6)
B_1'	Constant in equation (4.6)
C, C_0	Concentration of cellulose in waste pulp in terms of potential sugar
C	Sugar decomposition product in equation (5.1)
C_A, C_{AO}	Concentration of cellulose in waste pulp in terms of potential sugar in equation (5.5)
C_A	Concentration of sulphuric acid in equations (3.3) and (4.4) (%)
C_B, C_{BO}	Concentration of sugar in equation (5.3)
C_C, C_{CO}	Concentration of sugar decomposition product in equations (5.4) and (5.9)
C_1, C_2	Fixed capital costs of hydrolysis plant in equation (8.5)
e	Fractional vaporization
F	Mole of feed
F	Volumetric flow rate in equation (5.9)
H_L, H_V, H_F	Enthalpies of liquid, vapour and feed
ΔH, $\Delta H'$	Energy of activation

Symbol	Meaning
k	Rate constant
K	Capacity of hydrolysis plant
L	Mole of liquid
R	Universal gas constant
t	Time
T	Temperature
U	Overall heat transfer coefficient
V	Volume
V	Mole of vapour
x	Exponential factor

Greek Letters	
α	Constant in equation (4.3)
β	Constant in equation (3.3)
θ, θ_F	Temperature
π, $\Delta\pi$	Pressure and pressure difference
τ	Residence time

CHAPTER 1

INTRODUCTION

Cellulose and sugar, despite their apparent differences, are chemical twins. Both are carbohydrates, that is a combination of carbon and water, with sugar consisting of six carbon units bonded to six water units: $C_6(H_2O)_6$, while cellulose consists of six carbon units but only five water units: $C_6(H_2O)_5$. In order therefore to convert cellulose into sugar, a process known as saccharification, it is only necessary to add one water unit to each sugar molecule. Of these two carbohydrates, sugar is readily fermentable to alcohol and is useful as food, but cellulose, which is the world's most abundant organic raw material, is least useful as food and for industrial fermentation. Its utilization could, however, be enormously increased by prior conversion into sugar.

Work on converting cellulose to sugar dates back to the beginning of organic chemistry. Many saccharification processes have been developed and some of them used on industrial scale. In these processes wood cellulose, which is easily obtainable in large quantities in the form of sawdust, chips, shavings, and bark, was the principal source of cellulose. For that reason all the saccharification processes on industrial scale are called "WOOD HYDROLYSIS". The number of wood hydrolysis plants passed through a peak during the second world war because of increased demand for butadiene for the production of synthetic rubber.

Although after the war America and Western Europe did not revert to natural rubber - at present about 80 per cent of the annual rubber consumption in the United States is of synthetic origin - production of alcohol from wood came to a complete standstill. Even plants using conventional fermentation processes are now in danger of closure because of complete switch to synthetic alcohol production from ethylene. Currently, the latter source accounts for 91 per cent of the USA supply of alcohol whereas this value was 10 per cent in 1935(1). However, this trend may change with increasing shortage of raw materials for production of petrochemicals.

Despite the advantage which the synthetic production of alcohol gained over the conventional method of production there is one possibility which may help to revive the conventional fermentation process. This possibility exists as one of the several solutions to the waste disposal problem which has become a growing problem in the developed countries. However, before discussing the relation between waste disposal and alcohol a closer look will first be taken at the waste disposal problem.

The sources of waste could be divided into two groups: domestic waste and industrial waste. Although the composition of domestic waste varies Tables 1.1 and 1.2 give typical data for the United States and Great Britain.

Table 1.1 Municipal waste in America(2) 1965

Constituent	Weight Per cent (dry basis)
Paper	54
Garbage	15
Grass, leaves	10
Metals	7
Ashes	5
Glass	2
Rags	2
Wood	2
Misc.	3
TOTAL	100

Table 1.2 Domestic waste for the City of Bradford (1968)(3)

Constituent	Weight Per cent (dry basis)
Paper	41.48
Vegetable and Putrescible	34.78
Glass	7.49
Metal	5.85
Rags	3.02
Fine dust	1.28
Unclassified	6.13
TOTAL	100.00

The two tables reveal that more than half of the waste is paper and other cellulosic materials. It is thus a potentially valuable raw material for the production of alcohol. In recent years the utilization of waste or, in more precise terms, its cellulosic materials as raw material for the production of alcohol is gaining favour in the search for alternative methods to the conventional waste disposal by landfilling. Although the conventional disposal by landfilling is the cheapest way, it is slowly coming to a halt, due to unavailability of suitable sites.

The problem of industrial waste is more complex than that of domestic waste and peculiar to each industry. But part of the waste from paper and pulp mills has some similarity with domestic waste, since waste paper or pulp are its main constituents. And at some of these factories solid waste of cellulosic origin is as high as 250 ton/week and the most common method of its disposal is again by landfilling.

Summarizing, it can therefore be said that the whole approach to alcohol production from cellulosic materials has changed over the last three decades. Before and during the last war the prime object was to produce alcohol but today the prime concern is to utilize (or dispose of) the waste of cellulosic origin. Obviously, this requires data which can be used in the selection of the most suitable method of waste disposal.

The purpose of this work is therefore to assess the viability and feasibility of the production of alcohol from waste cellulosic materials. It involves the investigation of the kinetics of the reactions involved, study of the process engineering aspects and finally an economic assessment of the whole process.

CHAPTER 2

LITERATURE SURVEY

Wood cellulose was the main raw material used in the studies of the saccharification process. It is therefore relevant to start the literature survey with information on the composition of wood. This will be followed by a review of the production of alcohol from cellulose and the reaction kinetics of the saccharification process.

2.1 COMPOSITION OF WOOD

Main components of wood have been classified by Freeman(4) as follows:

I. Total carbohydrate fraction
    1. Cellulose
    2. Hemicellulose
        a. Pentosans
            (i) Xylans
            (ii) Arabans
        b. Hexosans
            (i) Mannans
            (ii) Glucosans
            (iii) Galactans
        c. Uronic acids

II. Lignin

The percentages of cellulose, hemicellulose and lignin vary according to the type of wood. Van Beckum and Ritter(5) analysed some wood types. Their results are shown in Table 2.1.

Table 2.1 Composition of certain wood species

Species	Cellulose (%)	Hemicellulose (%)	Lignin (%)
White Spruce	49.5	23.8	26.6
Red Spruce	48.3	24.6	26.6
Eastern Hemlock	48.2	20.3	31.5
Balsam Fir	44.0	25.9	30.1
Jack Pine	49.5	23.0	27.2
Aspen	50.7	31.8	17.3
Maple	50.0	26.3	23.5
White Oak	49.5	25.9	24.1

Of the two celluloses hemicellulose is hydrolyzed very easily in acidic solution while the other form of cellulose (sometimes called alpha-cellulose) resists acidic hydrolysis. Thus, the amount of sugars derived from wood depends on both the hydrolysis conditions and the types of wood used. This is illustrated in Table 2.2, which shows(4) compositions of the total hydrolyzates of some woods.

Table 2.2 Compositions of the total hydrolyzates of some woods

	Birch (%)	Jack Pine (%)	Spruce and Pine (%)
Glucose	67.7	67.6	61.9
Mannose	1.8	14.1	24.1
Galactose	0.0	6.2	4.0
Fructose	-	-	1.4
Xylose	30.0	8.9	8.0
Arabinose	0.4	3.2	-
Total	100.0	100.0	100.0

Alcoholic fermentability of sugars present in wood hydrolyzates is dependent on the pentosan content of hemicellulose and as pentose sugars are not fermentable to alcohol the higher the pentosan content of hemicellulose the lower the alcohol yield. In table 2.3 potential and fermentable sugar contents of various hard and softwoods are tabulated(6).

Table 2.3 Potential and fermentable sugar contents of various woods

Species	Potential reducing sugars (%)	Fermentability (%)	Potential fermentable sugars (%)
Hardwoods:			
American Beech	70.1	75.1	52.6
Aspen	75.1	76.3	57.3
Birch	69.9	67.8	47.4
Maple	68.2	71.0	48.4
Red Oak	63.6	63.0	40.2
Sweat Gum	66.4	73.8	49.0
Yellow Poplar	70.9	76.1	54.0
Softwoods:			
Douglas Fir	66.6	86.2	57.4
Eastern White Pine	66.5	86.3	57.4
Hemlock	66.1	88.2	58.3
Penderosa Pine	68.0	82.2	55.9
Redwood	52.4	77.1	40.4
Sitka Spruce	70.1	85.3	59.8
Southern Yellow Pine	64.8	82.0	53.2
Sugar Pine	64.3	82.4	53.0

2.2 PRODUCTION OF ALCOHOL FROM CELLULOSE

In 1819, Braconnot(7) reported that cellulose is transformed into sugar on treatment with concentrated sulphuric acid. In 1855, Melsens(8), realizing the difficulty of converting wood to sugar economically with strong acid made the first attempt to carry out the saccharification with dilute acid but did not succeed on a technical scale. First attempt to work under pressure with dilute acid was made by Simonsen(9). In his experiments Simonsen cooked chipped wood or sawdust for 15 minutes in 0.5 per cent sulphuric acid solution at a pressure of 9 bars and upon fermentation of the resultant sugar solution he obtained 5.95 kg alcohol from 100 kg dry wood. In 1900, Classen replaced the sulphuric acid with sulphurous acid and developed the process further. At Hattiesburg, Miss. a commercial-scale plant was erected based on the Classen Process. But the plant never operated(10). A number of wood saccharification plants constructed in Germany during World War I used a modified Classen sulphurous acid process(11). In these processes hydrochloric acid along with the sulphurous acid was used. Reaction was carried out at 165-170°C and 7-8 bars for 20 minutes. After fermentation 4-6 kg of alcohol was obtained per 100 kg of dry wood. Glesinger(12) claims that the first working wood-sugar factory ever built was in Georgetown, South Carolina, designed by Ewen and Tomlinson in 1910. Operational procedure was similar to that developed by Simonsen. They processed the sawdust and obtained 6 kg alcohol per 100 kg dry wood. But soon after the sawmills ran out of logs and the factory was closed down.

In 1926 Scholler succeeded in increasing the alcohol yield and at Tornesch in 1931 a commercial plant was erected. The number of such plants in Germany was estimated to be 20 in 1941(13). In the Scholler Process wood waste, consisting of sawdust and chips, was compressed in brick-lined steel percolators to approximately 180 kg/m^3 by low pressure steam and then preheated with live steam to 134°C. Successive batches (as many as twenty-four) of 8-11 m^3 of 0.5 per cent sulphuric acid were introduced through the bed beginning at 11.5 bars and reaching 12.4 bars in the final batch. Each batch remained in the percolator for approximately 45 minutes. Upon fermentation the yield was about 15 kg of alcohol per 100 kg of wood.

Numerous investigators have tried to use strong acid and thus to increase the yield. But only one of them, Bergius, succeeded and the so-called Bergius Process became, for a short period, industrially important. Bergius(14), using fuming hydrochloric acid, succeeded in dissolving all the cellulose in the wood at room temperature and then removed most part of the acid by vacuum distillation. By heating the remaining solution to 120°C he converted the dissolved cellulose to sugar without loss. In 1940, a full-scale plant was built at Regensburg, Germany, based on the Bergius Process. Although the yield, which was 23-27 kg alcohol per 100 kg dry wood, was high the process was abandoned very soon, because strong acid proved too corrosive for most standard-type equipment and in the end many parts had to be made of quartz and platinum which made the installation very expensive.

In 1943 Harris(15) and co-workers studied the Scholler Process on a pilot plant in America and were able to decrease the total hydrolysation time from 20 hours to 3 hours but unable to increase the yield. This improved process was called the Madison Process and in 1944, in Springfield, Oregon, a plant of 15,200 m^3 capacity was built. But the life of the plant was not long. Shortly after the end of the war the plant was shut down. Details of the Madison Process and difficulties encountered at the Springfield plant are well described in literature(13,16,17).

Sherrard and Gauger(18) tried to increase the sugar yield by introducing various organic and inorganic materials into the reaction vessel. They tried ferric sulphate, copper sulphate, sodium sulphate, cobalt sulphate, potassium aluminium sulphate, naphtolsulphonic acids, benzene, hydrogen peroxide etc. In no case did the yield increase; on the contrary in most cases it decreased in subsequent fermentation.

2.3 REACTION KINETICS

Most of the work done on the kinetics of cellulose hydrolysis involves strong acid and room temperature.

Freudenberg(19) hydrolysed pure cellulose in 50 per cent sulphuric acid solution at 18°C and 30°C and measured the rate constants. Sherrard(20) determined the rate of the reaction for cellulose of different origin in fuming hydrochloric acid and found some differences. Wolfram(21) studied the degradation of pure cellulose in fuming hydrochloric acid and, by following the change in polarimetric reading, predicted the yield and rate of the reaction.

More comprehensive observations were reported by Lüers(22,23). He claimed that both the hydrolysis of cellulose and the degradation of the sugar present in the hydrolyzate are monomolecular reactions. He further reported that rates of both reactions were equally affected by temperature and both rates were proportional to the acid concentration.

The most detailed work on the kinetics of both reactions was conducted by Saeman(24). He separately investigated the rates of hydrolysis of a number of wood species and decomposition of a number of sugars in dilute sulphuric acid at elevated temperatures. His main finding was that both reactions followed the laws of first order kinetics. Also, in the hydrolysis of different woods, he found small but marked differences in the rates of the reactions. He further reported that the effect of particle sizes over the range tested and effect of the solid-liquid ratio was minor. There were however big differences in the magnitudes of the rate constants in the decomposition of various sugars. Finally he confirmed the importance of temperature and acid concentration on the rates of the reactions.

CHAPTER 3

RATE EQUATION OF THE SACCHARIFICATION REACTION

3.1 INTRODUCTION

Cellulose which is a polysaccharide is composed of β-1,4 linked D-Glucopyranose units (Fig. 3.1) and only yields glucose, a monosaccharide, upon hydrolysis.

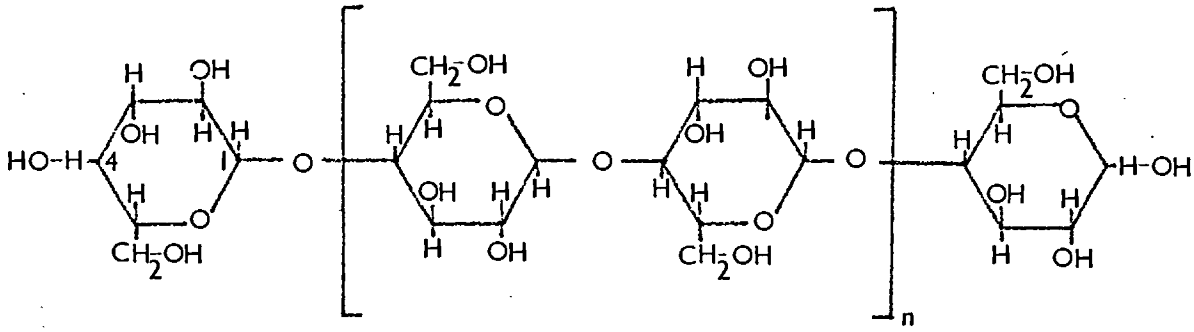


Fig. 3.1 Structural formula of a cellulose molecule

In shorthand notation the hydrolysis reaction may be written as:

$$\underset{\text{cellulose}}{(C_6H_{10}O_5)_n} + H_2O(H^+) \xrightarrow{k_1} \underset{\text{glucose}}{C_6H_{12}O_6}$$

with acid acting as catalyst.

The present chapter is devoted to the experimental study of the kinetics of the hydrolysis reaction using waste paper pulp as raw material. It also includes investigation of the effects of temperature and acid strength on the reaction.

3.2 RAW MATERIAL

The waste paper pulp was collected from the plant of the Reed Paper Group in Aylesford, Kent. It was brought to the College in plastic sacks and immediately was subjected to slow drying to prevent bacterial attack. The water content of the waste was thus reduced from its initial value of 75% to 4-6%. This was accompanied by hardening of the pulp pieces on account of dewatering of the clay present in the pulp. The pulp pieces had therefore to be ground before use. This was done by rubbing them between two files. Final sieving ensured a uniform particle size.

3.3 PRELIMINARY TESTS

A number of tests has been carried out prior to the reaction kinetics.

3.3.1 Organic Materials Content of the Waste Pulp

The waste paper pulp apart from cellulose and Lignin, which are organic, contained some inorganic materials added during the pulping process. This is primarily clay. As a first step towards finding the cellulose content of the pulp a number of samples were therefore taken and burned in porcelain crucibles. Results are given in Table 3.1

Table 3.1 Organic Material Content of the Waste Pulp

Run No.	Sample (g)	Residue after burning (g)	Cellulose + Lignin (%)
1	0.3328	0.0942	71.7
2	0.5425	0.1591	70.7
3	0.7412	0.2042	72.4
4	0.9190	0.2638	71.3
5	1.0137	0.2746	72.9

3.3.2 Acid Consumption of the Pulp (Neutralization Value)

The acid consumption of the waste pulp is very important for two different reasons: Firstly it must be allowed for in preparation of acid solutions acting as catalyst in kinetic experiments and secondly its cost must be taken into account in the economic analysis of the process. In order to find out whether the waste pulp would consume acid, several samples of about 0.7 g were treated with 10 ml of 1.6% sulphuric acid at several temperatures, ranging from 20°C to 180°C. The samples were then cooled, filtered and the resulting solutions titrated with N/10 sodium hydroxide solution. It was found that regardless of temperature 2.56 kg of sulphuric acid (100%) were needed to neutralize 100 kg of waste pulp.

3.3.3 Potential Sugar Content of the Waste Pulp

This test was carried out by using Saeman's method(25). Several samples were prepared in glass tubes by mixing about 0.4-1.0 g of waste pulp with 5 ml of 72% sulphuric acid. The tubes were then kept in a water bath at 30°C for 45 minutes. Subsequently the mixtures were washed into erlanmeyer flasks and made up to 140 ml volume with distilled water. The flasks were placed in an autoclave and were held there for 1 hour at 1 bar gauge pressure. Then they were cooled, neutralized with excess solid calcium carbonate and the solutions filtered off and finally analysed for sugar according to the method described in section 3.7. Results obtained are tabulated in Table 3.2.

Table 3.2 Potential Sugar Content of the Waste Pulp

Sample No.	Sample taken (g)	Sugar (%)
1	0.3752	46.7
2	0.4186	47.1
3	0.4642	45.6
4	0.5062	46.1
5	0.5580	46.3
6	0.6675	44.9
7	0.8360	45.9
8	0.9142	46.1
9	0.9672	47.1
10	1.0162	45.8
	AVERAGE:	46.1

3.4 PROCEDURE

Preliminary tests proved that hydrolysis of waste pulp in dilute acid is quite slow at low temperatures. For this reason 170°C, 180°C and 190°C were chosen as the reaction temperatures. Equipment limitations did not allow the use of higher temperatures. Three different sulphuric acid concentrations namely 0.4%, 0.8% and 1.6% were used.

A brief description of the apparatus used is given first, followed by experimental procedure and analysis of results.

3.4.1 Glass Tubes

A large number of 16 mm O.D. glass tubes were specially made from about 1.5 mm thick glass tubing. The upper parts of the tubes, about 5 cm from the top, were drawn to a small opening to make the final sealing of the tubes easy and efficient. First ground pulp was introduced, then one half of the acid solution was carefully added washing down the wall of the tube. The tube contents were mixed with a stainless steel rod and about 3 hours were allowed for the solution to wet and fill the porous parts of the pulp. The rest of the solution was then poured in and the tube was sealed.

3.4.2 Reaction Vessel

The vessel, as shown in Fig. 3.2, was essentially a cylindrical copper pipe 10 cm in diameter and 50 cm long. An air blower was placed at the bottom followed by an electrical heating wire coiled on an asbestos sheet. A heating coil (filament) was wound all round the vessel and finally the vessel was insulated with a thick layer of asbestos rope. Three thermometers were horizontally immersed into the vessel through specially cut holes in the wall. The control of the current and hence of temperature was made possible by the introduction of variac controllers into the heating wire and heating coil circuits.

3.4.3 Tube Holder

Three triangular metal sheets were soldered onto a steel rod at about 7 cm apart, in such a way that the rod would pass through the centers of the sheets. In the three corners of the top two sheets 16 mm holes were cut out to accommodate three tubes in each run. The holder was placed in the vessel about 8 cm away from the heating wire and was connected to a motor which was also controlled by a variac controller. The revolving

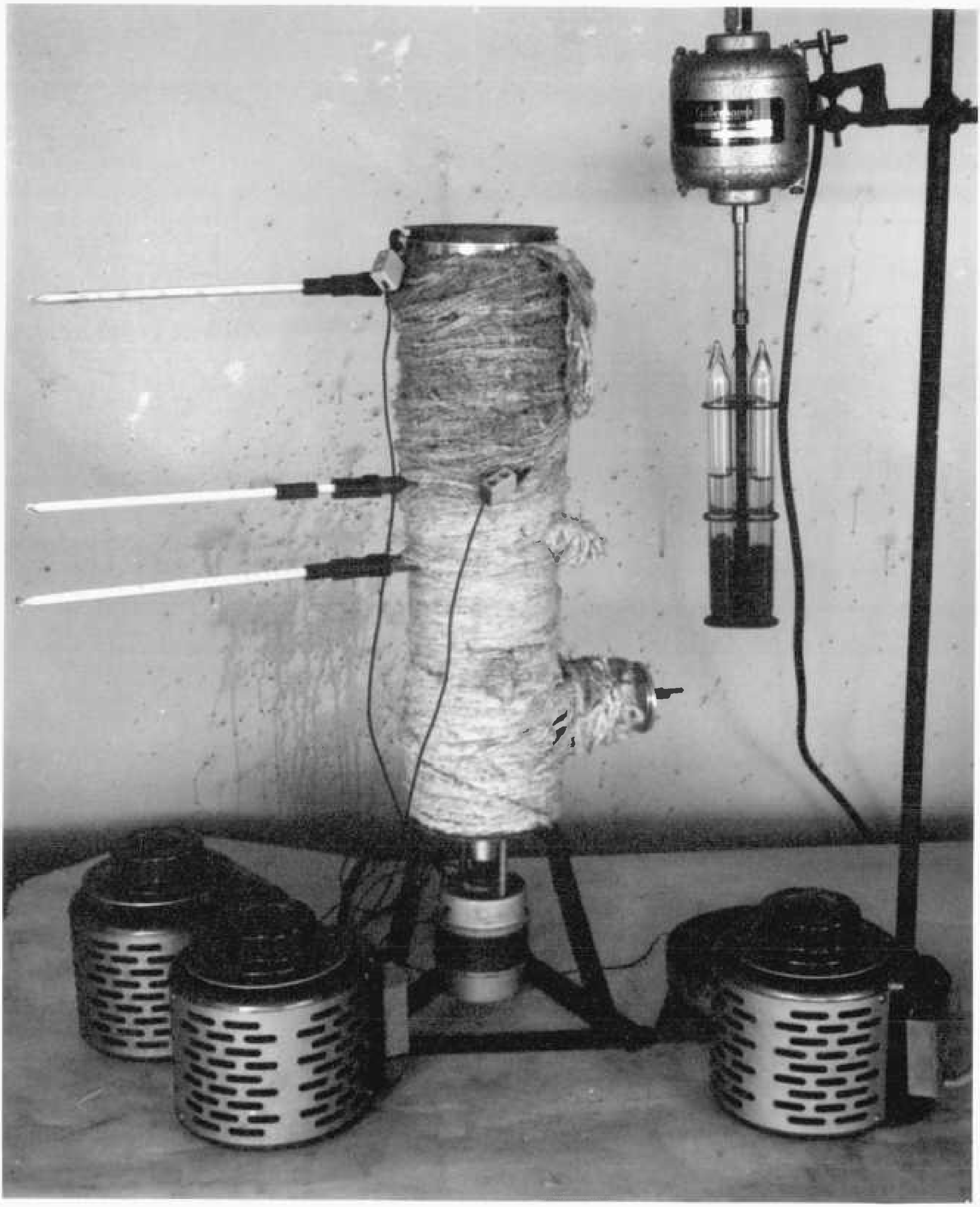


Fig. 3.2 Equipment for the Kinetic Study of Waste Pulp

holder induced therefore a stirring action in the tubes.

3.4.4 Experimental Procedure

The pulp particles used throughout the experiment were sub-36 mesh size. Concentration of the pulp, or in more precise terms solid-liquid ratio, was kept at 1/15 by weight. 0.6667 g of bone dry waste pulp and 10 g of acid solution were mixed in the tubes as described above. The tubes were then sealed and replaced in their places in the tube holder which was kept outside the vessel. Vessel temperature was brought up to the reaction temperature, the lid was quickly opened and the holder with tubes was immersed in the vessel. The lid was then closed and the holder put on motion. By adjusting the variac controllers, the temperature inside the vessel was kept at the desired value. After a certain time period the holder was taken out and the tubes cooled by immersing them in a cold water bath. Then the heads of the tubes were cut off, the liquid decanted and the residue washed several times. After drying, their potential sugar contents were determined according to the method described in section 3.3.3.

3.5 RESULTS

When the potential sugar contents of the residues, based on the initial waste pulp weight, were plotted on a semilog paper against time a series of straight lines of different slope were obtained. (Figures 3.3 and 3.4). These figures reveal that the hydrolysis reaction with respect to loss of potential sugar is a first order reaction and that temperature and acid strength both affect the reaction. Furthermore, since

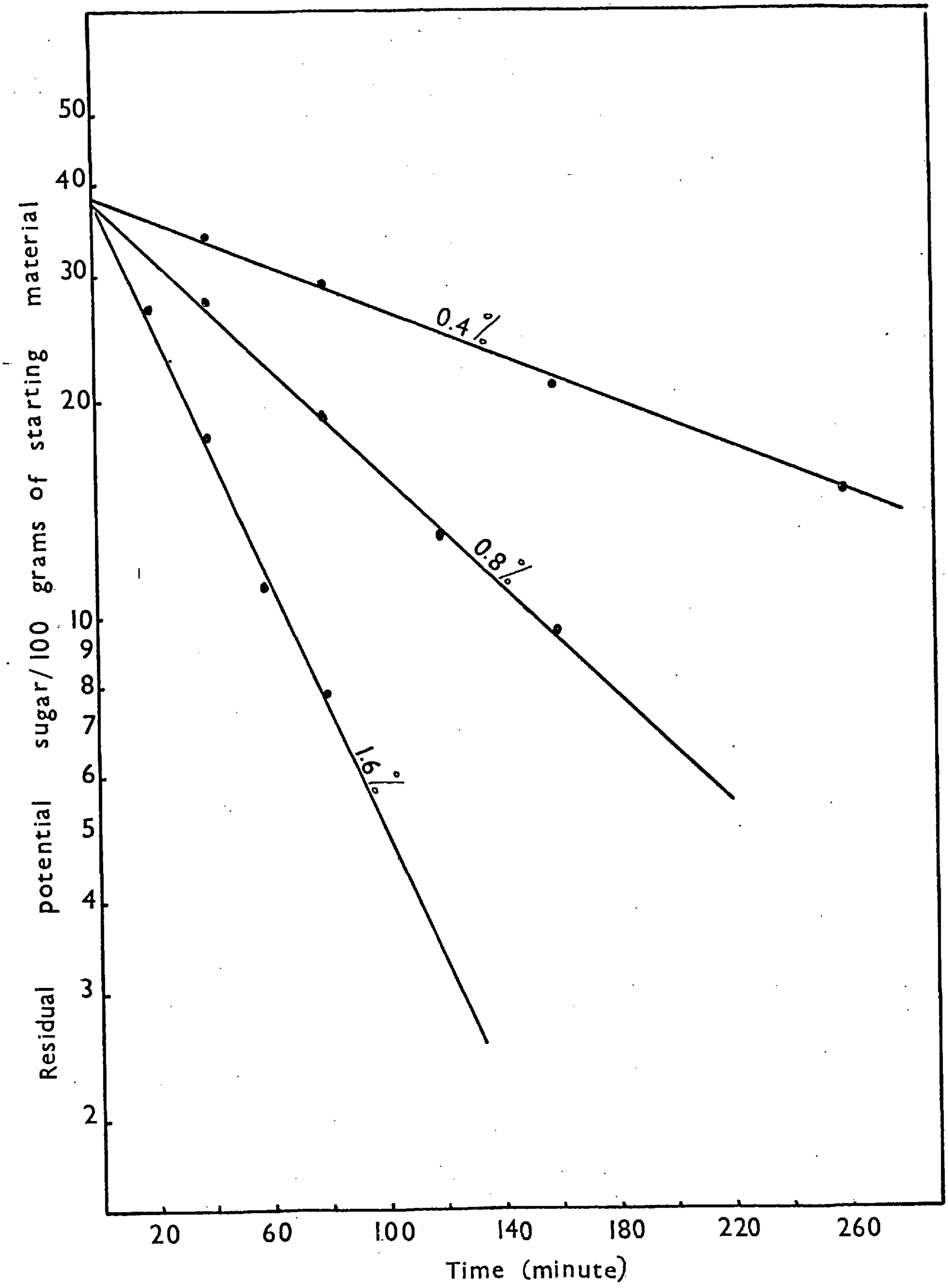
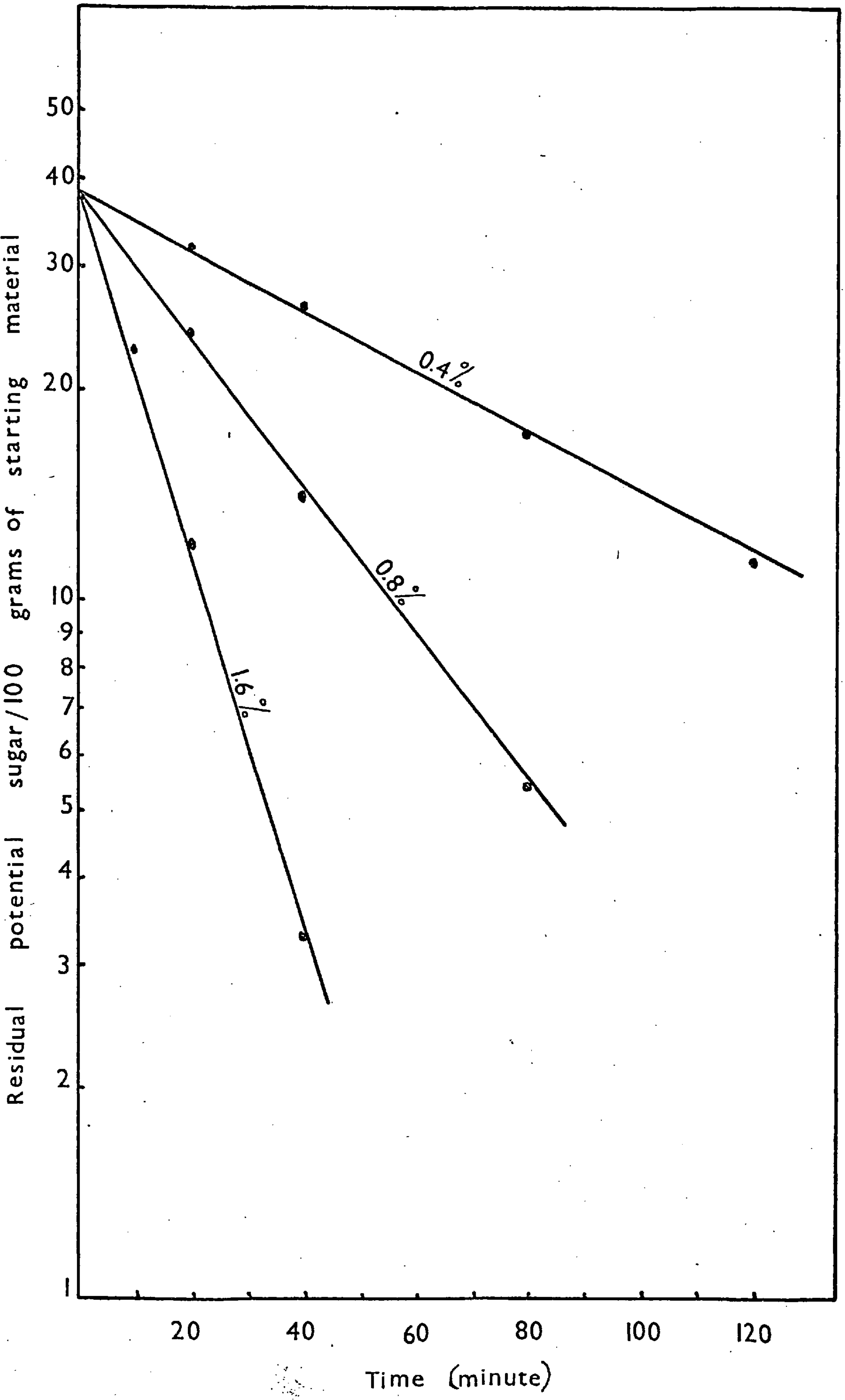


Fig. 3.3 Hydrolysis of Waste Paper Pulp at 170°C

Fig. 3.4 Hydrolysis of Waste Paper Pulp at 180°C



the extrapolated lines meet at a point which corresponds to a potential sugar of 38%, the hydrolysis reaction is rate controlling for the most of the cellulose content in the waste pulp. This indicates the difference in behaviour between cellulose in the waste pulp and wood cellulose employed by other workers$^{(24)}$. Up to 30% of the latter's cellulose content was found to be non-resistant to acid.

Hence, for the hydrolysis reaction, the rate equation can be written as

$$-\frac{dC}{dt} = k_1 C \qquad (3.1)$$

Upon rearrangement and integration

$$\log \frac{C}{C_0} = -2.303\ k_1 t \qquad (3.2)$$

is obtained.

Here C_0, C represent the concentrations of cellulose in the waste pulp expressed in terms of potential sugar at time zero and time t respectively.

By equating the slopes of the lines of figures 3.3 and 3.4 to $-2.303\ k_1$ values of rate constants have been calculated. Results are given in Table 3.3.

Table 3.3 Values of rate constants of hydrolysis reaction

Temperature (°C)	Acid (%)	k_1 (min^{-1})
170	0.4	0.00347
	0.8	0.00858
	1.6	0.02040
180	0.4	0.00995
	0.8	0.02250
	1.6	0.06110

3.5.1 Effect of Acid Concentration on the Reaction

When the logarithmic values of the rate constants of the hydrolysis reaction were plotted against the logarithmic values of the acid concentrations at constant temperatures straight lines of positive slope were obtained (Fig. 3.5).

Consequently,

$$k_1 = BC_A^{\beta} \tag{3.3}$$

where k_1 is the rate constant, C_A the concentration of sulphuric acid (%), while B and β are constants which are evaluated from the slopes and intercepts of the lines. Their values are given in the table overleaf.

Temp. (^oC)	B	β
170	0.01096	1.27
180	0.03193	1.28

3.5.2 Effect of Temperature on the Reaction

When the graph of rate constants versus reciprocal of absolute temperature was plotted on semilog paper for three different acid concentrations it produced a series of straight lines (Fig. 3.6).

Hence, assuming applicability of Arrhenius law

$$k_1 = A\, e^{-\frac{\Delta H}{RT}} \tag{3.4}$$

From the slopes of the lines ΔH, energy of activation, and from the intercepts the constant A can be calculated. The relevant results are given in the table below.

C_A (%)	ΔH (kJ/k mol)	A
0.4	175,500	1.89×10^{18}
0.8	171,700	4.60×10^{18}
1.6	179,700	20.1×10^{18}

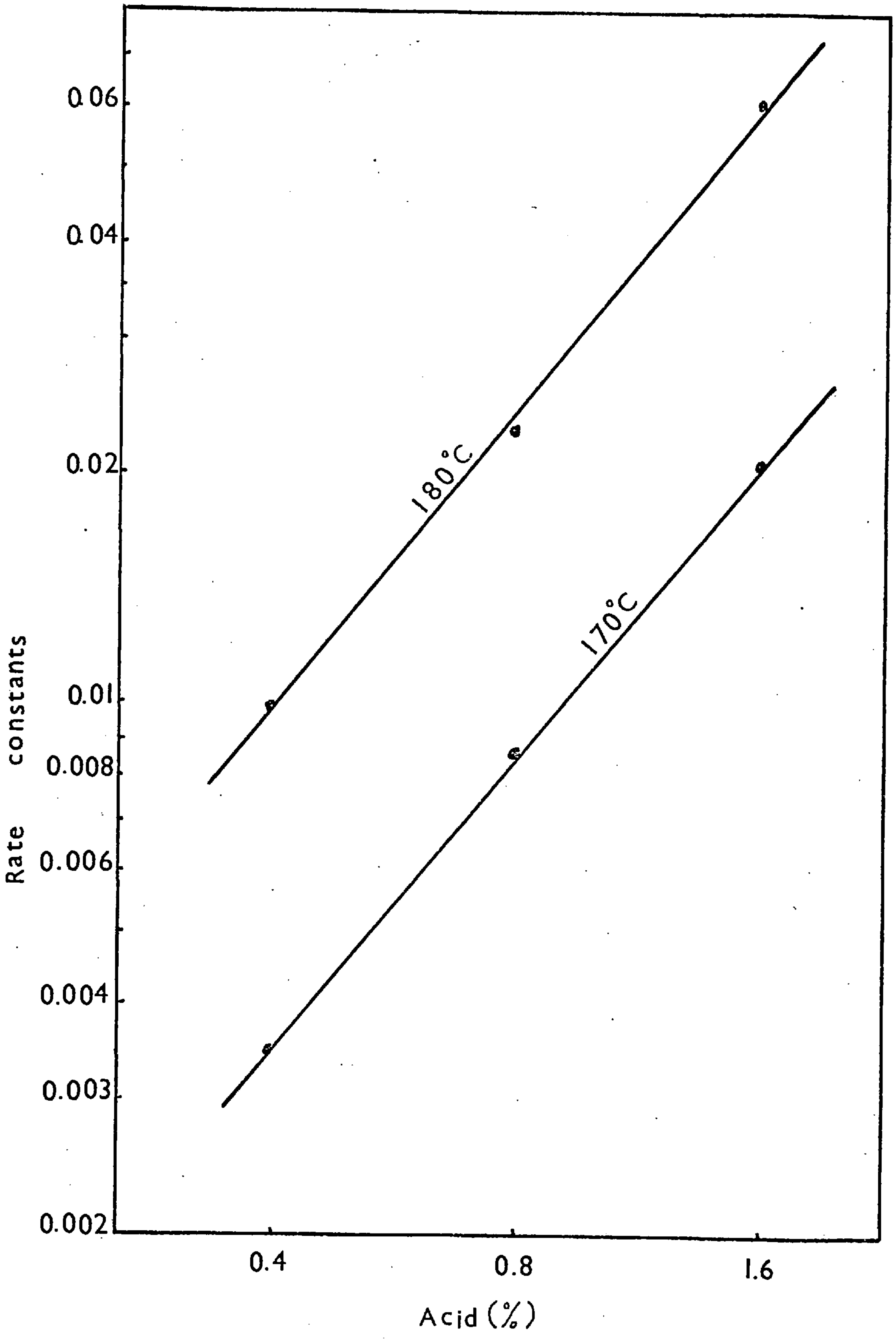


Fig. 3.5 Effect of Acid Concentration on First Order Reaction Constant in Hydrolysis of Waste Paper Pulp

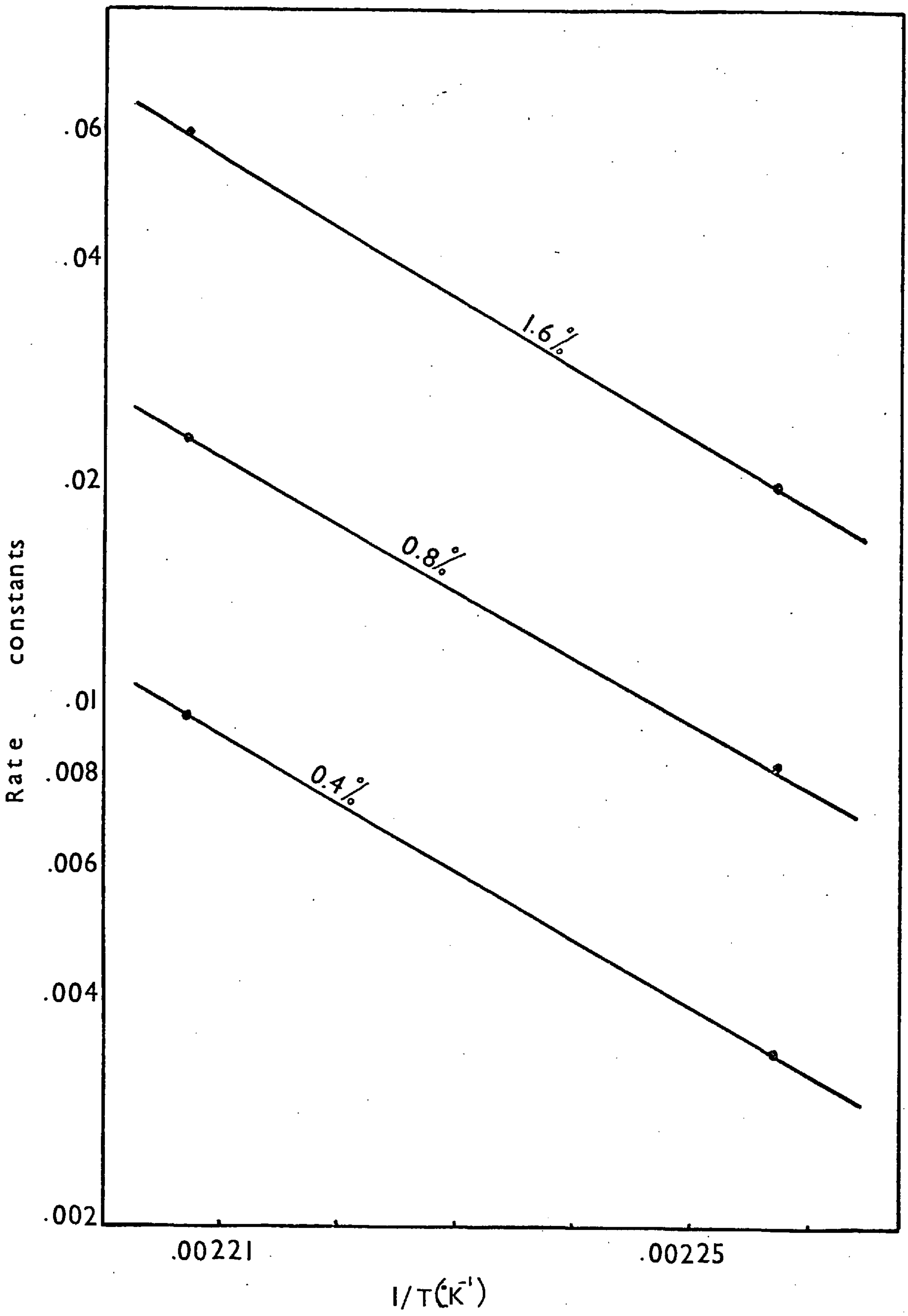


Fig. 3.6 Effect of Temperature on the First Order Reaction Constant in Hydrolysis of Waste Paper Pulp

3.5.3 Combination of the Two Effects: Generalized Rate Equation

From equations (3.3) and (3.4)

$$k_1 = A e^{-\frac{\Delta H}{RT}} = BC_A^{\beta} \qquad (3.5)$$

can be written.

The constant A thus incorporates the catalytic effect of the acid. Hence it can be expressed as

$$A = B_1 C_A^{\beta} \qquad (3.6)$$

On substituting into equation (3.4)

$$k_1 = B_1 C_A^{\beta} e^{-\frac{\Delta H}{RT}} \qquad (3.7)$$

is obtained.

By equations equations (3.7) and (3.4)

$$B_1 = B e^{\frac{\Delta H}{RT}} \qquad (3.8)$$

is found.

With known values of B and ΔH, B_1 is calculated as

$$B_1 = 6.15 \times 10^{18}$$

On substitution of known quantities into equation (3.7) and finally (3.1) the generalized rate equation is obtained as:

$$-\frac{dC}{dt} = 6.15 \times 10^{18} C_A^{1.275} \exp(-21,130/T)C \qquad (3.9)$$

3.6 DISCUSSION OF THE RESULTS

In order to check the reliability of equation (3.9) values of rate constants were computed from equation (3.7) with known values of B_1, β and ΔH at the conditions of experimental runs. Results are given in Table 3.4. Comparison of Tables 3.3 and 3.4 shows that measured and calculated values are in good agreement. Hence equation 3.7 and consequently equation 3.9 can be used to predict the values of rate constant at conditions outside the experimental range.

Table 3.4 Calculated values of rate constants of hydrolysis reaction

Temp. (°C)	Acid (%)	k_1 (min^{-1})
170	0.4	0.00357
	0.8	0.00863
	1.6	0.02088
180	0.4	0.01022
	0.8	0.02474
	1.6	0.05987

3.7 DETERMINATION OF SUGAR IN HYDROLYZATES

In determination of sugar in the solutions the Somogyi Method(26) was used.

In application of this method Reagent 50 containing 1 g of potassium iodide was used with a heating time of 30 minutes. The given empirical factor of 0.113 was not used. Instead an experimental factor was always determined by using pure glucose as reference whenever the analysis was carried out. The advantage of this method lies in the fact that sugar can be determined in very dilute solutions.

CHAPTER 4

RATE EQUATION OF THE GLUCOSE DECOMPOSITION REACTION

4.1 INTRODUCTION

Since glucose is the main product of the hydrolysis of cellulose in acidic solutions its behaviour in such solutions needs to be investigated.

In organic chemistry texts it is stated that glucose is decomposed in acidic solutions giving chiefly hydroxymethylfurfural, which further decomposes to levulinic and formic acids.

In shorthand notation the decomposition reaction may be written as:

$$\underset{\text{Glucose}}{C_6H_{12}O_6} + H_2O(H^+) \xrightarrow{k_2} \text{Products}$$

The objective of this chapter can thus be defined as:

(i) Study of the kinetics of the decomposition reaction,

(ii) Investigation of the effects of temperature and acid strength on the rate constant of the reaction.

4.2 PROCEDURE

Analar grade D-glucose was dissolved in sulphuric acid solutions in such a way that each fifteen ml of solution contained 1 g of glucose. 0.4%, 0.8% and 1.6% sulphuric acid solutions and temperatures of 170, 180 and 190°C were chosen as in the previous hydrolysis test. Same type of glass tubes, the same reaction vessel and the same experimental procedure were used.

4.3 RESULTS

When the percentages of residual glucose were plotted against reaction times on a semilog paper straight lines of different slope were obtained. (Figures 4.1, 4.2, 4.3) This confirms that the reaction follows first order reaction law.

Hence the rate equation can be written as:

$$-\frac{dC_B}{dt} = k_2 C_B \tag{4.1}$$

Upon rearrangement and integration,

$$\log \frac{C_B}{C_{BO}} = -2.303\ k_2 t \tag{4.2}$$

is obtained.

Here, k_2 is the rate constant of the decomposition reaction, C_B and C_{BO} are the glucose concentrations at time t and time zero respectively.

From the slopes of the lines the values of the rate constants were calculated. Results are tabulated in Table 4.1.

4.3.1 Effect of Acid Concentration on the Reaction

On plotting the logarithmic values of the rate constants against the logarithmic values of the sulphuric acid concentrations at fixed temperatures a series of straight lines were obtained. (Fig. 4.4).

These lines can be represented by the equation

$$k_2 = B' C_A^{\alpha} \tag{4.3}$$

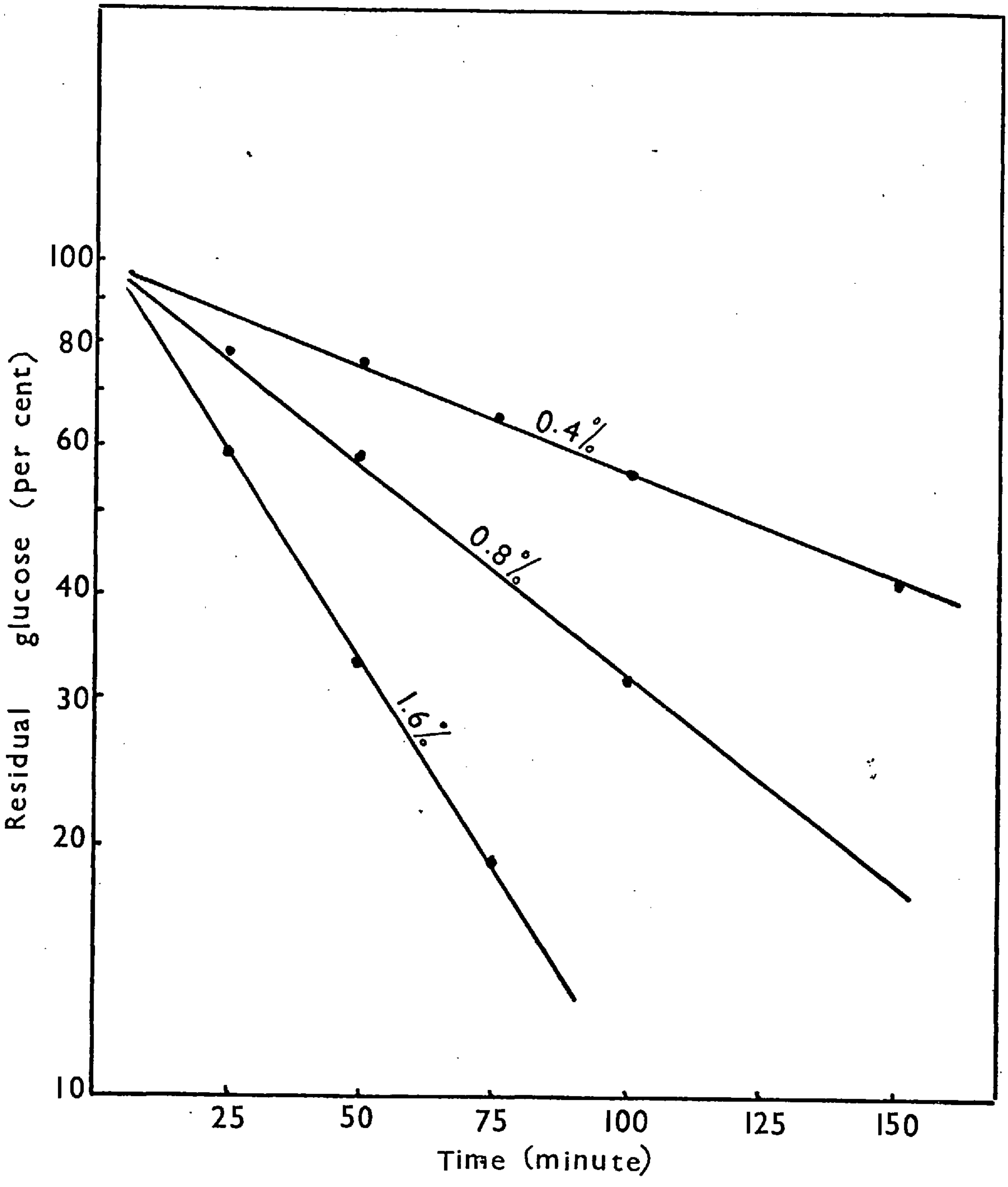


Fig.4.1 Decomposition of Glucose at 170°C

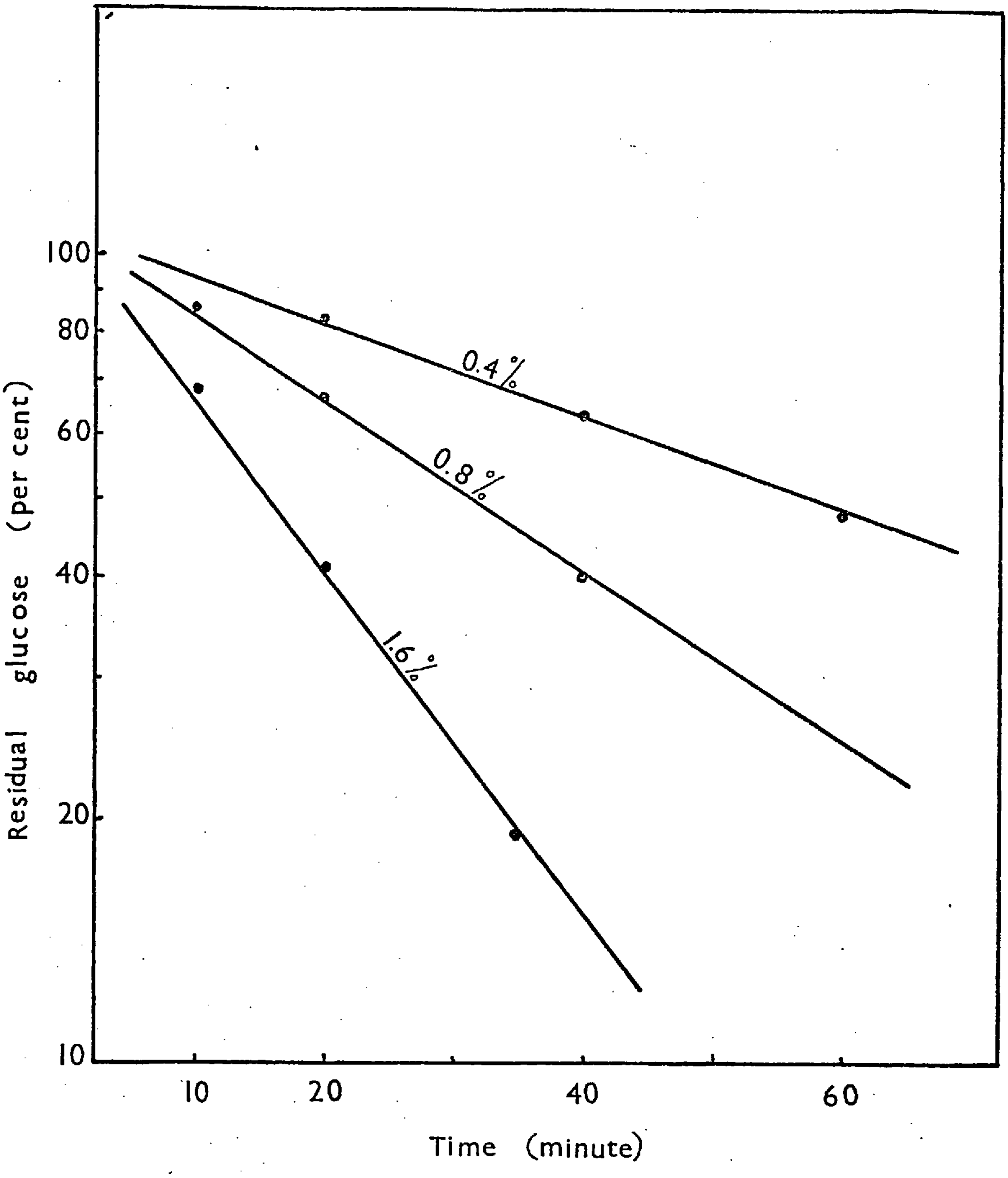


Fig. 4.2 Decomposition of Glucose at 180°C

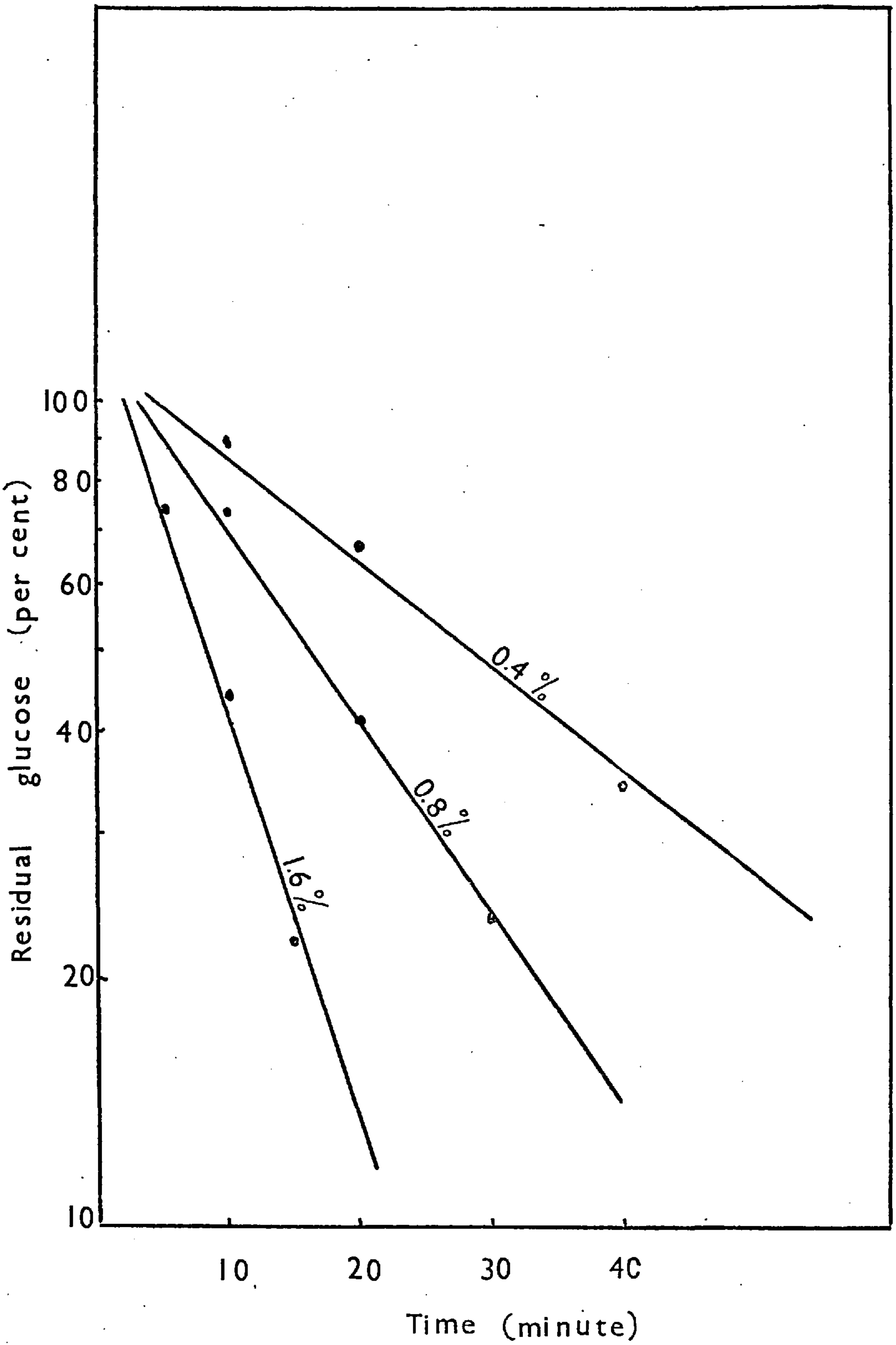


Fig. 4.3 Decomposition of Glucose at 190°C

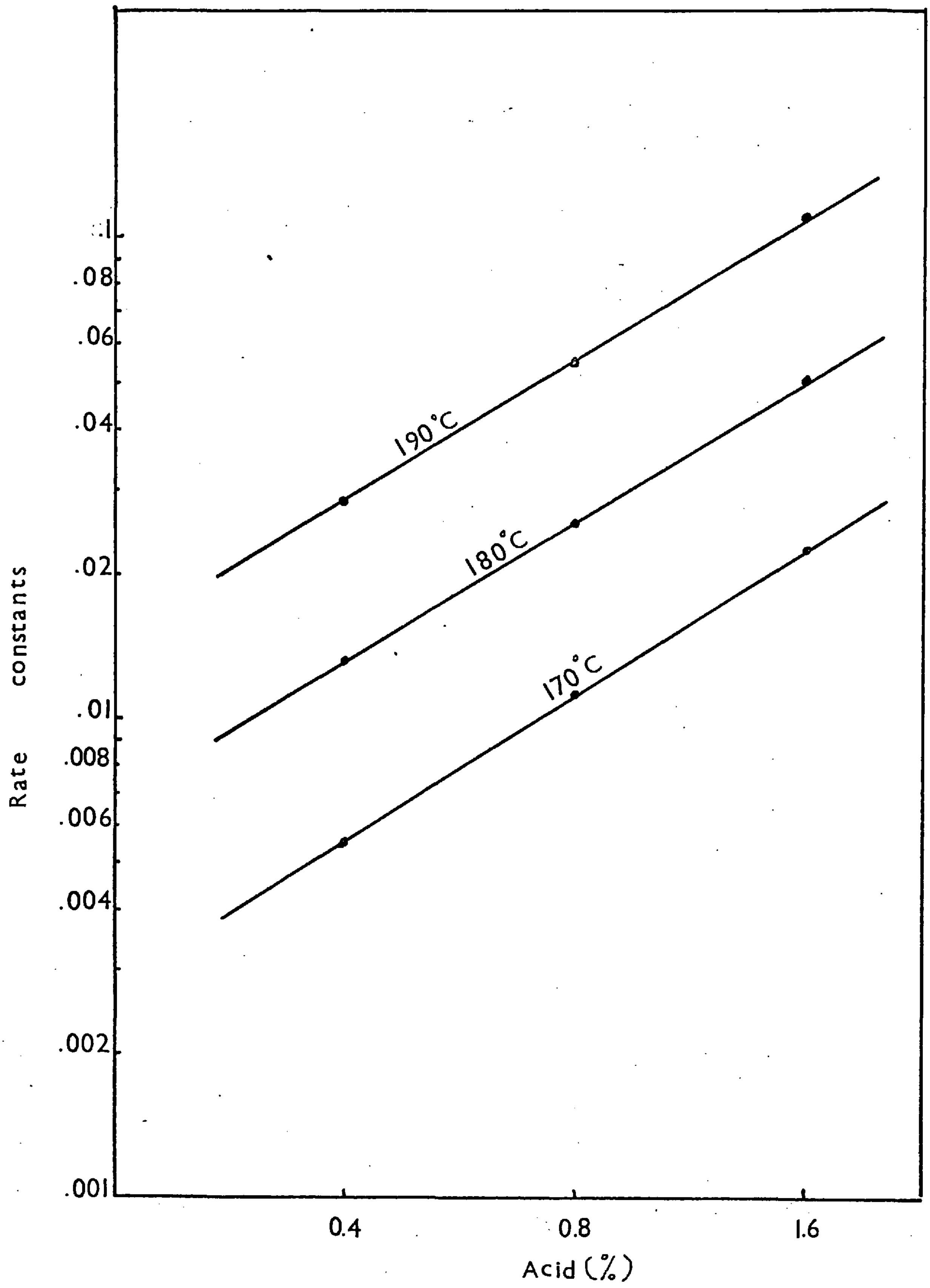


Fig. 4.4 Effect of Acid Concentration on First Order Reaction Constant in Decomposition of Glucose

Table 4.1 Measured values of the rate constants of decomposition reaction

Temp. (^{o}C)	Acid (%)	k_2 (min^{-1})
170	0.4	0.00558
	0.8	0.01124
	1.6	0.02290
180	0.4	0.0132
	0.8	0.0257
	1.6	0.0510
190	0.4	0.0286
	0.8	0.0550
	1.6	0.1110

where C_A is the concentration of sulphuric acid (%) while B' and α are constants. The values of the constants were determined from the slopes and the intercepts of the lines. Results are given in the table below.

Temp. (^{o}C)	B'	α
170	0.0230	1.010
180	0.0496	0.986
190	0.1105	0.993

4.3.2 Effect of Temperature on the Reaction

On plotting the logarithm of the rate constant against the reciprocal of the absolute temperature at fixed acid concentrations a series of straight lines were obtained (Fig. 4.5).

This graph confirms the applicability of Arrhenius Law. Hence,

$$k_2 = A' e^{-\frac{\Delta H'}{RT}} \qquad (4.4)$$

With the help of the graph ΔH', the energy of activation and A' were calculated. Results are given in the table below.

C_A (%)	ΔH' (kJ/k mol)	A'
0.4	136,700	5.25×10^{13}
0.8	132,900	11.20×10^{13}
1.6	137,500	22.70×10^{13}

4.3.3 Combination of the Two Effects: Generalized Rate Equation

From equations (4.3) and (4.4)

$$k_2 = A' e^{-\frac{\Delta H'}{RT}} = B' C_A^{\alpha} \qquad (4.5)$$

Here the constant A' includes the effect of the acid strength. Hence

$$A' = B_1' \, C_A^{\alpha} \qquad (4.6)$$

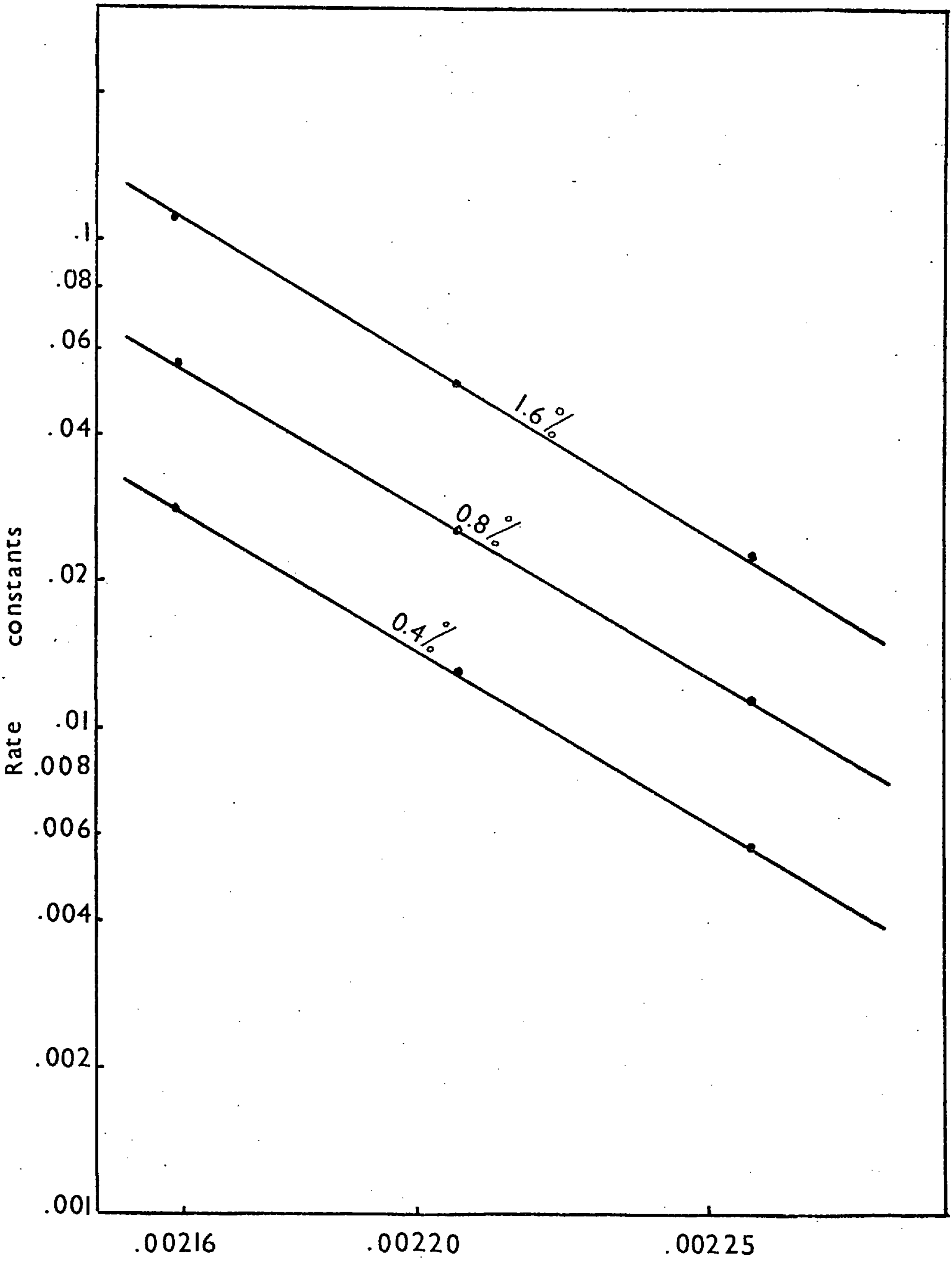


Fig. 4.5 Effect of Temperature on the First Order Reaction Constant in Decomposition of Glucose

On substituting into eq. (4.4)

$$k_2 = B_1' C_A^{\alpha} e^{-\frac{\Delta H'}{RT}} \qquad (4.7)$$

By equating eq. (4.7) and eq. (4.4)

$$B_1' = B_1 e^{\frac{\Delta H'}{RT}} \qquad (4.8)$$

With the known values of B_1 and $\Delta H'$, B_1' is calculated as:

$$B_1' = 1.42 \times 10^{14}$$

On substitution of all known quantities into equation (4.1) the general equation is obtained as:

$$-\frac{dC_B}{dt} = 1.42 \times 10^{14} C_A^{0.997} \exp(-16,300/T)\, C_B \qquad (4.9)$$

4.4 DISCUSSION OF THE RESULTS

As in the previous chapter, the reliability of equation (4.9) was checked. For this purpose the values of rate constants were computed from equation (4.7) with known values of B_1', α and $\Delta H'$ at the conditions of experimental runs. Results are given in Table 4.2.

Calculated values of rate constants compare well with the determined values. Hence, equation (4.7) and consequently equation (4.9) can be used to predict values of rate constants at conditions outside the experimental range.

Table 4.2 Calculated values of rate constants of decomposition reaction

Temp. (^oC)	Acid (%)	k_2 (min^{-1})
170	0.4	0.00545
	0.8	0.01087
	1.6	0.02170
180	0.4	0.01230
	0.8	0.02454
	1.6	0.04898
190	0.4	0.02679
	0.8	0.05348
	1.6	0.10673

4.5 DETERMINATION OF GLUCOSE CONTENT OF THE SOLUTIONS

In determination of the amount of glucose in the solution an automatic polarimeter (Fig. 4.6) was used. The working principle of the equipment can be outlined as follows: When a plane of polarised light passes through an optically active solution the plane of polarization is rotated. This deflection is made to cause a current to flow in the appropriate part of the equipment which is then compensated. This compensated current produces a rotation equal in magnitude but opposite in direction to that caused by the sample. Similarly, the voltage produced across a resistor and applied to a chart recorder will vary in direction and magnitude in proportion to the current.

Hence a permanent record of the reaction can be produced.

In determination of their glucose content the solutions, after heating in the reaction vessel, were made up to 100 ml with distilled water and then analysed by the polarimeter. Analar grade D-glucose solution was used as reference.

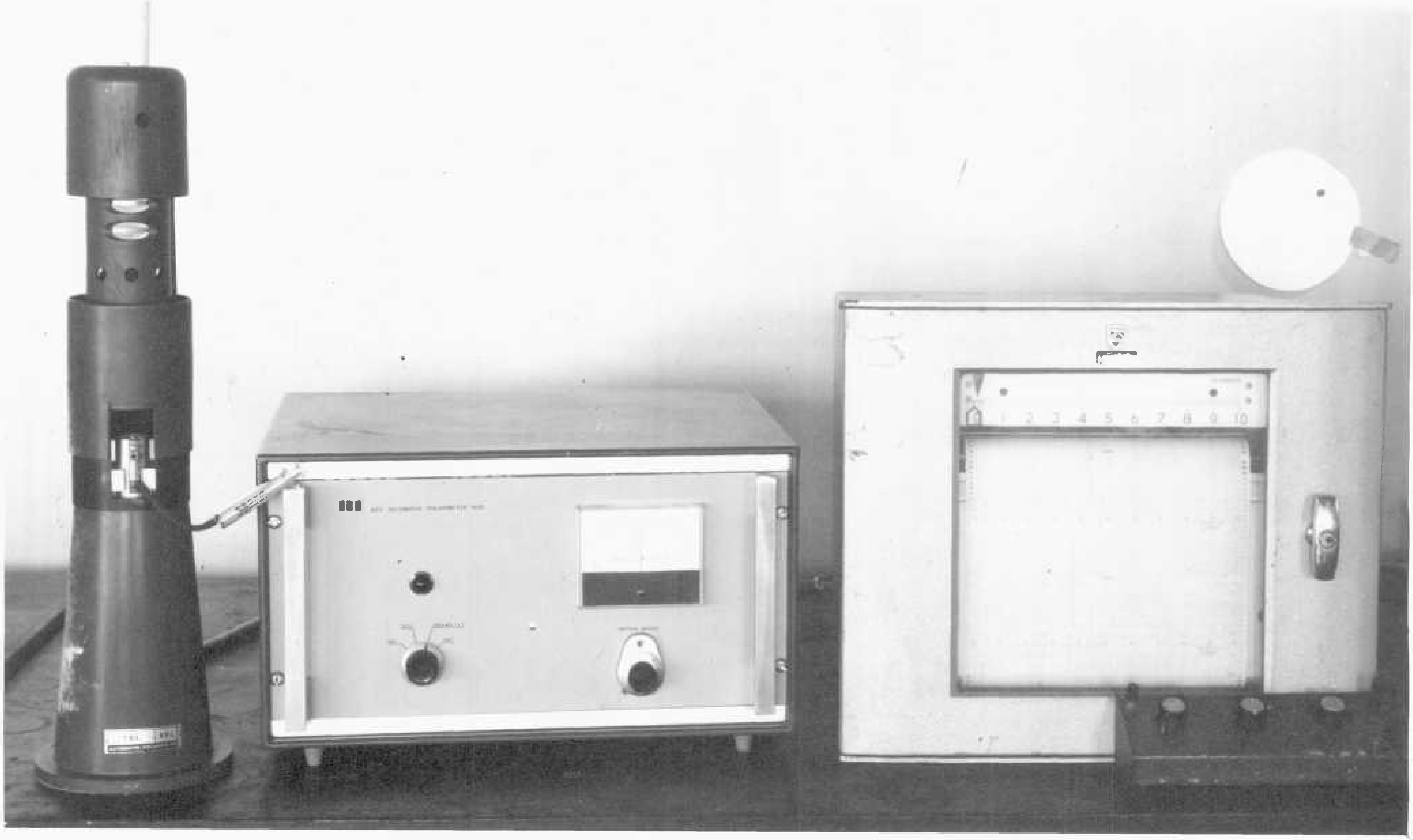


Fig. 4.6 Automatic Polarimeter

CHAPTER 5

DESIGN AND OPERATION OF SUGAR REACTOR

5.1 INTRODUCTION

In previous chapters it was shown that both the hydrolysis of cellulose in the waste pulp and the decomposition of glucose follow first order reaction laws. In cellulose hydrolysis of the waste pulp the cellulose concentration of the pulp was expressed in terms of potential sugar based on glucose and the change in this potential sugar was followed without paying much attention to the products. From these findings it was shown that this change followed the first order reaction law. Then, the decomposition of glucose in acidic solution at the same reaction conditions was investigated, keeping in mind that the hydrolyzate of cellulose contains predominantly glucose. This reaction too was found to follow the first order reaction law.

Consequently the overall hydrolysis reaction can be written as:

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C \qquad (5.1)$$

which is a first order consecutive reaction. Here A represents the cellulose in the waste, B the sugar and C the decomposition products.

In the light of equation 5.1 the objective of the present chapter can be outlined as follows: Firstly, equation (5.1) will be assumed to be valid and theoretical analysis conducted of the process for various types of reactors using the experimentally determined values of rate constants. Secondly, the process will be operated batchwise in a bench scale reactor and the yields determined experimentally. The comparison of experimentally determined and theoretically evaluated results will serve as a test of the validity of equation 5.1 and of the reactor models.

5.2 THEORETICAL ANALYSIS

5.2.1 Analysis of Batch and Plug Flow Reactors(27)

When the initial concentrations of B and C are zero the relevant rate equations are:

$$r_A = \frac{dC_A}{dt} = -k_1 C_A \qquad (5.2)$$

$$r_B = \frac{dC_B}{dt} = k_1 C_A - k_2 C_B \qquad (5.3)$$

$$r_C = \frac{dC_C}{dt} = k_2 C_B \qquad (5.4)$$

From equation (5.2) upon integration

$$C_A = C_{AO} e^{-k_1 t} \qquad (5.5)$$

is obtained. On substitution into eq. (5.3) and integration

$$\frac{C_B}{C_{AO}} = \frac{k_1}{k_2 - k_1} (e^{-k_1 t} - e^{-k_2 t}) \qquad (5.6)$$

The maximum value of C_B is found by taking the derivative of C_B in eq. (5.6) with respect to time and equating it to zero. This yields

$$(\frac{C_B}{C_{AO}})_{max} = \left[\frac{k_1}{k_2}\right]^{\frac{k_2}{k_2-k_1}} \qquad (5.7)$$

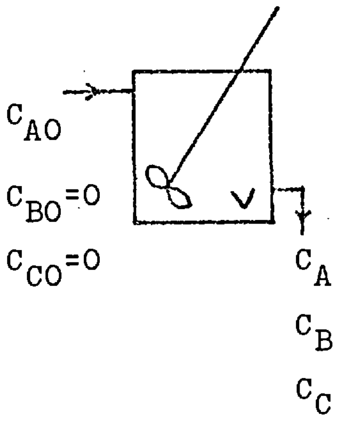
The time τ at which C_B reaches its maximum value is found by equating equations (5.6) and (5.7) and solving for τ

$$\tau = \frac{\log \frac{k_2}{k_1}}{k_2 - k_1} \qquad (5.8)$$

5.2.2 Analysis of Constant Flow Stirred Tank Reactor(27)

If F represents the volumetric flow rate, the overall material balance for steady-state conditions can be written as:

$$FC_{AO} + FC_{BO} + FC_{CO} = FC_A + FC_B + FC_C \qquad (5.9)$$



Material balance on A yields

$$FC_{AO} = FC_A + k_1C_AV \qquad (5.10)$$

Material balance on B yields

$$FC_{BO} + k_1C_AV = FC_B + k_2C_BV \qquad (5.11)$$

From equation (5.10), noting that t = residence time = $\frac{V}{F}$

$$\frac{C_A}{C_{AO}} = \frac{1}{1 + k_1t} \qquad (5.12)$$

is obtained.

On substituting the value of C_A in eq. (5.12) into equation (5.11) noting that $C_{BO} = 0$

$$\frac{C_B}{C_{AO}} = \frac{k_1t}{(1 + k_1t)(1 + k_2t)} \qquad (5.13)$$

is found.

For maximum value of C_B the derivative of C_B in eq. (5.13) with respect to time is set to zero and this gives

$$\left(\frac{C_B}{C_{AO}}\right)_{max} = \frac{1}{\left[\left(\frac{k_2}{k_1}\right)^{\frac{1}{2}} + 1\right]^2} \qquad (5.14)$$

The time at which yield reaches its maximum value is found by equating equations (5.13) and (5.14) and solving for τ. When this is done

$$\tau = \frac{1}{\sqrt{k_1 k_2}} \qquad (5.15)$$

In the above equations C_{AO} is the concentration of the cellulose expressed in terms of potential sugar in 100 g of starting waste material (g/100 g waste) C_B is the amount of sugar obtained from 100 g of starting waste material (g/100 g waste).

5.3 PREDICTION OF THE YIELD

Equations (5.7) and (5.14) can be used to predict the maximum yield of the process as represented by eqn. 5.1 for different types of reactors, whereas equations (5.6) and (5.13) are helpful to follow the change of the yield with time. Equations (5.8) and (5.15) are referred to whenever the time required to attain maximum yield is needed.

It follows from the relevant equations that the maximum yield and the corresponding time, regardless of the type of the reactor, is only a function of the rate constants. But the rate constants, as was shown previously, are functions of temperature and acid concentration. Thus, the maximum yield is dependent only on temperature and acid concentration. Their dependence is indicated in Table 5.1. The data in Table 5.1 were calculated from equations (5.7), (5.8), (5.14) and (5.15) with the help of equations (3.7) and (4.7) by digital computation on a CDC 6400 computer. (See Appendix A)

It follows from Table 5.1 that the yield increases as the temperature and/or acid concentration increase, that corresponding residence times become shorter, that batch and plug flow reactors give higher yield than the constant flow stirred tank reactor, although the residence times for both type of reactor remain approximately identical, at the same reaction conditions.

5.4 EXPERIMENTAL RESULTS

5.4.1 Equipment

The equipment set up for the experimental runs consisted mainly of three parts (Fig. 5.1): reactor, pump and acid feed tank.

Reactor: The reactor was a cylindrical vessel constructed from EN 58J grade stainless steel. Its dimensions were 15 cm I.D., 25 cm overall length and 0.8 cm wall thickness. The bottom was welded to the cylinder while the top was secured in its place by 16 high tensile bolts and nuts so that the vessel could be opened whenever needed. Several pipes of 1.9 cm O.D. were welded to the vessel at various locations to enable the introduction of acid solution and live steam and withdrawal of sugar solution. The drain pipe was a double pipe heat exchanger

Table 5.1 Maximum yield and corresponding residence time at various conditions for batch and constant flow stirred tank reactors

Reaction conditions		Batch and plug flow reactors		Constant flow stirred tank reactor	
Temp. °C	Acid %	Maximum yield (%)	Residence time (min)	Maximum yield (%)	Residence time (min)
170	0.4	29.3	225.2	20.0	226.9
	0.8	32.6	103.0	22.2	103.2
	1.6	36.1	47.0	24.5	47.0
180	0.4	33.4	89.1	22.7	89.2
	0.8	36.9	40.6	25.1	40.6
	1.6	40.5	18.4	27.6	18.5
190	0.4	37.6	36.5	25.6	36.5
	0.8	41.2	16.6	28.0	16.6
	1.6	44.9	7.5	30.6	7.6
200	0.4	41.7	15.5	28.4	15.5
	0.8	45.4	7.0	31.0	7.1
	1.6	49.1	3.2	33.7	3.2
210	0.4	45.8	6.8	31.2	6.8
	0.8	49.5	3.1	33.9	3.1
	1.6	53.2	1.4	36.7	1.4
220	0.4	49.7	3.1	34.1	3.1
	0.8	53.4	1.4	36.8	1.4
	1.6	57.0	0.6	39.6	0.6
230	0.4	53.4	1.4	36.8	1.5
	0.8	57.0	0.6	39.7	0.7
	1.6	60.6	0.3	42.5	0.3
240	0.4	56.9	0.7	39.6	0.7
	0.8	60.5	0.3	42.4	0.3
	1.6	64.0	0.1	45.3	0.1
250	0.4	60.3	0.3	42.2	0.4
	0.8	63.7	0.1	45.0	0.2
	1.6	67.0	0.1	47.9	0.1

so that the sugar solution was cooled on discharge from the reactor. A turbine propeller made of the same steel and driven by a gear motor at desired speed was fitted to the vessel through a high pressure compression gland located at the centre of the top cover. An immersion heater of 3 kW capacity was also placed in the vessel through two special compression fittings located in the top cover. The heater coil was encased in EN 58J grade stainless steel sheet to protect it from acid corrosion. Finally a thermocouple and a pressure gauge were attached to the reactor. The side wall of the reactor was insulated with lagging material.

Pump: The pump was a stainless steel gear pump. It was driven by an electric motor of 3 H.P. through a reduction gear unit. The pump had a capacity range of 0.27 m^3/h - 0.90 m^3/h. The maximum obtainable discharge pressure was about 35 bars. The pump was connected to the inlet pipe of the reactor at one end and to the acid feed tank at the other end.

Acid Feed Tank: This was made of graduated glass cylinder in order to be able to pump a measured quantity of acid solution to the reactor. It was connected to the suction side of the pump by a plastic tube.

5.4.2 Experimental Procedure

The conditions at which experiments conducted were chosen as 170°C and 180°C with 0.4%, 0.8% and 1.6% sulphuric acid concentrations and 10 to 1 liquid-solid ratio. The reason for this choice lies in the fact that experiments to determine the kinetics of both the hydrolysis and decomposition reactions

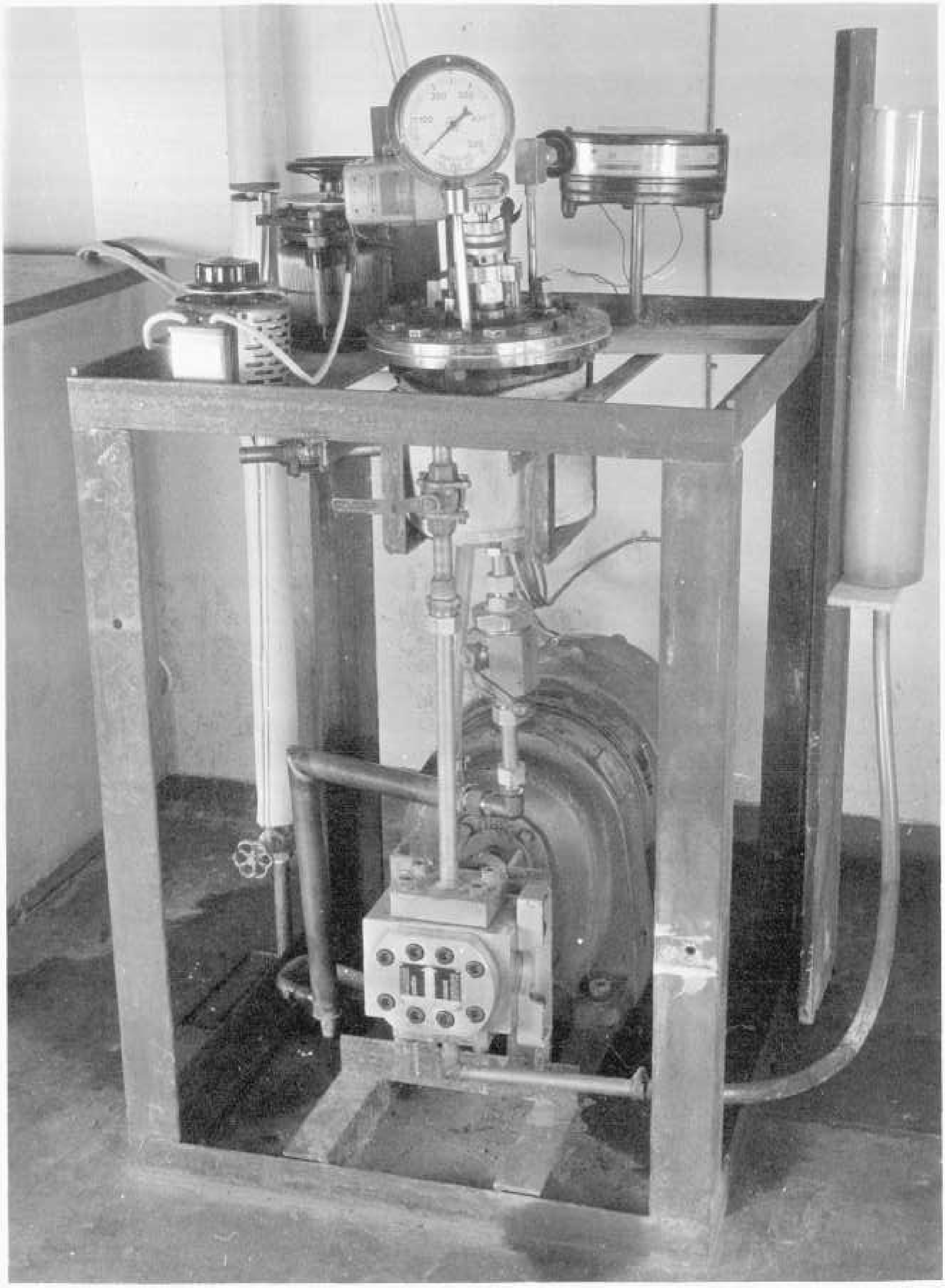


Fig. 5.1 Experimental Set Up

were conducted at these conditions.

The maximum steam pressure available in the laboratory where experiments were carried out was 6.9 bars. Hence the maximum temperature reached by using live steam was 170°C. For the tests conducted at 180°C the rest of the heat was supplied by the immersion heater which was controlled by a variac controller.

In the experiments the waste pulp was first introduced into the vessel and a measured amount of water was added, the cover was then closed and bolts tightened up. The steam valve was opened and live steam was allowed to enter. At this time the turbine propeller was started and a small valve at the top of the reactor was opened, for a short period, to vent the air in the vessel. Steam intake continued until the temperature and pressure in the reactor rose to the steam pressure and the steam temperature. Then, the steam valve was closed and the acid solution introduced. This caused a small drop in temperature and pressure of the reactor because the acid solution was at room temperature. But, these were restored to their original values by switching on the heater for a short period of time. When operating at 180°C the heater was switched on after the steam valve was closed and kept on until the temperature in the reactor reached 180°C. The acid solution was then introduced. After the desired time interval the drain valve at the bottom was opened and the sugar solution withdrawn.

The reaction times were recorded from the moment the acid solution was introduced to the opening of the drain valve.

The waste pulp used throughout the experiments was taken from the same batch of waste pulp from which samples had been taken for the experiments mentioned in Chapter 3. The waste pulp was first boiled in 2% sulphuric acid solution in a beaker for about 1 hour to remove the non-acidic resistant part. It was then washed for several times, dried and potential sugar content of it was determined.

After several runs it was found that working with the quantities given below was satisfactory in getting reproducible results.

Waste pulp charge to the reactor: 0.220 kg (5% moisture content)
Initial water charge : 1.0 kg
Amount of acid solution introduced: 0.2 kg

These quantities ensured a liquid-solid ratio of 10 in the reactor with 10% deviations (The total liquid charge was 1.2l kg. The rest of the liquid to bring the liquid solid ratio to 10/1 came from the condensed steam). When the deviation was greater than 10% the run was discarded. The concentration of the acid solution was chosen so that when this solution mixed with the water already present in the reactor the concentration of the final solution attained the desired value. This has been checked by titrating the drained sugar solutions with sodium hydroxide. Runs with deviations of more than 10% were discarded.

Table 5.2 Results of experiments

170°C - 0.4% sulphuric acid

REACTION TIME (MINUTE)	50	100	200	300	400	500
YIELD (%)	16.05	23.1	27.5	26.5	22.0	16.5

170°C - 0.8% sulphuric acid

REACTION TIME (MINUTE)	25	50	100	150	200	250
YIELD (%)	18.6	24.9	30.5	28.1	23.0	16.1

170°C - 1.6% sulphuric acid

REACTION TIME (MINUTE)	10	20	40	70	100
YIELD (%)	18.3	28.4	33.0	30.0	21.5

180°C - 0.4% sulphuric acid

REACTION TIME (MINUTE)	20	50	100	150	200
YIELD (%)	17.5	28.7	30.1	26.5	18.7

180°C - 0.8% sulphuric acid

REACTION TIME (MINUTE)	10	30	50	70	90
YIELD (%)	19.6	31.4	32.1	27.4	18.5

180°C - 1.6% sulphuric acid

REACTION TIME (MINUTE)	10	20	30	40
YIELD (%)	33.3	38.2	32.5	23.9

5.4.3 Results and Discussion

The results of the experiments are tabulated in Table 5.2.

In order to compare the experimentally determined values with the predicted ones equation 5.6 was plotted in Figures 5.2, 5.3 and 5.4 at the conditions at which experiments were conducted. The results in Table 5.2 were also indicated on the graphs. The close agreement found between the determined and predicted values confirms that the kinetic picture of the overall hydrolysis reaction agrees with the proposed $A \rightarrow B \rightarrow C$ reaction mechanism. Hence, equations (5.6), (5.7), (5.13), (5.14) can be used with confidence to calculate the yield at any condition provided that the values of rate constants at these conditions are known.

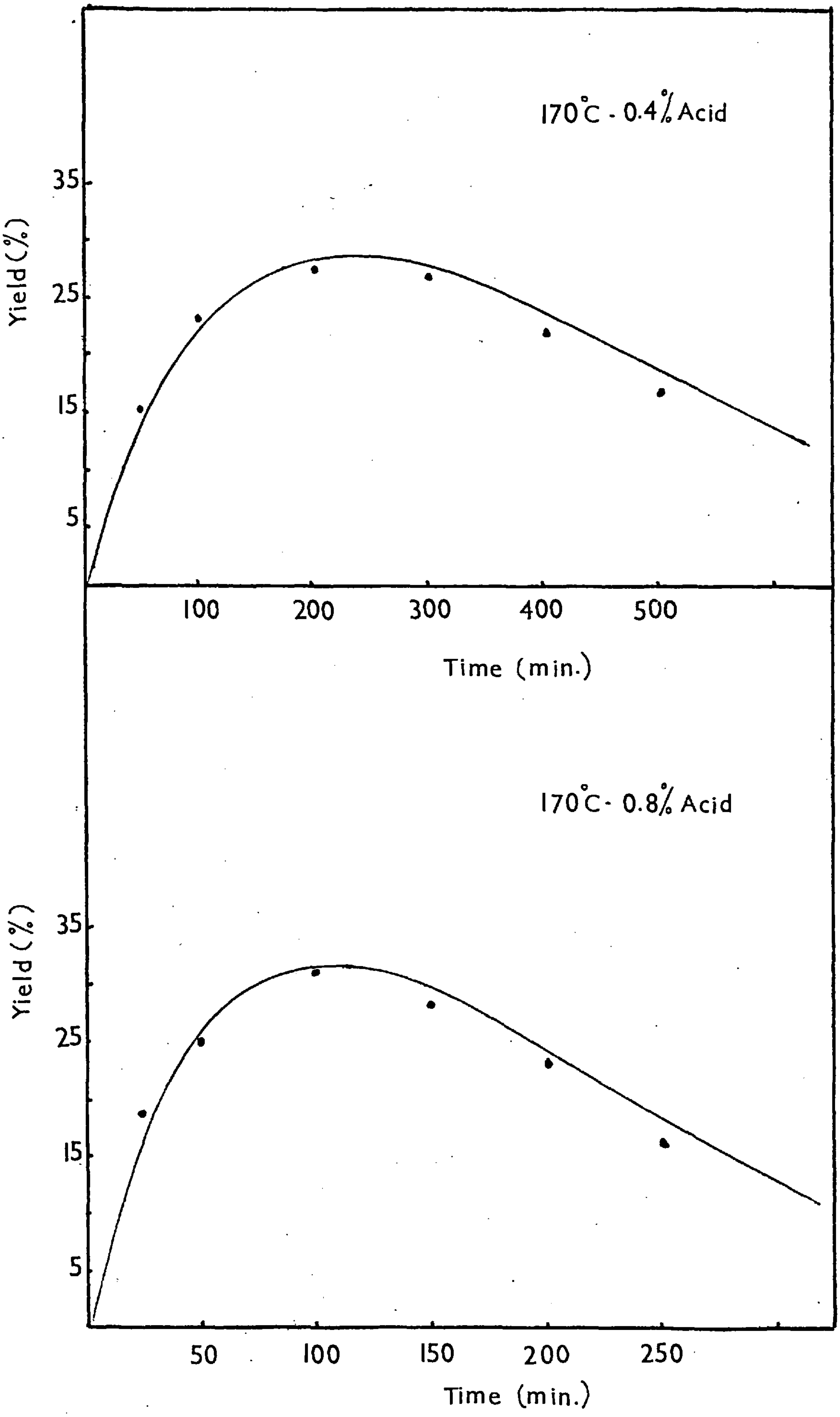


Fig. 5.2 Calculated and Determined Yields of the Hydrolysis Reaction

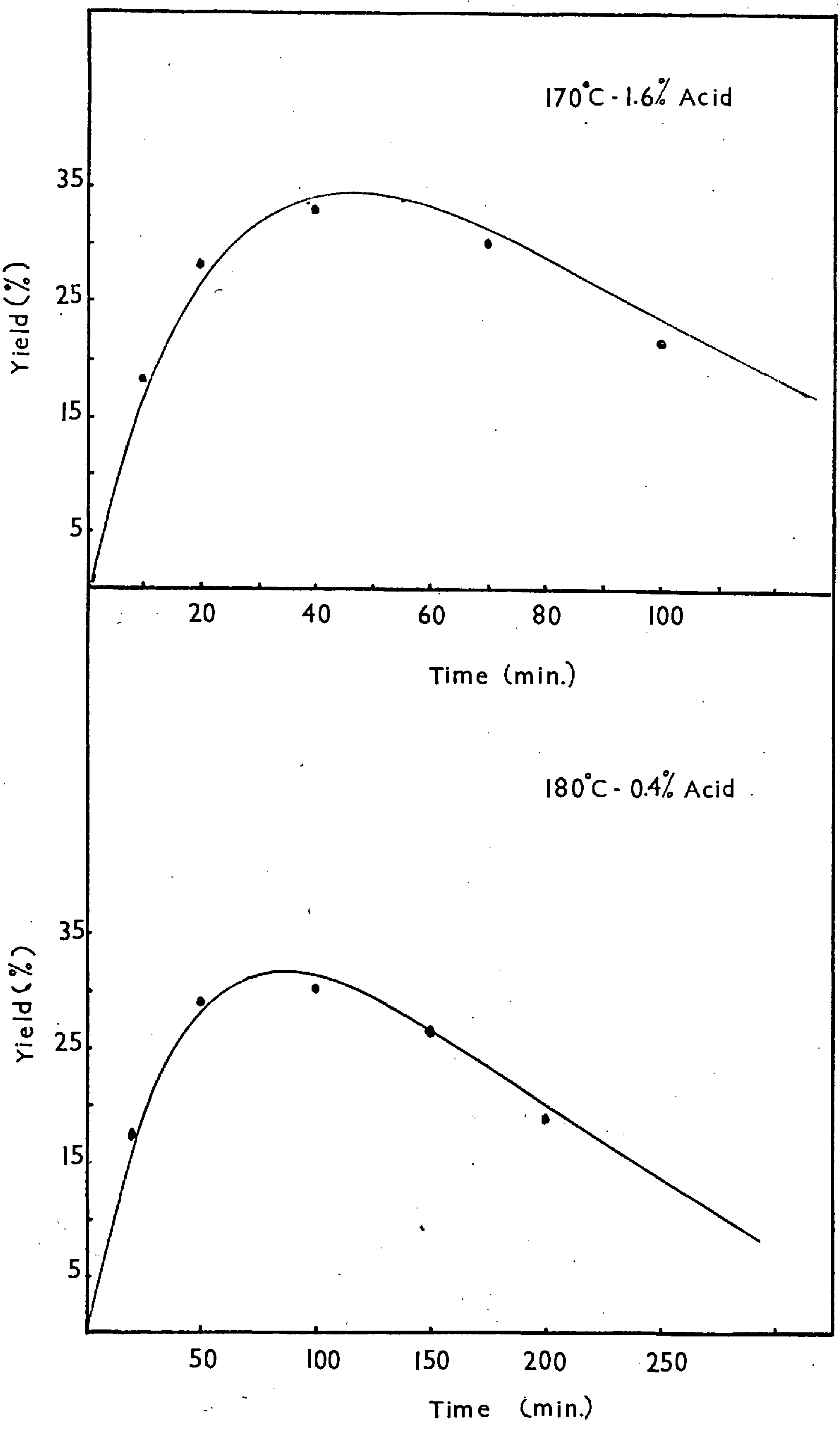


Fig. 5.3 Calculated and Determined Yields of the Hydrolysis Reaction

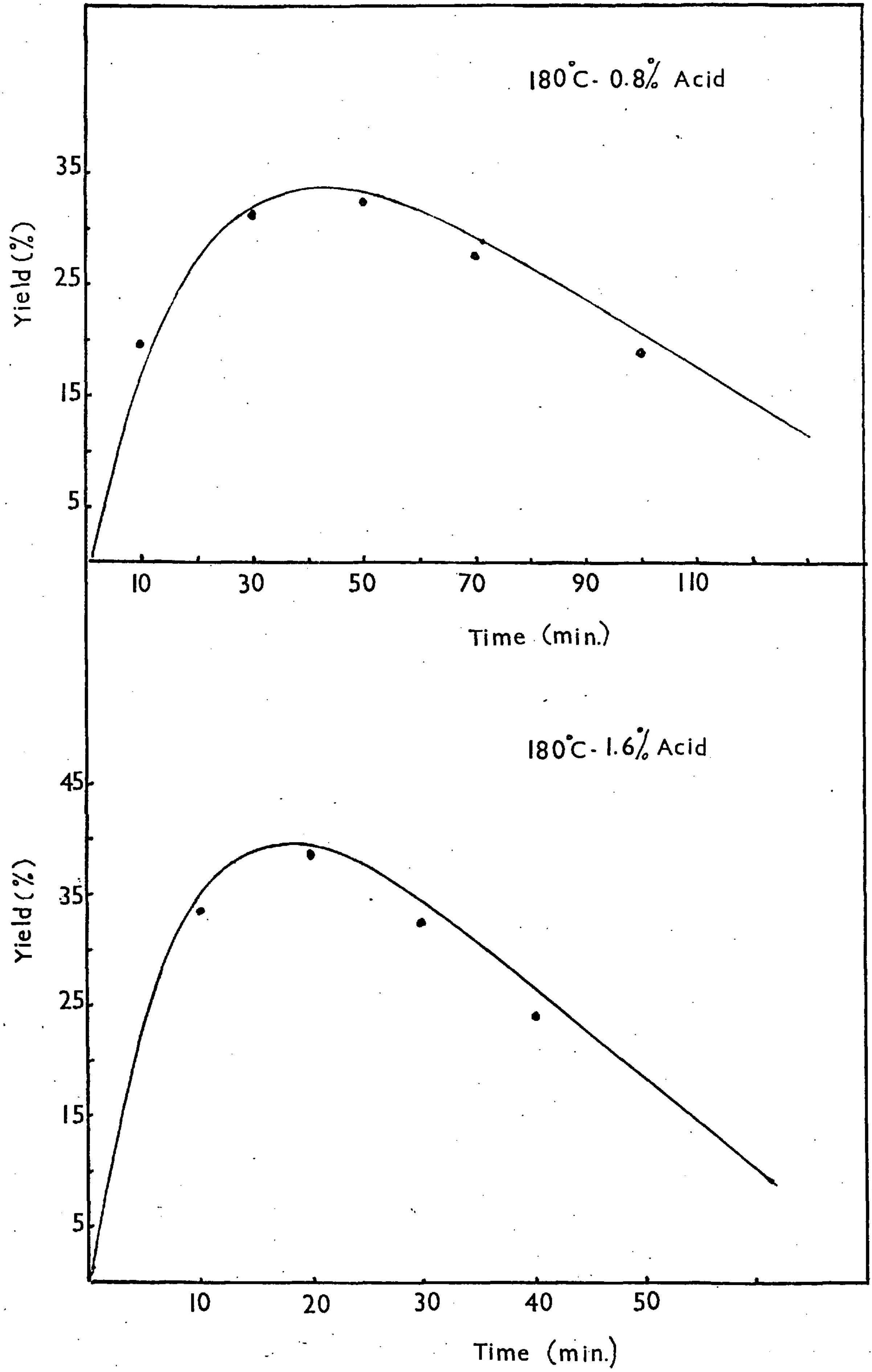


Fig. 5.4 Calculated and Determined Yields of the Hydrolysis Reaction

CHAPTER 6

FERMENTATION OF WASTE CELLULOSE HYDROLYZATE

6.1 INTRODUCTION

As was stated in Chapter 1 the purpose of this work was to investigate the utilization of cellulose in the waste for the production of industrial ethanol. As a first step towards this goal the production of sugars from the cellulose in the waste pulp was investigated in the preceding chapters. In this chapter the fermentation of the hydrolyzates obtained from the cellulose in waste pulp is looked at.

When the production of alcohol from the wood gained momentum during the Second World War research into the fermentation of wood hydrolyzate into alcohol increased and a number of workers made valuable contributions in this field. Their work had been summarized by Underkofler and Hickey(28). At the beginning some difficulties were encountered which were not found in the fermentation of molasses. This was attributed to the toxic materials present in the hydrolyzate. But these difficulties were overcome by modifying the fermentation procedure either by pretreating the hydrolyzate or increasing the yeast amount. The fermentation of wood hydrolyzate was then successfully carried out on laboratory and industrial scales both batchwise and continuously.

Wood hydrolyzate and hydrolyzate obtained from the cellulose in waste pulp contain the same chemical compounds, because the original raw materials are the same and they undergo the same process. Only the relative amounts of these compounds in the two cases may differ. Consequently hydrolyzate obtained from cellulose in the waste pulp can be fermented in the same way as wood hydrolyzates. Hence, lengthy study of fermentation of the hydrolyzate obtained from the cellulose in waste pulp is not necessary. Only the fermentability or, in other words, the percentage of sugars present in the hydrolyzate that can be fermented to alcohol needs to be determined in order to be able to assess of whole process.

6.2 FERMENTABILITY OF THE HYDROLYZATE

The fermentability of the solution obtained from the hydrolysis of cellulose in waste pulp was determined by using the yeast sorption method developed by Saeman and co-workers(29). This has been conducted as follows: Acidic sugar solution obtained from quantitative hydrolysis of waste pulp was neutralized with excess calcium carbonate and filtered off. The clear solution was then diluted to a concentration of about 1.5 g/l and reducing sugar content of it was determined by the Somogyi method. Samples of 20 ml were collected in glass tubes with glass stoppers and to each tube about 1 g of compressed baker's yeast (Saccharomyces Cerevisiae) was added. The stoppers were firmly closed and the tubes shaken by a shaking machine at 30°C for various periods of time. At the end of these times the mixtures in the tubes were centrifuged and clear solutions were pipetted off and analysed for reducing sugar. The difference between readings taken before and after fermentation gave the amount of fermented sugar. The ratio of the amount of fermented sugar to the original sugar amount gave the fermentability. The results are collected in Table 6.1.

Table 6.1 Fermentability of waste cellulose hydrolyzate

Run no.	FERMENTABILITY (%)		
	30 minutes shaking	60 minutes shaking	90 minutes shaking
1	76.4	86.6	86.6
2	81.0	87.4	86.9
3	79.6	88.3	88.0
4	78.3	88.0	87.4
5	79.9	86.7	88.3
6	77.7	87.2	86.9
Average	-	87.4	-

It follows from Table 6.1 that 60 minutes is enough for the fermentation of all the fermentable sugars in the hydrolyzate, since further increase in shaking time does not increase the fermentability. The average of fermentabilities obtained with 60 minutes shaking time was taken as the maximum fermentability of the hydrolyzate and economic calculation was based on this figure in Chapter 8, because Saeman and co-workers(29) proved that fermentability obtained by the yeast sorption method can in fact be realized in an actual fermentation process.

As is seen, the fermentability of the waste pulp hydrolyzate into ethanol is quite high. This is not found surprising if it is remembered that the pulp during the pulpation process is freed of its hemicellulose which gives pentose sugars upon acidic hydrolysis and alcoholic fermentation of which is not possible.

CHAPTER 7

WASTE DISPOSAL

7.1 INTRODUCTION

At a plant converting either waste pulp or waste paper into ethanol via acidic hydrolysis followed by fermentation two kinds of waste will be encountered: solids waste and liquid waste.

SOLID WASTE

This will mainly be composed of unreacted cellulose, lignin, filling materials, calcium carbonate and calcium sulphate. To this will be added the uncellulosic materials such as listed in Tables 1.1 and 1.2, if municipal waste is used as raw material instead of waste pulp. Hence, the amount of solid waste to be disposed of will depend on the source of waste cellulosic material as well as on plant capacity. In order to estimate the amount of solids to be encountered at a plant using the waste pulp as raw material the waste pulp was subjected to total saccharification and the residual solids were dried and weighed. It was found that approximately 32% of the original waste pulp formed a solid residue. In the chapter dealing with the design of hydrolysis plant this figure was taken as the basis for calculation of the daily solid disposal cost.

LIQUID WASTE

This comes mainly from the bottoms of the distillation column and has a substantially high B.O.D (Biochemical Oxygen Demand), because it will contain unfermented sugar and unrecovered ethanol together with the decomposition products of sugar. The amount of these dissolved materials needs to be reduced so that when the effluent of the plant is discharged into rivers or lakes the oxygen depletion caused by their presence should not exceed the difference between the oxygen saturation value and the minimum permissible concentration of dissolved oxygen. For each chemical compound there is a permissible concentration which, when exceeded, upsets the biological equilibrium in water. In Table 7.1 the threshold doses of certain chemical compounds in water are given.

Table 7.1 Threshold doses of certain compounds in water

Compound	Threshold dose (mg/l)
Ethanol	250
Methanol	32,000
Sugar	35

The exact treatment of the effluent obviously requires the knowledge of composition of the effluent as well as of the conditions of the stream into which the effluent is to be discharged. But 5-day B.O.D is an accepted standard measure to estimate any effluent treatment. The 5-day B.O.D. is defined as the amount of free oxygen consumed by aerobic microorganism at 20^{o}C for 5 days. In this chapter this 5-day B.O.D procedure has been used to determine the amount of noxious material present in the effluent, in terms of oxygen demand of the effluent. The dilution method, which is one of the several methods used to measure the 5-day B.O.D of any waste liquid, was employed.

7.2 DETERMINATION OF THE 5-DAY B.O.D OF THE EFFLUENT BY THE DILUTION METHOD

7.2.1 Preparation of Dilution Water

Standard dilution water was prepared by adding small quantities of inorganic salts to distilled water. The composition of the standard dilution water prepared is given below.

Salts	P.P.M
$FeCl_3$	0.06
$CaCl_2$	30.0
$MgSO_4$	14.7
$KNaHPO_4$)) KH_2PO_4)	47.5
$(NH_4)_2SO_4$	1.87

Dilution water was seeded by adding 5 ml soil suspension to each litre of dilution water.

Soil Suspension

One part of garden soil was mixed with two parts of water (by weight) and shaken for 10 minutes. The mixture was then filtered until a clear filtrate was obtained. This solution was kept in the refrigerator.

7.2.2 Preparation of Samples and Procedure

Waste pulp samples of about 0.6 g were subjected to quantitative saccharification. The resultant solutions were made up to 250 ml and neutralized with calcium carbonate. They were subsequently fermented to ethanol with baker's yeast (Chapter 6). The mixtures were then centrifuged and 20 ml samples were taken from the clear solutions. These solutions were made up to 250 ml with dilution water and transferred to 250 ml glass bottles with glass stoppers. The bottles were kept at 20°C for 5 days (120 h).

7.2.3 Calculation and Results

At the end of the 5-day period samples of 200 ml from the bottles were taken and dissolved oxygen in the samples determined by the permanganate modification of the Winkler method(30). The volumes of 0.025 N sodium thiosulphate solution consumed by each sample and a blank are indicated in Table 7.2.

Analysis of the chemical reaction occurring during the titration of the samples with sodium thiosulphate shows that when 200 ml samples are taken from the bottles and titrated with 0.025 N sodium thiosulphate solution the dissolved oxygen content of the samples in parts per million is numerically the same as the required volume of 0.025 N thiosuphate expressed in millilitres. Thus, in order to find the B.O.D of the

Table 7.2 The 5-day B.O.D of the effluent based on 10 to 1 liquid-solid ratio

Sample no.	0.025 N $Na_2S_2O_3$ spent (ml)	5-Day B.O.D based on 10 to 1 liquid-solid ratio (p.p.m)
1	9.5	2080
2	9.8	1920
3	10.1	1770
4	8.5	2600
5	9.7	1970
Blank	13.5	Ave: 2070

original solution all that needs to be done is to multiply the difference between the required volumes of 0.025 N thiosulphate solutions for the blank and the sample by the overall dilution ratio.

In the determination of the overall dilution ratio an assumption needs to be done regarding the original amount of liquid in order to prevent misunderstanding. The original liquid amount was taken as the amount of liquid which would give a liquid-solid ratio (by weight) of 10. Thus, for 0.6 g waste pulp taken the original liquid amount is 6 g. Hence the overall dilution ratio is: $\frac{250}{6} \times \frac{250}{20} = 520$. The B.O.Ds of the original liquids based on liquid-solid ratio of 10 were calculated by using this figure and the relevant results were added to Table 7.2.

At a plant using this waste pulp as raw material the B.O.D of the effluent can now be estimated as follows: First, by dividing the amount of liquid coming from the bottom of the distillation column to the amount of waste pulp input to the plant the liquid-solid ratio is found. Then, this ratio is divided by 10/1 and the reciprocal of the result is multiplied by the average value of B.O.D in Table 7.2.

CHAPTER 8

PROCESS DESIGN AND ECONOMIC ANALYSIS OF THE PROCESS

8.1 INTRODUCTION

The aim of the preceding chapters was to clarify the kinetics of the hydrolysis reaction and to collect the necessary kinetic data. In addition, fermentability of the resultant sugar solution into ethanol and biochemical oxygen demand of the effluent stream have been determined. In this chapter, in the light of these results, the process engineering aspects and then the economic assessment of the whole process are investigated. At the end of the chapter, conditions are discussed which must be met in order to make the whole process profitable.

In this country the daily waste pulp output of the largest paper mill is somewhere around 30 tons(31). Thus, a plant working only on the cellulose waste of an individual paper mill can not exceed a capacity of 30 tons/day. Wastes of several mills can of course be combined. But this procedure can only become a practical proposition if the distance over which waste is to be transported is not too long. On the other hand, a plant utilizing cellulosic part (waste paper) of the municipal waste can have a capacity of several hundred tons depending upon its location.

Thus, two different approaches to suit two different sets of conditions were adopted: First a high capacity plant based on continuous process conditions was investigated and secondly, a small capacity plant based on a batch process was studied.

This was followed by comparative assessment of capital requirement and profitability of the two plants.

8.2 CONTINUOUS PROCESS

In the following calculations the design capacity was chosen as 200 ton/day. The main reasons for choice of such a high capacity can be outlined as follows:
(i) High liquid-solid ratio makes high fixed capital costs inevitable. (ii) The potential sugar content of the wastes, especially of waste pulp, is rather low. (iii) Maximum yield of the sugar producing reaction is not very high: This is about 50% under practical working conditions. (iv) Selling price of the ethanol is rather low.

8.2.1 Reaction Conditions

It follows from Table 5.1 that the smaller the residence time the higher the yield. Thus small residence times are favourable from yield point of view. But on the other hand, the presence of a non-homogeneous slurry does not permit the achievement of real residence times less than a certain threshold time. In other words at this residence times a small variation in the flow conditions causes large fluctuations in the yield. Experimental evidence suggests that this time limit is about 1 minute.

(a) Temperature and Acid Strength: At a fixed residence time the same yield can be obtained by two different combinations of the two parameters, acid percentage and temperature: either by lower acid concentration and higher temperature or by higher acid concentration and lower temperature. The choice can only be made on economic considerations. In Fig. 8.1 are shown the annual costs of the required fuel oil and sulphuric acid for a fixed yield and fixed liquid-solid ratio (50% and 8 to 1). This graph has been constructed by making energy balances around the reactor, flash drum and evaporators (Fig. 8.3) at various temperatures and acid concentrations which give the same conversion. The energy balances around the fermenters and distillation column remain constant, as it is assumed that flow rates and concentrations after the evaporators will not change. Thus, the cost of the fuel oil required at these stages is not affected by changes in reactor conditions and it is therefore not included in the fuel oil cost shown in the graph. The cost of the acid required to neutralize the waste is similarly disregarded, since it is not a function of the reaction conditions. It can be seen that the cost of acid rapidly increases as the concentration increases. But the cost of the fuel oil remains more or less constant. This is due to the fact that recovery and re-use of the heat throughout the process can be made possible whereas the acid cannot be recovered. Thus, lowest possible acid concentration for a fixed yield is favourable from the economic point of view. In the following design calculations this was chosen as 0.4%, the lowest acid concentration successfully used throughout the experiments. Concentrations smaller than this value cannot be relied upon because small variation in the neutralization value of the waste results in marked differences in the yield. With the above considerations in mind optimum reaction conditions

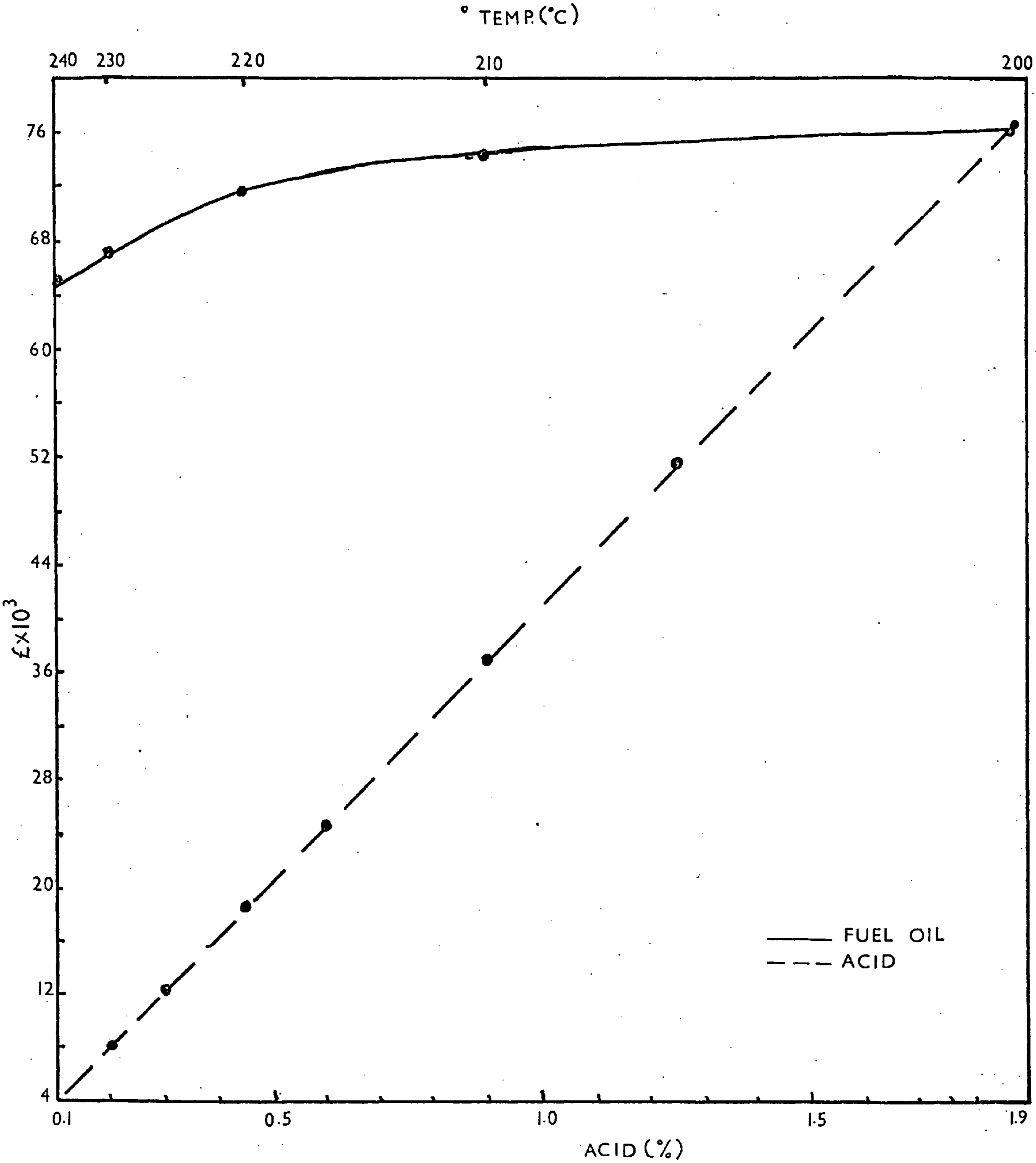


Fig. 8.1 Annual Costs of Required Fuel Oil and Acid for 50% Yield at Various Conditions

were chosen with the help of Table 5.1 as 230°C and 0.4% sulphuric acid.

(b) Liquid-Solid Ratio: Ratios 15 to 1 and 10 to 1 were tested and showed no marked difference in the yields of sugar. This means that yield is not significantly affected by the liquid-solid ratio. High liquid-solid ratios have the advantage of more even distribution and easy pumping but cause excessive dilution of the sugar produced. On the other hand, low liquid-solid ratios introduce a number of operational problems such as bad wetting of the waste during short times of contact, difficulty in pumping, clogging and loss of sugar in the solution entrained by the unreacted solids. Tests showed that an 8 to 1 liquid-solid ratio (by weight) is suitable for continuous processing. Hence, this ratio was used in subsequent calculations.

8.2.2 Process Engineering and Cost

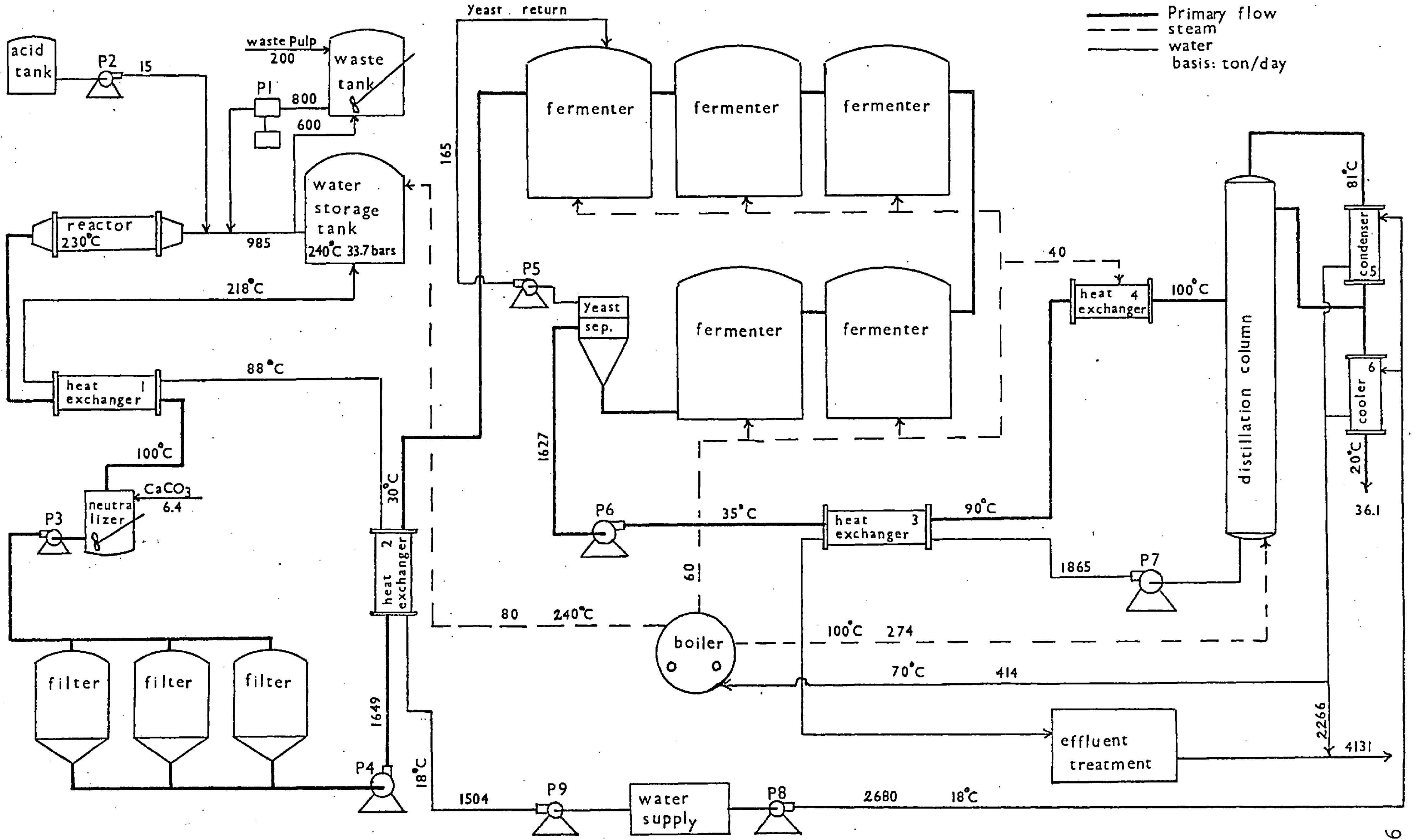
A hydrolysis plant can roughly be regarded as consisting of three sections: (i) Reactor, in which the hydrolysis reaction takes place, (ii) Fermenter, where fermentation of the sugar solution is carried out, and (iii) Distillation section where dilute alcohol solution is rectified to produce industrial alcohol. The solution leaving the reactor will be rather dilute. This solution can be fermented as it is or, before introducing it to the fermentation unit, it can be concentrated by evaporation. Installation of evaporators affects the required capital cost as well as the utilities cost. At first look it seems to increase the capital requirement.

But this may not be the case because, due to the reduction in the quantity of the solution, subsequent fermentation and distillation units will obviously be reduced in size and hence in cost. Also some heat exchangers, which will be required for the heat economy as well as be dictated by the process conditions will be excluded. As for the utilities cost, steam requirement for the distillation column and condenser duty will be reduced for the concentrated solution. But certain amount of steam will also be required for the evaporation unit. All these points justify a detailed study of the processes with and without evaporators in order to determine their relative economic advantages. Flow diagrams of the two proposed continuous processes, with flow rates and conditions marked in, are shown in Figures 8.2 and 8.3.

8.2.3 Process Without Evaporators

According to this process, the waste material is discharged into a waste tank and mixed there with part of the feed water to make it suitable for pumping. The resulting slurry is pumped into the reactor which is also supplied by feed water and acid. The stream leaving the reactor is cooled to 100°C by water in a series of heat exchangers. At this temperature it is neutralized in the neutralizer with calcium carbonate which is then filtered off. The clear stream leaving the filters is further cooled in a second series of heat exchangers down to the fermentation temperature of 30°C. After its pH had been adjusted it flows into the fermenters. Fermentation is continuous and is completed in 20 hours. In

Fig. 8.2 Flow Diagram of the Continuous Process (without evaporators)



the end of this time yeast is separated for reuse and dilute alcohol solution is heated to its boiling point temperature by passing it through two series of heat exchangers. In the first, part of the sensible heat of the bottom product of the distillation column is used to heat the solution. The second exchanger employs live steam. In the final part of the process, the solution is distilled to produce a 60% (by weight) alcohol solution.

I - COST OF INDIVIDUAL ITEMS OF EQUIPMENT

The costing is preliminary in nature and all the prices given in this chapter are 1972 prices.

(1) Waste Material Tank

Daily waste pulp (paper) flow is 200 tons. Water, three times this weight, is fed into this tank from the water storage tank. This helps to preheat the waste material and gets the slurry pump working. A capacity sufficient to produce slurry flow rate for half an hour can be relied upon to ensure continuous operation. Thus, a 17 m^3 capacity tank, fitted with an agitator, is required. The material of construction is stainless steel. Cost including agitator and drive is £7,000(32).

(2) Reactor

This will be a plug flow type reactor made of EN 58J grade stainless steel. The working conditions are 230°C and 27.2 bars. Its capacity can be found as follows: Total flow rate is 1800 ton/day. For an average density of 1000 kg/m^3 the hourly flow rate is 75 m^3. Residence time is 1.4 minutes. Thus the capacity is $\frac{75}{60} \times 1.4 = 1.75\ m^3$. The cost is £12,500(32).

(3) Neutralizer

This will be a stainless steel tank with agitator. Design capacity will be taken as twice the capacity of the reactor to ensure complete neutralization. Purchasing cost, including agitator and drive, is £3,500(32).

(4) Acid Storage Tank

The capacity of the acid tank is made equal to the daily acid requirement. The daily acid requirement is 5.12 tons for neutralization purposes and 6.4 tons for the hydrolysis reaction. Thus, total acid consumption is 11.52 ton/day (100%). Acid is assumed to be available at 77% (= 1690 kg/m^3) concentration. This means a tank of 9 m^3 is required. Construction material will be stainless steel. Purchasing cost is £2,700(32).

(5) Water Storage Tank

This tank acts as a reservoir for the process water. It will be made of mild steel. Working temperature is 240°C and pressure 33.7 bars. A capacity sufficient to give the required water flow rate to the reactor for half an hour is considered satisfactory for continuous operation. This is determined as follows: Daily flow rate to the reactor is 1585 tons (this, with 15 tons acid solution, brings the liquid-solid ratio in the reactor to 8 to 1). Amount discharged in half an hour is 33 m^3. Purchasing cost is £4,600(33).

(6) Filters

Bed filters operating under positive pressure will be used. Total flow rate to the filters is 75 m^3/h. Required filter area, for a 0.4 m^3/m^2h flow rate, is 190 m^2. Thus three filters with a 95 m^2 area each will be needed. It is assumed that two will be in operation while the third one is discharged and cleaned. Purchasing cost of each filter is £12,000 making a total of £36,000(3).

(7) Fermentation Unit

Liquid leaving the filters contains about 2.8 g sugar per 100 g of solution and after pH adjustment and cooling to 30°C it is introduced into the fermentation vats. Fermentation is continuous and the time required for its completion is approximately 20 hours. Total flow rate to the fermenter is about 1600 m^3/day. Thus, required capacity (with 10 per cent excess) is about 1500 m^3. Five redwood vats, each of 300 m^3 capacity, are required. Purchasing cost of each vat with agitator and drive is £5,000(32,34) giving a total of £25,000. Apart from fermentation vats, pumps, a centrifugal separator as well as tanks for yeast growing, lime, sodium hydroxide, sulphuric acid and nutrient salts are needed to complete the fermentation unit. Another £25,000 is estimated to be required for these ancillary equipment. Thus, the total cost of the fermentation section is £50,000.

(8) Distillation Column

The liquid stream coming from the fermenters contains about 1.25 g ethanol per 100 g of solution. The solution will enter the column as liquid at its boiling point. Open steam will be used thus eliminating the need for a reboiler. It is assumed that 99 per cent of the alcohol present in the feed will be recovered. From graphical construction it was found that a minimum reflux ratio of 10 is needed to produce 60% alcohol as top product. Optimum reflux ratio was calculated to be 1.3 times the minimum reflux ratio(35). Thus, R_{DOP} = 13. Using the McCabe-Thiele method and the Kremser equation(36) the number of ideal plates was found to be 22. From Kirschbaum's work(37) plate efficiency was estimated to be 0.80 which gives an overall column efficiency of 0.82(36). Hence, the number of actual plates is 27. For a 0.60 m plate spacing(38) the height of the column needs to be 18.5 m (with 10% excess).

Estimation of column diameter: From the Souders Brown equation(38) allowable vapour velocities were calculated as 1.37 m/s and 1.87 m/s at the top and the bottom of the column respectively. Corresponding diameters are 2.16 and 1.87 m. Hence, design diameter was taken as 2.0 m.

Purchasing cost of the shell is	£7,000(32)
Installed cost of the plates is	£11,500(32)
Total cost is	£18,500

(9) Heat Exchanger

All the required heat exchangers showing the relevant flow rates as well as inlet and outlet temperatures of the streams are indicated in Fig. 8.2. Required surface areas, overall heat transfer coefficients (U) used in the calculations and costs of the separate units are tabulated in Table 8.1.

Table 8.1 Cost of heat exchangers

Heat exch. no.	U ($W\ m^{-2}\ {}^{o}K^{-1}$)	Surface area (m^2)	Cost(33) £
1	1700	470	24,000
2	1700	280	13,000
3	1700	240	10,500
4	2840	3	600
5	1140	200	10,000
6	570	28	3,500
		Total cost:	£61,600

(10) Boiler

Daily steam requirement has been calculated as 420 tons. Hence a package boiler capable of producing 450 tons of steam at 33.7 bars pressure is required. The cost of such a boiler is £50,000(33). However, if sufficient process steam is available on the site, this cost will be considerably reduced.

(11) Pumps

It follows from Fig. 8.2 that a number of pumps are needed throughout the plant. In order to find their cost and the power required to drive them, their capacities, physical properties of the liquids they handle and the pressure drop along the pipes, fittings and valves must be known. Only the first two are known from process conditions but an estimation is required of the last one. This was conducted as follows: From the economic pipe diameter chart(39) the pipe diameters were determined. Then, with the known values of the economic pipe diameters and flow rates, pressure drops due to friction were found from the pipe-flow chart(39). These two values were averaged as 0.13 m and 0.011 bar/m. Subsequently, from the sizes of the relevant items of equipment the heads and the equivalent lengths of pipe were estimated. For each heat exchanger an average pressure drop of 0.14 bars was assumed. With all the necessary data determined, the required pump work and horse power was calculated from the conventional pump work formulae. For all pumps 60% efficiency had been assumed. Results of the calculations for each pump with its cost are collected in Table 8.2. Total cost of pumps was taken as £20,000 to make allowance for a number of subsidiary pumps which were overlooked in the design for simplicity sake.

(12) Effluent Treatment Unit

Effluent coming from bottom of the distillation column will have a high B.O.D and it must be treated before leaving the plant. This will be done by the activated sludge process. Daily effluent rate will be 1865 m^3. Hence the capacity of the unit will not be less than this figure. Installed cost of the unit is £85,000(32).

II - BUILDING

A two-storey standard steel building with a floor area of 2,000 m^2 will be needed to accommodate all the process equipment with the exception of the distillation unit, which will be housed next to the main building. Cost, including lighting, heating and plumbing is £118.5 per m^2 (32). Thus, total cost is: 118.5 x 2,000 = £237,000.

III - PIPING COST

The true assessment of the piping cost can only be made after the detailed design of the plant has been completed. However, the cost of piping can be predicted using the accepted procedure based on the type of process plant(32). Hydrolysis plant can be regarded as a solid-liquid process plant with the liquid handling part dominating. Thus, piping cost can be taken as 40% of the purchased equipment cost. This figure is about 10% higher than the recommended percentage for the solid-liquid process plant(32). Hence, total piping cost is about £106,500.

IV - INSTRUMENTATION COST

The instrumentation cost for a liquid - solid chemical process plant can be taken as 13% of the purchased equipment (32) cost. Thus, the cost is £34,600.

V - INSTALLATION COST

The installation cost of the separate items of equipment varies from equipment to equipment as well as from size to size.

Table 8.2 Cost of pumps

Pump No.	Capacity m^3/h	Pressure diff. bar	Equivalent length m	Elevation m	Required H.P.	Type of pump	Approximate cost (pump + drive)(£)	Cost data reference
1	33.4	26.2	20	2.5	56	Positive displ.	5,000	40, 33
2	0.037	26.2	20	2.5	1.5	Metering	300	
3	75.0	4.8	30	4.0	25.0	Centrifugal	1,450	33
4	68.0	-	50	5.0	4.0	Centrifugal	800	33
5	7.0	-	70	5.0	1.0	Centrifugal	400	33
6	68.0	-	50	10.0	8.0	Centrifugal	1,000	33
7	75.0	-	100	4.0	3.0	Centrifugal	800	33
8	110.0	-	100	15.0	13.0	Centrifugal	1,400	33
9	63.0	32.7	200	50	140.0	Centrifugal (multiple)	5,000	33
					251.5		16,100	

It is usually expressed as percentage of the purchased equipment cost. A typical variation is shown in Table 8.3 for the relevant types of equipment(32). The total installation cost was determined by adding up separate installation costs for each equipment, which were calculated by multiplication of the relevant purchase cost by a suitable percentage for that particular equipment. Thus, total installation cost is £85,000.

Table 8.3 Installation costs of some types of equipment as percentage of the purchase cost

Type of equipment	Installation cost (%)
Metal tanks	20-40
Pumps	10-50
Wood tanks	30-60
Evaporators	10-40
Filters	25-45
Heat exchangers	10-35
Towers	25-50
Centrifugal separators	10-35
Boilers	40-50

VI - WORKING CAPITAL

The working capital required for the plant is estimated using a standard procedure(32).

(i) Cash kept on hand for wages and salaries for one month:	£5,500
(ii) Raw material and utilities cost for one month:	£20,500

(iii)	Finished product in stock for one month:	£36,500
(iv)	Credit given to customers for one month:	£51,000
(v)	Insurance cost for three months:	£ 2,500
	TOTAL :	£116,000

VII - TOTAL CAPITAL COST

The total capital cost required was arrived at as shown in Table 8.4. In its determination, engineering and supervision cost, and contractor's fee were assumed as 15% of the physical plant cost and 4% of the direct plant cost respectively. A contingency of 15% of the direct plant cost was also included.

VIII - DAILY MATERIAL AND UTILITIES REQUIREMENT AND COST

Daily material and utilities requirement and their unit costs are given below.

SULPHURIC ACID: 5.12 tons (100%) sulphuric acid is required for neutralization purposes; another 6.4 tons is needed for the preparation of 1600 tons of 0.4% sulphuric acid solution for the reaction. Acid is assumed to be available at 77%. Thus, acid requirement is 15 tons. Cost is £6.0 per ton(3).

CALCIUM CARBONATE: 6.4 tons of calcium carbonate is required to neutralize the acidic sugar solution. Bulk price of calcium carbonate is approximately £2.7 per ton(3).

WATER: A total of 4,200 tons of water is required for the preparation of reaction solution, for condenser duty and product cooling. Cost is £0.01 per ton.

ELECTRICITY: Approximate required horsepower is 400; this also

Table 8.4 Total capital cost

	£	
Purchase costs of separate items of equipment		
1 - Waste material tank	7,000	
2 - Reactor	12,500	
3 - Neutralizer	3,500	
4 - Acid storage tank	2,700	
5 - Water storage tank	4,600	
6 - Filters	36,000	
7 - Fermentation unit	50,000	
8 - Distillation unit	18,500	
9 - Heat exchangers	61,600	
10 - Pumps	20,000	
11 - Package boiler	50,000	
Total cost of equipment		266,400
Piping cost	106,500	
Installation and instrumentation cost	119,600	
Installed effluent treatment unit	85,000	
Building	237,000	
Physical plant cost		814,500
Engineering and supervision cost	122,200	
Direct plant cost		936,700
Contractor's fee	37,500	
Contingency	140,500	
Fixed capital cost		1,114,700
Working capital	116,000	
Total capital		1,230,700

includes lighting requirement. 400 H.P. is equivalent to an energy of 7,000 kWh per day. Cost is £0.007 per kWh.

FUEL OIL: Total energy needed is found by adding up the energies required at several steps of the process. These are shown below:

(i) Water entering the water storage tank is at 218°C. This temperature will be raised to 240°C by condensing live steam in it. Thus, when the water is mixed with the waste material and acid solution in the reactor (both originally at 18°C) the temperature falls to the reaction temperature of 230°C. Amount of steam to be condensed in the water storage tank is calculated to be 80 tons/day (saturated at 240°C). The energy needed to produce this steam is:

$$Q_1 = 80 \times 10^3 \times 4.18 \times (670-70) = 200 \times 10^6 \text{ kJ.}$$

(ii) Energy needed to heat up the alcohol solution from 90°C to 100°C prior to the distillation column

$$Q_2 = 1626 \times 10^3 \times 1 \times 4.18 \times (100-90) = 67.9 \times 10^6 \text{ kJ}$$

(iii) Energy needed to produce steam for the fermentation unit(41).

$$Q_3 = 20 \times 10^3 \times 4.18 \times (640-70) = 47.6 \times 10^6 \text{ kJ.}$$

(iv) Energy needed to produce steam for the distillation column

$$Q_4 = 274 \times 10^3 \times 4.18 \times (640-70) = 652.9 \times 10^6 \text{ kJ.}$$

Thus, total energy required is 968.4×10^6 kJ. This needs 29.2 m^3 of fuel oil of calorific value 39×10^6 kJ/m^3, assuming a boiler efficiency of 85%. Cost of the fuel oil is £11.5/m^3 (3).

SOLIDS DISPOSAL AND B.O.D REDUCTION: The quantity of solids to be disposed of is somewhere around 80 tons. Its disposal is to be carried out by landfilling. Current cost is £0.50 per ton. The B.O.D of the waste liquor coming from the bottom of the distillation column was calculated to be 2200 ppm for this dilution. This value will be lowered to 200 ppm because, when water coming from the condenser is added to this stream, the final stream leaving the plant will have an approximate B.O.D value of 100 ppm. Thus, daily removal of B.O.D is 3680 kg. Cost is £0.03 per kg B.O.D removed(3). Daily costs of materials and utilities are tabulated in Table 8.5.

IX - ECONOMIC ANALYSIS OF THE PROCESS

The daily production of 60% ethanol from 200 tons of waste material of 46% potential sugar content at the optimum conditions is given in Table 8.6. The economic analysis and the profitability of the process is shown in Table 8.7. In the preparation of the table (i) A working year of 330 days was assumed to be realized. (ii) A total of 36 men for three shifts work has been estimated to be required. At each shift 12 men including a shift supervisor will be employed. Their averaged wage was taken as £1,800 per year per man. (iii) A credit of £0.60 per ton of waste, which is required to be disposed of by other means, was assumed on the income side. (iv) Overhead costs were assumed as 50 % of the expenses for labour, supervision and maintenance.

Table 8.5 Daily material and utilities cost

Material or utility	Quantity	Cost per unit £	Cost £
Sulphuric acid	15.0 tons	6/ton	90.0
Calcium carbonate	6.4 tons	2.7/ton	17.0
Water	4,200 tons	0.01/ton	42.0
Electricity	7,000 kWh	0.007/kWh	49.0
Fuel oil	29.2 m^3	11.5/m^3	336.0
Solids disposal	80 tons	0.50/ton	40.0
B.O.D removal	3,680 kg	0.03/kg	110.0
		TOTAL:	£ 684.0

Table 8.6 Daily ethanol yield

	t
Potential sugar in the waste : 200 x 0.461	92.2
Net sugar yield : 92.2 x 0.53	48.8
Fermentable sugar : 48.8 x 0.874	42.6
100 per cent ethanol yield : 42.6 x $\frac{92}{180}$	21.7
60 per cent ethanol yield : 21.7 x $(\frac{1}{0.60})$	36.1

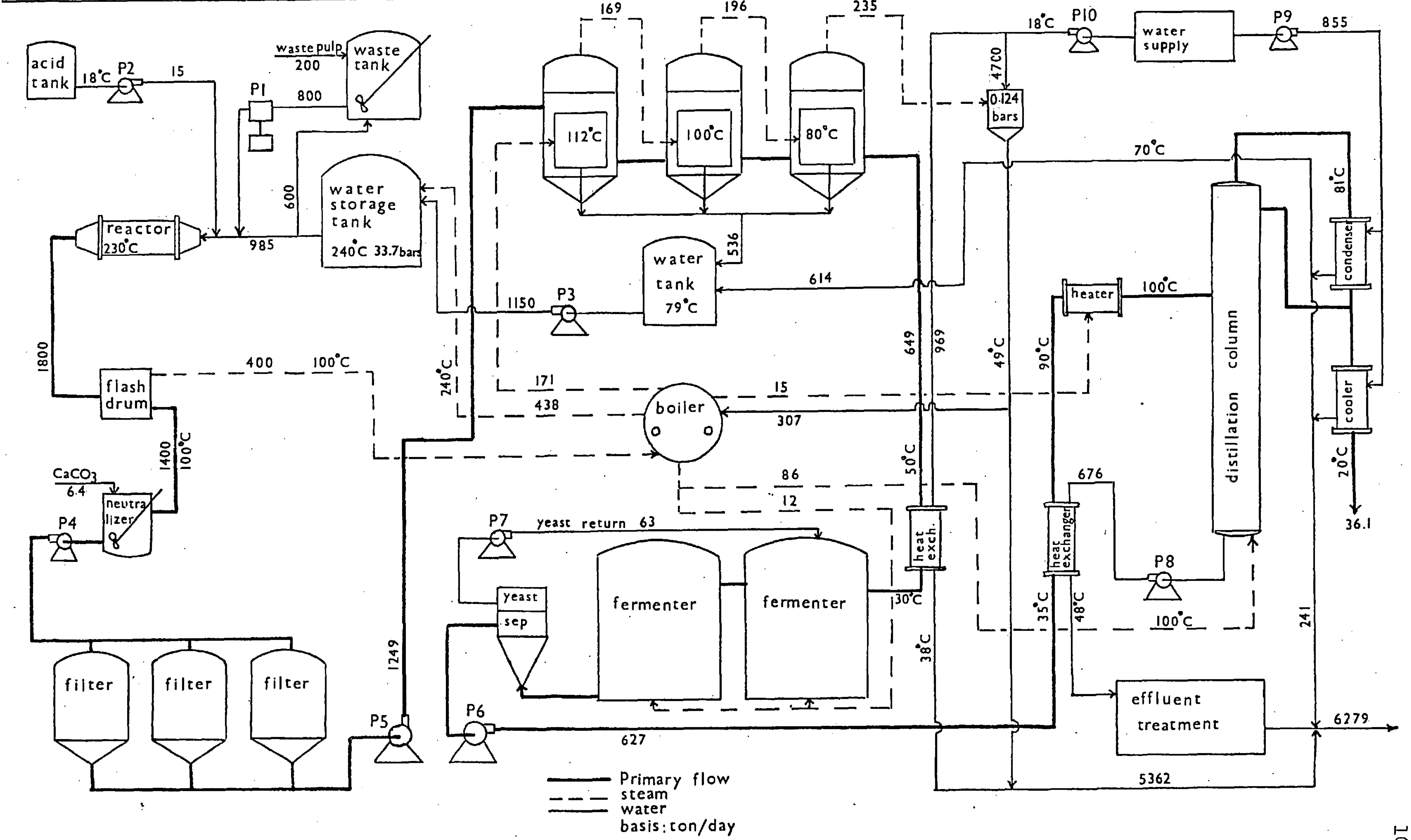
Table 8.7 Economic analysis of the process

	£	
Annual revenue at £47 per ton selling price : 36.1 x 330 x 47	559,200	
Credit on hand £0.6 per ton of waste :	39,600	
Material and utilities cost : 684 x 330		225,700
Depreciation : 10% of fixed capital		111,500
Maintenance : 4% of fixed capital		44,600
Labour and supervision cost : 1800 x 36		64,800
Overhead costs:		54,700
Insurance : 1% of fixed capital		11,100
Net profit per year :	86,400	
Profit per ton of product :	7.3	
Profit per ton of waste :	1.32	
Annual percentage return on total investment :	7.8	

8.2.4 Process with Evaporators

In this case the layout of the plant (Fig. 8.3) differs from the previous one only in the following ways (i) Sugar solution leaving the reactor is flashed to atmospheric pressure and thus leaves part of its sensible heat and by evaporation concentrates itself. (ii) It is further concentrated through the evaporators after filtration. These produce savings in the size and hence in the cost of the filters, fermentation unit, distillation column, heat exchanger surface and effluent treatment unit. But it brings in additional costs of the flash drum and evaporators. The sizes of the reactor, neutralizer,

Fig. 8.3 Flow Diagram of the Continuous Process (with evaporators)

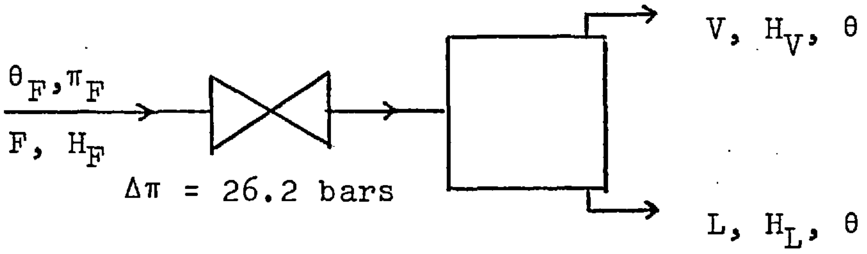


waste material, acid and water storage tanks, building and pumps remain unchanged. The costs of the items of equipment reduced in size were found by using the same data as in previous sections.

I - COST OF NEW PROCESS EQUIPMENT

(1) Flash Drum

The stream leaving the reactor will be flashed to atmospheric pressure. Partial vaporization (e) is found by setting up material and enthalpy balances around the drum



Overall material balance:

$$F = V + L \tag{8.1}$$

Enthalpy balance:

$$FH_F = VH_V + LH_L \tag{8.2}$$

By definition, fractional vaporization:

$$e = \frac{V}{F} \tag{8.3}$$

Simultaneous solution of equations 8.1, 8.2 and 8.3 gives

$$e = \frac{H_F - H_L}{H_V - H_L} \tag{8.4}$$

Inserting the known values of H_F, H_L, H_V into eq. (8.4) e = 0.25 is found. Thus, 25% of the entering liquid is vaporized. This gives 1600 x 0.25 = 400 ton/day vapour leaving 1200 ton/day liquid behind. The cost of the flash drum is included in the evaporator cost.

(2) Filters

The total flow rate to the filters is 58.5 m^3/h. For the same filtration rate, as used in the previous section, required filter area is 146 m^2. Thus, three filters, each with a 75 m^2 area, will be needed. Purchase cost is £31,000.

(3) Evaporators

A triple effect evaporator unit will be used to concentrate the sugar solution prior to the fermenters. Half of the water contained in the solution coming from the filters will be vaporized. Thus, liquid entering the fermenters will contain 7.2 g of sugar per 100 g of solution. This figure is within the range of widely used sugar concentration for fermentation. The flow rates and the conditions of the liquid, steam and vapour entering and leaving the evaporators are shown in Fig. 8.3. In the design calculation boiling point rise of the solutions was neglected and heat transfer coefficients of 4,000, 2,850 and 1,420 $W\ m^{-2}\ {}^{o}K^{-1}$ for the first, second and third effects respectively have been assumed. Because the feed temperature is reasonably high forward feed arrangement is the most suitable arrangement from steam consumption and economy points of view(38). From the usual material and enthalpy balances around the evaporators, by trial and error procedure, the required total surface was found to be 300 m^2. To this a surface area equal to one effect was added to account for the flash drum and condenser costs. Thus, required area is 400 m^2. The installed cost of a standard vertical tube evaporator unit of this capacity, with C.I. body and copper tubes is £60,000(32).

(4) Fermentation Unit

The flow rate to the fermenters is about 650 m^3/day. For a 20 hours fermentation time the required capacity is 540 m^3. Two redwood vats each with a capacity of 300 m^3 will do the job. Each costs £5,000 (with agitator and drive). Total estimated cost of the fermentation unit including yeast separator and ancillary tanks and pumps is £25,000.

(5) Distillation Column

Alcohol solution entering the column will contain about 3.17 g of alcohol per 100 g of solution. If the same procedure is employed as used in the previous design a column of 1.20 m diameter with 41 actual plates is found to be required. In this case optimum reflux ratio is 3. For a 0.46 m plate spacing the height of the column needs to be 20 m (with 10% excess). Total purchase cost is £8,000.

(6) Heat Exchangers

The required heat exchangers with their capacities and costs are shown in Table 8.8.

Table 8.8 Costs and capacities of the heat exchangers

Heat exch. no.	U (W m^{-2} $^oK^{-1}$)	Surface area (m^2)	Cost (£)
1	1140	70	5,900
2	1700	90	6,600
3	2840	3	600
4	570	28	3,500
5	1140	60	5,400
		Total:	£22,000

(7) Water Tank

Condensates from the evaporators and part of the water used as coolant in the condenser of the distillation column will be used as process water. This will be collected in a water tank and pumped to the water storage tank. The capacity of the water tank can be taken as equal to the half-hourly flow rate of the water to the water storage tank. Thus, capacity is $\frac{1150}{24 \times 2} \doteq 24$ m^3. Material of construction is mild steel. Cost is £3,600(33).

(8) Boiler

A package boiler with a capacity of 322 ton/day steam of 33.7 bars is required. Purchase cost is £35,000.

(9) Effluent Treatment Unit

Daily effluent to be treated is 680 m^3. Hence the installed cost of the unit is £37,000.

II - INSTRUMENTATION COST

The instrumentation cost, at 13 % of the purchased equipment cost, is £30,500.

III - PIPING COST

40% of the equipment cost is taken as the piping cost. This is £94,000.

IV - INSTALLATION COST

With the help of Table 8.3 total installation cost of the process equipment was found to be £60,000.

V - WORKING CAPITAL

The working capital for this case was calculated to be £115,000.

VI - TOTAL CAPITAL COST

Total capital required is shown in Table 8.9.

VII - DAILY MATERIAL AND UTILITIES COST

The required quantities of sulphuric acid, calcium carbonate and electricity will be the same as before. Water, fuel oil and B.O.D removal costs will, however, change. Fuel oil cost is found from energy balances. In the calculations, steam coming from the flash drum is taken into consideration. The procedure is the same as outlined in section 8.2.3. In the effluent treatment unit, the B.O.D of the 680 tons effluent is only required to be lowered to 970, because the water flow rate coming from the condensers is high enough to lower this figure to the accepted 100 when it joins the stream leaving the effluent treatment unit. Daily cost is shown in Table 8.10.

Table 8.9 Total capital cost

	£	
Costs of the separate items of equipment:		
1 - Waste material tank	7,000	
2 - Reactor	12,500	
3 - Neutralizer	3,500	
4 - Acid storage tank	2,700	
5 - Water storage tank	4,600	
6 - Water tank	3,600	
7 - Flash drum and evaporators	60,000	
8 - Filters	31,000	
9 - Fermentation unit	25,000	
10 - Distillation column	8,000	
11 - Heat exchangers	22,000	
12 - Pumps	20,000	
13 - Package boiler	35,000	
Total cost of equipment		234,900
Piping cost	94,000	
Installation and instrumentation cost	90,500	
Installed effluent treatment unit	37,000	
Building	237,000	
Physical plant cost		693,400
Engineering and supervision cost	104,000	
Direct plant cost		797,400
Contractor's fee	31,900	
Contingency	119,600	
Fixed capital cost		948,900
Working capital	115,000	
TOTAL CAPITAL		1,063,900

Table 8.10 Daily material and utilities cost

Material or utility	Quantity	Cost per unit (£)	Cost (£)
Sulphuric acid	15.0 tons	6/ton	90.0
Calcium carbonate	6.4 tons	2.7/ton	17.0
Water	6,500 tons	0.01/ton	65.0
Electricity	7,000 kWh	0.007/kWh	49.0
Fuel oil	24.2 m^3	11.5/m^3	278.0
Solid disposal	80 tons	0.50/ton	40.0
B.O.D removal	3,350 kg	0.03/kg	100.0
		TOTAL:	£639.0

VIII - ECONOMIC ANALYSIS

The economic picture of the process is summarized in Table 8.11.

Table 8.11 Economic analysis of the process

	£	
Annual revenue at £47 per ton selling price: 36.1 x 330 x 47	559,900	
Credit on hand £0.6 per ton of waste :	39,600	
Material and utilities cost : 639 x 330		210,900
Depreciation : 10% of fixed capital :		94,900
Maintenance : 4% of fixed capital :		37,900
Labour and supervision cost :		64,800
Overhead costs		51,400
Insurance : 1% of fixed capital :		9,500
Net profit per year :	130,100	
Profit per ton of product :	11.0	
Profit per ton of waste :	1.98	

Annual percentage return on total investment: 12.3

IX - EFFECT OF PLANT CAPACITY ON PROFITABILITY

In order to find the effect of capacity on profitability, a determination was conducted of the total cost, economic picture and profitability of a plant of the same design but of a capacity of 100 tons of waste material. The results are given as a summary in Tables 8.12 and 8.13. The capacities of all the process equipment have been determined as described in the previous sections. Same cost data were used. The piping, installation, engineering and supervision, contractor's fee and working capital costs were all estimated in the same manner.

For the two plants of different capacity, the process plant configurations, the unit operations involved and the materials of construction of the process equipment are the same. Hence, the power factor method applied to plant capacity ratio(32) for estimating capital investment can be regarded to hold. This is expressed as:

$$C_2 = C_1\left(\frac{K_2}{K_1}\right)^x \qquad (8.5)$$

where C_1 and C_2 are the fixed capital investments and K_1 and K_2 the capacities of the two plants. With the help of Tables 8.10 and 8.11 the exponent x is found as :

$$x = \frac{\log \frac{948,900}{615,800}}{\log \frac{2}{1}} = 0.62$$

This value of x was used in the equation (8.5) to determine the fixed capital requirements of hydrolysis plants of different

Table 8.12 Total capital cost for a plant of capacity of hundred tons waste material

	£	
Equipment cost	152,300	
Piping cost	60,900	
Installation and instrumentation cost	57,800	
Installed effluent treatment unit	21,000	
Building cost	158,000	
Physical plant cost		450,000
Engineering and supervision cost	67,500	
Direct plant cost		517,500
Contractor's fee	20,700	
Contingency	77,600	
Fixed capital cost		615,800
Working capital	64,800	
Total capital		680,600

Table 8.13 Economic analysis

	£	
Annual revenue at £47 per ton selling price :	279,900	
Credit on hand £0.6 per ton of waste :	19,800	
Material and utilities cost		105,500
Depreciation :		61,600
Maintenance		24,600
Labour and supervision		43,200
Overhead costs		33,900
Insurance :		6,200
Net profit per year	24,700	
Profit per ton of product :	4.2	
Profit per ton of waste	0.76	
Annual percentage return on total investment :	3.7	

capacities. Results are tabulated in Table 8.14 alongside the known results of the 100 and 200 tons/day capacity plants. The working capital of each plant was also determined and included in the table. Finally, profits per ton of product and waste and annual returns on total investment were calculated and attached to the table.

8.3 BATCH PROCESS

As was stated before a hydrolysis plant working on a single paper mill's waste can have a maximum capacity of 30 ton/day in this country. The figures in Table 8.14 reveal that a plant of that capacity based on continuous process condition will not be economic. Thus, in this part the design and economic pictures of hydrolysis plants based on batch process condition are investigated with specific attention being paid to the capacity range which was proved to be uneconomic for the continuous case.

8.3.1 Process Conditions and Procedure

Under the continuous process conditions, high temperature and low acid concentration were proved to be most favourable from the economic point of view. By analogy, this fact was assumed to hold for the batch process conditions as well and 0.4% sulphuric acid concentration was selected as in the continuous case. In the continuous process conditions the realization of small residence time helped to attain high temperature and hence high yield. But, batch operation of the reactor does not allow such small residence times to be

Table 8.14 Comparison of various capacity hydrolysis plant (continuous process)

Capacity (tons/day)	100	150	200	250	300
Fixed capital (£)	615,800	790,000	948,900	1,084,000	1,220,000
Working capital (£)	64,800	85,800	116,000	134,000	156,000
Total capital (£)	680,600	875,800	1,063,900	1,218,000	1,376,000
Profit per ton of product (£)	4.2	6.7	11.0	13.7	15.6
Profit per ton of waste (£)	0.76	1.21	1.98	2.48	2.80
Annual per cent return on total investment	3.7	6.9	12.3	16.8	20.2

realized in practice. The threshold time in this case was chosen as 5 minutes and times smaller than this were assumed to be unrealiable. The close check of Table 5.1 reveals that maximum temperature that can be attained without violating this time limit is 210°C. The corresponding yield of 45.8% seems very low to secure the profitability of small capacity plant because, in the continuous case, even a 53% yield was not sufficient for economic operation of such plants. However, if considerable savings in capital, material and utilities costs can be achieved in batch operation, small capacity plants may become profitable, in spite of such a low yield. But this - as will be shown in later sections - is not the case. Thus, for a profitable operation, methods have to be found to somehow increase the yield. This can be done by introducing the dilute acid solution intermittently into the reactor, already filled with a batch of waste cellulosic material, in a number of injections rather than all at once. These injections will be referred to henceforth as acid batches to distinguish them from the batches of cellulosic material which will be called solids batches. The process is conducted in such a way that each acid batch is drained before the next acid batch is introduced. The time interval of each acid batch in the reactor will be referred to as the residence time of the acid batch. The residence times of acid batches may or may not be equal in the treatment of a given solids batch.

The intermittent introduction of acid will not cause excessive dilution of the sugar produced, because the use of high liquid-solid ratio in the reactor, which was inevitable in the continuous case - partly due to difficulties in pumping and clogging - is no longer necessary. For practical purposes a liquid-solid ratio of 2 was assumed to be satisfactory.

Although 210°C gives the highest yield for single acid batch conditions, this temperature may not give the highest yield for multibatch introduction of acid. Hence the relation between temperature and number of acid batches per solids batch has to be investigated. A suitable computer program was written (see Appendix A) using temperature levels of 180, 190, 200 and 210°C at up to 4 acid batches per solids batch and with various acid residence times in each solid batch. The complete list of results is given in Appendix B. Extracts from this list were collected in Table 8.15.

It follows from Table 8.15 that equal residence times of each acid batch do not necessarily give the highest yield. The highest yield occurs at 200°C - not at 210°C - when the number of batches is equal to four, each with progressively increasing residence times.

The optimum number of acid batches is governed by economic considerations. In the calculation below 4 acid batches at 200°C are taken as basis. The effect of number of acid batches will be investigated in later sections. The residence time of each acid batch will be taken such that the total yield is to be highest. These are 5, 5, 10 and 15 minutes for the first, second, third and fourth acid batches respectively.

The design capacity is chosen as 30 ton/day, because that

Table 8.15 The yield of sugar producing reaction at various temperatures for conditions of 3 and 4 acid batches per solids batch

Residence times of acid batches (MINUTE)					Total yields (%)	
Temp. °C	First batch	Second batch	Third batch	Fourth batch	At the end of three batches	At the end of four batches
180	10	10	10	10	24.8	31.5
	20	10	10	10	30.5	36.6
	30	10	10	10	34.7	40.1
	40	40	40	40	54.9*	62.5*
	50	10	10	10	39.6	44.0
	50	20	10	40	43.4	54.9
190	10	10	10	10	49.5	58.7
	10	10	20	20	55.9	66.5
	10	20	20	40	59.8	69.0*
	20	20	40	10	63.1*	65.4
	30	30	20	40	58.9	62.9
	40	30	20	40	54.0	57.1
200	5	5	5	5	57.7	66.5
	5	5	10	15	63.4	73.0**
	5	5	10	20	63.4	72.6
	5	10	10	10	65.9	72.0
	5	10	15	5	67.0*	70.0
	10	5	5	5	60.0	66.1
210	5	5	5	5	68.2	70.9
	5	5	5	7	68.2	71.1
	5	5	7	7	68.5**	70.4
	6	5	5	5	65.7	67.9
	7	5	5	5	62.5	64.4

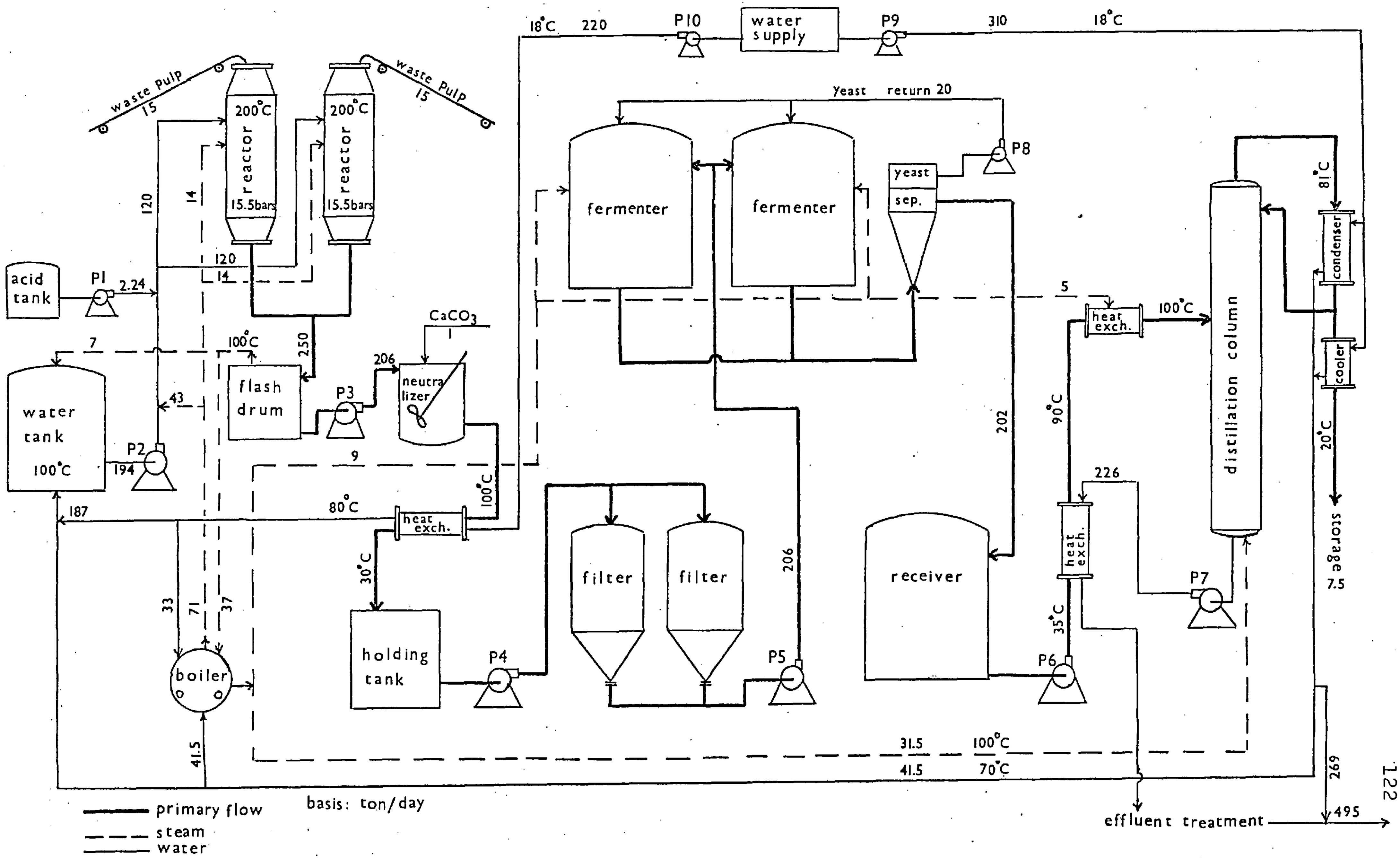
(*) Shows the best condition at a particular temperature

(**) Shows the best condition for all temperatures amount of waste pulp is available at one paper mill. As in the continuous case, the effect of plant capacity on profitability will be assessed at a later stage.

8.3.2 The Layout of the Process Plant

The layout of the proposed batch process plant is shown in Fig. 8.4. According to this layout, the waste material collected in an open tank is carried into the reactor by conveyor belts. There, it is heated to the reaction temperature by live steam. Steam is then shut off and hot dilute acid solution is introduced into the reactor. At the end of the reaction time the solution is withdrawn to a flash drum where it is flashed to atmospheric pressure. The reactor with its content is brought up again to the reaction temperature by live steam and the second batch of fresh hot acid solution is introduced. This is repeated as many times as desired. Unreacted waste is then discharged from the reactor and a fresh batch of waste material is introduced into it. The flashed solution is pumped to the neutralizer where it is neutralized by calcium carbonate at about 100°C. Through a heat exchanger the solution is cooled down to the fermentation temperature of 30°C and flows into a holding tank. After filtration the clear stream is admitted to the fermenters for batchwise alcoholic fermentation. At the end of the fermentation time the yeast is separated for reuse and the alcoholic solution then is pumped through two series of heat exchangers to heat it up to its boiling point temperature. In the first exchanger part of the sensible heat of the bottom

Fig. 8.4 Flow Diagram of the Batch Process



product of the distillation column is used to heat the solution. The second exchanger employs live steam. In the final section of the process, the alcohol solution is rectified to produce 60% alcohol.

8.3.3 Process Engineering and Cost

I - COST OF INDIVIDUAL ITEMS OF EQUIPMENT

(1) Reactors

Two cylindrical reactors made of stainless steel are employed. Their capacities were found as follows: The total reaction time is 35 minutes. Another 100 minutes is estimated to be needed for filling, emptying, steaming, introducing and withdrawing the solutions. Thus total time for each solids batch is 135 minutes. This means that $\frac{24 \times 60}{135} \simeq 10$ batches can be treated in a day. Hence, the amount of waste material treated in each batch is (30/10 =) 3 tons. For dried waste pulp of an average density of 300 kg/m^3 the total volume of 3 tons of waste pulp is 10 m^3. A volume twice as big as this figure is considered sufficient to hold 3 tons of waste pulp and reaction solution. Hence the capacity of each reactor is taken as 10 m^3. Cost of each is £7,500(32) making a total of £15,000.

(2) Belt Conveyors

Waste pulp is transported to the reactors from the waste tank by belt conveyors. Two 15 m long belts of 0.35 m width are estimated to be sufficient. Cost is £2,500(32).

(3) Water Tank

Water used in the heat exchanger immediately after the neutralizer as coolant and thus heated up to 80°C will be collected in the water tank to be used in the preparation of dilute acid solution. A capacity of 15 m^3 is sufficient for the water tank, to ensure smooth operation. Material of construction is mild steel. Cost is £2,700(33).

(4) Acid Tank

Total daily acid requirement is 1.73 tons (% 100). A capacity sufficient to hold the daily acid requirement is considered satisfactory. Since the acid is assumed to be available at 77% the volume of the tank requires to be 1.3 m^3. Material of construction is stainless steel. Cost is £1,300(32).

(5) Flash Drum

Maximum amount of solution charged at a time is 3 m^3. Hence a tank of 3 m^3 capacity is sufficient. Material of construction is stainless steel. Cost is £2,700(32).

(6) Neutralizer

This will be a stainless steel tank fitted with an agitator. Capacity is 3 m^3. Cost, including agitator and drive, is £3,500(32).

(7) Holding Tank

This tank will act as a reservoir for the filters. A capacity of 10 m^3 will be sufficient to ensure the uninterrupted working of the reactors. Material of construction is carbon steel. Cost is £1,200(32).

(8) Filters

Bed filters with positive pressure will be employed. Total liquid to be filtered is 196 m^3/day (because, on flashing the solution to atmospheric pressure from a pressure of 15.5 bars 18.2% of the total amount is vaporized). For a 0.4 m^3/m^2h filtration rate the required area is 21 m^2. Two bed filters each with an area of 21 m^2 are required. Cost of each filter is £4,700 making a total of £9,200.

(9) Fermentation Unit

Fermentation will be carried out in batch fashion with a 20 h fermentation time. Two redwood vats each of 200 m^3 capacity will be needed. While the one is being filled fermentation will be progressing in the other. Cost of each vat with agitator and drive is £4,000. To complete the fermentation unit, a yeast separator, a number of small tanks and pumps will be needed. Another £7,000 is estimated for the purchase of these items. Thus, total cost is £15,000.

(10) Receiver

The fermented solution will be emptied into this tank from the fermenters. The capacity of this tank will be taken equal to daily flow rate: 196 m^3. Material of construction is carbon steel. Cost is £6,000(32).

(11) Distillation Column

The solution pumped to the distillation column from the receiver will approximately contain 2.3 g ethanol per 100 g of solution and enter the column at its boiling point temperature. Open steam will be used. It is assumed that 99% of the ethanol present in the feed will be recovered. With the help of the methods mention in section 8.2.3 the number of actual plates and design diameter of the column were found to be 20 and 0.9 m respectively. For a plate spacing of 0.3 m the height of the column needs to be 6.6 m (with 10% excess). Total cost of the column is £4,000(32).

(12) Heat Exchangers

The necessary heat exchangers are indicated in Fig. 8.4. With the same methods and data used in section 8.2.3 the total cost was calculated to be £6,300.

(13) Pumps

Major pumps required throughout the plant are shown in Fig. 8.4. Using the same criteria and data mentioned in section 8.2.3, their costs add up to £7,000.

(14) Boiler

Daily steam requirement is 82 tons. Hence, a package boiler capable of producing 90 tons of steam at 15.5 bars pressure is required. Cost is £10,500(32).

(15) Effluent Treatment Unit

Amount of effluent to be treated daily is 230 m^3. The installed cost of a unit of this capacity is £16.000$^{(32)}$.

II - INSTRUMENTATION COST

The instrumentation cost, at 13 % of the purchased equipment cost, is £11,300.

III - BUILDING

A two-storey standard steel building with a 600 m^2 floor area will be sufficient to accommodate all the equipment. Cost, at £118.5 per m^2, is £71,100.

IV - PIPING COST

The piping cost, at 40% of the purchases equipment cost, is found to be £34,700.

V - INSTALLATION COST

With the help of Table 8.3 total installation cost was found to be £27,500.

VI - FIXED CAPITAL COST

The fixed capital cost of the plant was obtained by following the same procedure as used in the continuous case. This gave the fixed capital requirement as £338,700.

VII - EFFECT OF PLANT CAPACITY ON FIXED CAPITAL COST

In the continuous process calculations in section 8.2.4 the effect of plant capacity on capital cost was found by applying "the power factor method applied to plant capacity ratio". The exponential factor was then determined with the help of the fixed capital costs found for two different capacity plants using the calculated cost data. This gave a power factor of 0.62. The same method using the same exponential factor can be applied to determine the effect of plant capacities on the capital costs for batch process plants without causing great error, because of the great similarities which exist between the two process conditions, equipment and unit operation involved.

The fixed capital costs of plants of 60 and 90 tons/day waste pulp capacity employing the same process conditions as the 30 ton/day capacity plant - namely a liquid-solid ratio of 2 and 4 acid batches per solids batch - were thus found by using the fixed capital cost determined for 30 tons/day capacity plant as basis. Results are given in Table 8.16.

VIII - EFFECT OF NUMBER OF ACID BATCHES ON FIXED CAPITAL

As the number of acid batches per batch of waste pulp is increased, keeping the liquid-solid ratio constant in each batch, the capacities and hence the costs of process equipment increase, due to the increased liquid quantity although the waste pulp input remains constant. This affects the required capital cost. The effect of this change on the capital cost for a fixed waste pulp input can also be estimated by the power factor method, because the ratio of waste pulp quantities of plants of two different capacities is equal to the ratio of sugar solutions produced in these plants for the same liquid-solid ratios and number of acid batches per solid batch. For example, for the case of plants of 30 and 60 tons/day of waste pulp capacity the amount of sugar solutions produced are 240 and 480 tons/day respectively, for a four acid batches per solids batch condition. And it is obvious that $\frac{60}{30}$ is equal to $\frac{480}{240}$. Hence, the power factor method used with solids ratio replaced by liquids ratio produces the same result. This fact can be exploited to estimate the capital costs for plants of the same waste pulp capacity but different amounts of reaction solution or in other words different number of acid batches per solids batch.

The fixed capital costs of plants of capacities of 30, 60 and 90 tons/day were determined in this way for numbers of acid batches of 3 and 5. Results are collected in Table 8.16.

IX - WORKING CAPITALS

The working capitals for plants of capacities of 30, 60 and 90 tons were determined according to the procedure outlined in section 8.2.3. Results are given in Table 8.16.

X - MATERIAL AND UTILITIES COST

Daily material and utilities requirement and their cost for a plant of 30 tons capacity with 4 acid batches per solid batch condition are described below.

SULPHURIC ACID: A total of 2.25 tons of sulphuric acid of 77% is calculated to be required for both neutralization and the preparation of 240 tons of 0.4% sulphuric acid solution. Cost, at £6 per ton, is £13.5.

CALCIUM CARBONATE: Amount of calcium carbonate needed to neutralize the acidic sugar solution is found on the basis that

Table 8.16 Effect of waste pulp amount and the number of acid batches per solids batch on capital cost

CAPACITY (Ton/day)	30			60			90		
Number of acid batches per solids batch	3	4	5	3	4	5	3	4	5
Amount of dilute acid solution (Ton/day)	180	240	300	360	480	600	540	720	900
Fixed capital cost (£)	283,000	338,700	389,000	434,000	520,000	596,000	560,000	670,000	768,500
Working capital (£)	23,000	26,300	30,200	39,700	45,700	50,500	55,500	64,100	71,200
Total capital (£)	306,000	365,000	419,200	473,000	565,700	646,500	615,500	734,100	839,700

approximately one mole of calcium carbonate is equivalent to one mole of sulphuric acid. In this case, this is about 1 ton and its cost, at £2.7 per ton, is £2.7.

WATER: 530 tons of water is found to be required for the preparation of the acid solution, for heat exchangers, condenser duty and product cooling. Cost, at £0.01 per ton, is £5.3.

ELECTRICITY: Total horse power including the allowance for lighting is estimated to be 75. This amounts to an energy of 1800 kWh. Cost, at 0.007 per kWh, is £12.6.

FUEL OIL: Daily consumption of fuel oil is found by looking at energy balances at various stages of the process and the temperature of available water. These are:

(i) Steam obtained from the flash drum is sufficient to meet the demands of the distillation column and the fermenters.

(ii) 50 tons of steam (saturated at 200°C) is needed to inject into 190 tons of dilute acid solution originally at 80°C to obtain the reactant solution at 200°C. This steam is raised from water at 70°C coming from the condenser of the distillation column. Thus, energy required is:

$$Q_1 = 50 \times 10^3 \times 4.18 \times (666-70) = 124.5 \times 10^6 \text{ kJ.}$$

(iii) Certain amount of steam is needed for steaming the reactors at the beginning of each solids batch as well as at the intervals of the acid batches to bring the temperature and the pressure of the reactors to the reaction conditions prior to the introduction of dilute acid solutions. This amount can be estimated as follows: The reactor itself which is made of steel and the waste pulp will be heated to the reaction temperature from $20^{o}C$ at the beginning of each batch. Since there are 10 batches a day this requires an energy of:

$$[10{,}500 \times 0.12 \times (200-20) + 3{,}000 \times 0.32(200-20)] \times 10 \times 4.18$$
$$= 16.7 \times 10^{6} \text{ kJ}.$$

When a cycle is over, sugar solution is withdrawn from the reactor. This causes a temperature drop in the reactor. Hence, before the next acid batch is introduced temperature and pressure of the reactor have to be restored to their original values. This is done by steaming. At each interval a temperature drop of $50^{o}C$ is assumed. In four acid batches there are 3 intervals. For 10 solids batches a day this means a total of 30 intervals. Hence, the amount of energy needed is:

$$(10{,}500 \times 0.12 \times 50 + 3{,}000 \times 1 \times 50) \times 30 \times 4.18$$
$$= 26.8 \times 10^{6} \text{ kJ}.$$

The addition of these two energies with an assumed 25% energy loss gives a total of 52.2×10^{6} kJ. This energy is supplied from the latent heat of the steam saturated at $200^{o}C$. Thus, amount of steam required is: $\frac{52.2 \times 10^{6}}{1940} = 27{,}000$ kg. This steam is raised from water at $70^{o}C$ coming from the condenser. Thus energy required to raise that amount of steam is:

$$Q_2 = 27{,}000 \times 4.18 \times (660-80) = 66.2 \times 10^{6} \text{ kJ}.$$

(iv) The energy needed to heat the alcoholic solution prior to the distillation column from $90^{o}C$ to $100^{o}C$ is:

$Q_3 = 1.96 \times 10^5 \times 4.18 \times (100-90) = 8.2 \times 10^6$ kJ.

Total energy is $\Sigma Q = Q_1 + Q_2 + Q_3 = 198.9 \times 10^6$ kJ. This needs 6 m^3 of fuel oil of calorific value 39×10^6 kJ/m^3, assuming a boiler efficiency of 85%. Cost, at £11.5/m^3, is £69.

SOLID DISPOSAL AND B.O.D REDUCTION: Amount of solids to be disposed of is estimated to be 9 tons. Cost, at £0.50/ton, is £4.5. The B.O.D of the bottoms of the distillation column was found to be 2,600 ppm for this dilution. This requires only to be reduced to 200 ppm because the amount of water coming from the condenser is sufficient enough to reduce this value further down to the accepted discharge value. Thus, daily B.O.D removal is 550 kg. Cost, at £0.03 per kg B.O.D removed, is £16.5.

By following up the same procedure daily material costs for any capacity and condition can be found. This has been done for a plant of capacity of 30 ton/day with 3 and 5 acid batches per solids batch as well as for 60 and 90 tons/day capacity plants with 3, 4, and 5 acid batches per solids batch and results are tabulated in Table 8.17.

Table 8.17 Daily material and utilities costs for plants of different capacities and different number of acid batches

CAPACITY (ton/day)	30			60			90		
Number of acid batches per solids batch	3	4	5	3	4	5	3	4	5
Daily cost (£)	102	124.1	146.9	204	244.2	293.8	306	368.3	440.7

XI - ECONOMIC ANALYSIS OF THE PROCESS

The daily amount of 60% ethanol produced at 200°C and 0.4% sulphuric acid conditions from 30 tons of waste pulp of 46.1 potential sugar content is shown in Table 8.18.

Table 8.18 Daily ethanol yield from 30 tons of waste pulp at 200°C and 0.4% acid conditions

The number of acid batches per solids batch	3	4	5
Potential sugar (tons)	13.8	13.8	13.8
Net sugar yields (tons)	9.26	10.10	10.65
Fermentable sugars (tons)	8.09	8.82	9.30
100 per cent ethanol (tons)	4.12	4.50	4.75
60 per cent ethanol (tons)	6.85	7.50	7.91

The yields of plants of capacities of 60 and 90 tons/day are found by simply doubling and tripling the relevant figures in Table 8.18.

The economic analysis and the profitability of the process were determined for plants of three capacities with three different number of acid batches per solids batch. The procedure is illustrated in Table 8.19 for the 60 tons/day capacity plant with 4 acid batches per solids batch condition. Other results are summarised in Table 8.20. In the preparation of the tables (i) A working year of 330 days was assumed to be realized. (ii) A total of 18 men for work on three shifts have been estimated to be required. Their averaged wage was

taken as £1,800 per year per man. (iii) A credit of £0.60 per ton of waste, which is required to be disposed of by other means, was assumed on the income side.
(iv) Overhead costs were assumed as 50 % of the expenses for labour, supervision and maintenance.

Table 8.19 Economic analysis of a plant of 60 tons/day waste pulp capacity with 4 acid batches per solids batch

	£	
Annual revenue at £47 per ton selling price :	232,600	
Credit on hand £0.6 per ton of waste	11,800	
Material and utilities cost : 244.2 x 330		80,600
Depreciation : 10% of fixed capital		52,000
Maintenance : 4% of fixed capital		20,800
Labour and supervision cost : 1800 x 18		32,400
Overhead costs		26,600
Insurance : 1% fixed capital		5,200
Net profit per year	26,800	
Profit per ton of product	5.4	
Profit per ton of waste pulp	1.1	
Annual percentage return on total investment :	4.7	

8.4 DISCUSSION OF THE RESULTS

In above sections process engineering, costs and the profitabilities of hydrolysis plants working both on continuous and batch process conditions have been looked at. The findings can be outlined as follows:

It has been shown that in the continuous process case the inclusion of evaporators increases the profitability margin,

Table 8.20 Economic comparison of plants of different capacities (batch process)

Capacity (tons/day)	30			60			90		
Number of acid batches per solids batch	3	4	5	3	4	5	3	4	5
Profit per ton of product (£)	-8.0	-9.8	-13.2	5.4	5.4	2.3	9.7	11.0	7.8
Profit per ton of waste pulp (£)	-1.83	-2.4	-3.5	1.22	1.1	0.55	2.2	2.7	2.0
Annual per cent return on total investment	-5.9	-6.6	-8.2	5.1	4.7	1.6	10.6	11.1	7.3

because of savings in both fixed capital and material costs. It was also found that the capacity of the plant has an important effect on the profitability. Analysis of Table 8.14 shows that for continuous process conditions a plant of capacity less than 200 tons/day is far from being profitable. The profitability margin increases as the capacity of the plant increases. The reasons for this are: (i) fixed capital costs of hydrolysis plants are high, (ii) the potential sugar content of the waste on which calculations are based is low. (iii) yield of the reaction is not high. (iv) industrial ethanol is a rather cheap product.

The 200 tons/day limit is strictly applicable to the plant for which the potential sugar content of the waste input is 46.1%. As this figure changes the limit changes. Indeed, the potential sugar content of a waste is an important factor for a hydrolysis plant to be profitable, because three of the above given reasons - at least for the present - are unlikely to change but the potential sugar content of the waste may change depending upon the source of it. In the case of this waste coming from paper mills it is unlikely that it will increase. But, it may increase if the source of the waste is municipal waste. Indeed, if the cellulosic part of the municipal waste can be separated successfully from the rest, this figure can go up to 60 or even 70 per cent. In Table 8.21 the economic picture of plants of same capacity working on waste celluloses of 55 and 65% potential sugar content respectively are shown. It can be seen that annual percentage returns on total investment increase dramatically and 100 tons/day capacity plants become profitable. However, the additional cost, which will occur in the separation operation has not been taken into account.

In the batch process profitability of the plants is affected by the number of discrete batches of acid solution as well as by the amount of waste input.

Plants of capacities of 30 and even 60 tons/day of waste cellulose were found to be far from being profitable for a waste cellulose of 46.1 potential sugar content. But a 90 tons/day capacity plant, contrary to the continuous process case, may become viable for a waste cellulose of 46.1 potential sugar content. This is due to the fact that introduction of dilute acid solution in a number of discrete batches - rather than at once - almost doubles the sugar yield.

Again, the economic picture of plants of the same capacity are expected to change with the change of potential sugar content of the waste. This is indicated in Table 8.22. It follows from the table that a plant of 60 tons/day capacity may become economic when the potential sugar content of the waste reaches 55%.

This shows that hydrolysis plants of small capacities which are uneconomic to operate as a continuous process may become profitable when working under batch conditions.

Table 8.21 Effect of potential sugar content of waste on the profitability (continuous process)

Capacity (tons/day)	100		150		200		250		300	
Potential sugar content of waste (%)	55	65	55	65	55	65	55	65	55	65
Profit per ton of product (£)	11.1	16.7	13.2	18.5	16.8	21.4	19.0	23.5	20.7	24.7
Profit per ton of waste	2.4	4.2	2.9	4.7	3.6	5.5	4.1	6.1	4.5	6.3
Annual percentage return on total investment	11.6	20.6	16.1	26.7	22.5	34	27.8	40.5	32.2	45.4

Table 8.22 Effect of potential sugar content of waste on the profitability (batch process with 3 acid batches per solids batch)

Capacity (tons/day)	30		60		90	
Potential sugar content of waste (%)	55	65	55	65	55	65
Profit per ton of product (£)	1.2	7.9	14.4	19.0	18.0	22.1
Profit per ton of waste (£)	0.2	2.6	3.9	6.1	4.9	7.1
Annual per cent return on total investment	1.0	8.3	16.3	25.4	23.4	34.5

CHAPTER 9

SUMMARY AND CONCLUSIONS

The results of the present study may be summarized as follows:

(1) The waste paper pulp was expressed in terms of potential sugar and the change in this potential sugar in acid solution was investigated. It was found that this change followed first order reaction law.

(2) Decomposition of glucose in acid solution was also investigated. It was shown that this reaction too obeyed first order reaction law.

(3) Effect of acid concentration and the temperature on both reactions were assessed. Both reactions were found to be affected, although to a different extent, by the changes in acid concentration as well as in temperature. For both reactions generalized rate equations, taking into account the effects of acid concentration and temperature, were derived.

(4) The overall hydrolysis reaction was assumed to be represented by first order consecutive reaction mechanism and the process was analysed theoretically on this assumption for different types of reactors and the yield was predicted. Experiments were then conducted and yield determined. The good agreement which was obtained between observed and predicted values was taken as confirmation of the proposed mechanism.

(5) The fermentability of the solution obtained from the hydrolysis into ethanol was determined. It was found that the

fermentability was higher than those of hydrolyzates of most species of wood.

(6) The B.O.D of the solution left after fermentation was determined. It was found that the effluent has a high B.O.D and would require treatment before discharge into rivers or lakes.

(7) The process design was carried out and the economic merits of plants converting waste pulp into industrial ethanol were assessed. Two different approaches were made: A large capacity continuous plant and a small capacity batch plant were separately investigated. From the economic considerations optimum reaction conditions were determined. It was found that working at high temperature with low acid concentration is favourable. In the batch process case, introduction of dilute acid solution into reactor in a number of discrete batches was found to increase the yield and hence profitability. It was established that continuous process plant needs to have large capacity in order to be economically feasible. The batch process plant was found to be economic at relatively smaller capacity.

The potential sugar content of the waste was found to be the most important factor in determining the economic capacity of a plant. In batch process, in addition, the number of acid batches per solids batch was found to be important.

Recommendation for future work

(1) Because of equipment limitation kinetic data could not be obtained at temperatures higher than 190°C. Working at high temperature would enable a more precise prediction of the overall reaction yield.

(2) The reaction should be conducted continuously in a larger scale reactor at higher temperatures.

(3) An attempt should be made to apply multivariable optimization technique to economic analysis of the process both for continuous and batch process conditions, in order to produce more precise and detailed results.

APPENDIX A

COMPUTER PROGRAMMES

Two computer programmes have been written to facilitate the calculation of the yield of hydrolysis reaction. Both programmes were written in FORTRAN IV Language and run on a CDC 6400 computer.

(1) This programme was written to calculate the yield of hydrolysis reaction for batch, plug and constant flow stirred tank reactors at various conditions. With the help of this programme the values of both rate constants can also be evaluated at desired conditions. The listing of the programme is given below.

```
   PROGRAM KIN(INPUT,OUTPUT,TAPE5=INPUT,TAPE6=OUTPUT)
   T=433.16
15 T=T+10.
   BT=T-273.16
   A1=1./EXP(42030./(1.987*T))
   A2=1./EXP(32480./(1.987*T))
   DO 5 I=1,4
   IF(I.EQ.3) GO TO 5
   C=0.4*FLOAT(I)
   AK1=6.15*(1.E18)*(C**1.275)*A1
   AK2=1.42*(1.E14)*(C**0.997)*A2
   RAK1K2=AK1/AK2
   RAK2K1=AK2/AK1
   PW=AK2/(AK2-AK1)
   AP=100*(RAK1K2**PW)
```

```
   AL=ALOG(RAK2K1)
   TPMAX=AL/(AK2-AK1)
   AB=100/(RAK2K1**0.5+1)**2
   TBMAX=1./(AK1*AK2)**0.5
   WRITE(6,10)BT,C,AP,TPMAX,AB,TBMAX
10 FORMAT(25X,F5.1,F7.1,4F10.1)
 5 CONTINUE
   IF(T.LT.523.) GO TO 15
   STOP
   END
```

(2) At multistage batch process case, the yield of hydrolysis reaction was calculated with the help of the programme given below. This programme was written in general form for the condition of 4 acid batches per solids batch. It can be run at any acid concentration, temperature and residence time of each acid batch. The yield, remaining potential sugar of waste can be determined at the end of each acid batch for different number of residence times. The listing of the programme is:

```
   PROGRAM YIELD(INPUT,OUTPUT,TAPE5=INPUT,TAPE6=OUTPUT)
   DIMENSION CA1(4),CA2(4,16),CA3(4,16,64)
   DIMENSION CB1(4),CB2(4,16),CB3(4,16,64),CBU(64),CBD(64)
   DIMENSION AT2(4),AT3(4,16),AT4(4,16,64),ATU(64),ATD(64)
   DIMENSION CBUY(64),CBDY(64)
   T=443.16
15 T=T+10.
   BT=T-273.16
```

```
      C=0.4
      A1=1./EXP(42030./(1.987*T))
      A2=1./EXP(32480./(1.987*T))
      AK1=6.15*(1.E18)*(C**1.275)*A1
      AK2=1.42*(1.E14)*(C**0.997)*A2
      AN=0.0
   10 CONTINUE
      AN=AN+1
      AT1=AN*10.
      CA=46.1*EXP(-AK1*AT1)
      CBO=46.1*(AK1/(AK2-AK1))*(EXP(-AK1*AT1)-EXP(-AK2*AT1))
      AAT2=0.
      DO 1 M=1,4
      AT2(M)=AAT2+10.
      CA1(M)=CA*EXP(-AK1*AT2(M))
      CB1(M)=CA*(AK1/(AK2-AK1))*(EXP(-AK1*AT2(M))-EXP(-AK2*AT2(M)))
      AAT2=AT2(M)
    1 CONTINUE
      DO 2 M=1,4
      AAT3=0.
      DO 3 N=1,4
      AT3(M,N)=AAT3+10.
      CA2(M,N)=CA1(M)*EXP(-AK1*AT3(M,N))
      CB2(M,N)=CA1(M)*(AK1/(AK2-AK1))*(EXP(-AK1*AT3(M,N))-EXP
     1 (-AK2*AT3(M,N)))
      AAT3=AT3(M,N)
    3 CONTINUE
    2 CONTINUE
      KB=0.
```

```
      DO 4 M=1,4
      DO 5 N=1,4
      AAT4=0
      DO 6 K=1,4
      AT4(M,N,K)=AAT4+10.
      KB=KB+1
      CA3(M,N,K)=CA2(M,N)*EXP(-AK1*AT4(M,N,K))
      CB3(M,N,K)=CA2(M,N)*(AK1/(AK2-AK1))*(EXP(-AK1*AT4(M,N,K))-
     1EXP(-AK2*AT4(M,N,K)))
      ATU(KB)=AT1+AT2(M)+AT3(M,N)
      ATD(KB)=AT1+AT2(M)+AT3(M,N)           +AT4(M,N,K)
      CBU(KB)=CB0+CB1(M)+CB2(M,N)
      CBD(KB)=CB0+CB1(M)+CB2(M,N)+CB3(M,N,K)
      CBUY(KB)=100*(CBU(KB)/46.1)
      CBDY(KB)=100*(CBE(KB)/46.1)
      WRITE(6,20)AT1,AT2(M),AT3(M,N),AT4(M,N,K),CBUY(KB),CBDY(KB)
   20 FORMAT(30X,4F8.1,2X,2F9.2)
      AAT4=AT4(M,N,K)
    6 CONTINUE
    5 CONTINUE
    4 CONTINUE
      IF(AT1.LT.64) GO TO 10
      STOP
      END
```

List of Symbols Used in the Computer Programmes

FORTRAN Symbol	Meaning
T	Temperature (^{o}K)
BT	Temperature (^{o}C)
C	Concentration of acid (%)
AK1	Rate constant of hydrolysis reaction (min^{-1})
AK2	Rate constant of sugar decomposition reaction (min^{-1})
AP	Maximum yield of batch and plug flow reactors (%)
TPMAX	Residence time when the yield is at its maximum in batch and plug flow reactors (min.)
AB	Maximum yield of constant flow stirred tank reactor (%)
TBMAX	Residence time when the yield is at its maximum in constant flow stirred tank (min.)
AT1,AT2,AT3,AT4	Time (min)
CA,CA1,CA2,CA3	Concentration(g)
CBO,CB1,CB2,CB3	Concentration (g)
ATU	Total of residence times of the first three acid batches (min.)
ATD	Total of residence times of the four acid batches (min.)
CBU	Total amount of sugar produced from 100 g of waste pulp in the first three batches (g)
CBD	Total amount of sugar produced from 100 g of waste pulp in the four batches (g)

Symbol	Meaning
CBUY	Sugar obtained in the first three batches as percentage of potential sugar
CBDY	Sugar obtained in four batches as percentage of potential sugar

APPENDIX B

Yield of Overall Hydrolysis Reaction for Multibatch Conditions

The yield of overall hydrolysis reaction at various temperatures for the conditions of 3 and 4 acid batches per solids batch is given below. Acid concentration was kept constant at 0.4%.

Temp.	Residence times of acid batches (Minute)				Total yields (%)	
°C	First Batch	Second Batch	Third Batch	Fourth Batch	At the end of three batches	At the end of four batches
	10.0	10.0	10.0	10.0	24.83	31.55
	10.0	10.0	10.0	20.0	24.83	36.34
	10.0	10.0	10.0	30.0	24.83	40.93
	10.0	10.0	10.0	40.0	24.83	44.01
	10.0	10.0	20.0	10.0	30.69	36.76
	10.0	10.0	20.0	20.0	30.69	41.53
	10.0	10.0	20.0	30.0	30.69	45.23
	10.0	10.0	20.0	40.0	30.69	48.01
	10.0	10.0	30.0	10.0	35.22	40.72
	10.0	10.0	30.0	20.0	35.22	45.01
	10.0	10.0	30.0	30.0	35.22	45.34
	10.0	10.0	30.0	40.0	35.22	50.36
	10.0	10.0	40.0	10.0	38.63	43.58
	10.0	10.0	40.0	20.0	38.63	47.47
	10.0	10.0	40.0	30.0	38.63	50.48
	10.0	10.0	40.0	40.0	38.63	52.75
	10.0	20.0	10.0	10.0	30.60	35.67
	10.0	20.0	10.0	20.0	30.60	41.44
	10.0	20.0	10.0	30.0	30.60	45.13
	10.0	20.0	10.0	40.0	30.60	47.32
	10.0	20.0	20.0	10.0	35.89	41.37
	10.0	20.0	20.0	20.0	35.89	45.56
	10.0	20.0	20.0	30.0	35.89	49.01
	10.0	20.0	20.0	40.0	35.89	51.53
	10.0	20.0	30.0	10.0	39.98	44.32
	10.0	20.0	30.0	20.0	39.98	48.32
	10.0	20.0	30.0	30.0	39.98	51.93
	10.0	20.0	30.0	40.0	39.98	54.09
	10.0	20.0	40.0	10.0	43.05	47.53
	10.0	20.0	40.0	20.0	43.06	51.14
	10.0	20.0	40.0	30.0	43.06	53.76
	10.0	20.0	40.0	40.0	43.06	55.31
	10.0	30.0	10.0	10.0	34.96	40.45
	10.0	30.0	10.0	20.0	34.96	44.75

180	10.0	30.0	10.0	30.0	34.96	48.03
	10.0	30.0	10.0	40.0	34.96	50.50
	10.0	30.0	20.0	10.0	39.74	44.69
	10.0	30.0	20.0	20.0	39.74	48.58
	10.0	30.0	20.0	30.0	39.74	51.59
	10.0	30.0	20.0	40.0	39.74	53.35
	10.0	30.0	30.0	10.0	43.43	47.39
	10.0	30.0	30.0	20.0	43.43	51.41
	10.0	30.0	30.0	30.0	43.43	54.13
	10.0	30.0	30.0	40.0	43.43	56.17
	10.0	30.0	40.0	10.0	46.21	50.24
	10.0	30.0	40.0	20.0	46.21	53.42
	10.0	30.0	40.0	30.0	46.21	55.87
	10.0	30.0	40.0	40.0	46.21	57.72
	10.0	40.0	10.0	10.0	38.15	43.10
	10.0	40.0	10.0	20.0	38.15	46.99
	10.0	40.0	10.0	30.0	38.15	50.00
	10.0	40.0	10.0	40.0	38.15	52.27
	10.0	40.0	20.0	10.0	42.47	46.93
	10.0	40.0	20.0	20.0	42.47	50.45
	10.0	40.0	20.0	30.0	42.47	53.16
	10.0	40.0	20.0	40.0	42.47	55.21
	10.0	40.0	30.0	10.0	45.80	49.83
	10.0	40.0	30.0	20.0	45.80	53.00
	10.0	40.0	30.0	30.0	45.80	55.45
	10.0	40.0	30.0	40.0	45.80	57.31
	10.0	40.0	40.0	10.0	48.31	51.35
	10.0	40.0	40.0	20.0	48.31	54.82
	10.0	40.0	40.0	30.0	48.31	57.03
	10.0	40.0	40.0	40.0	48.31	58.70
	20.0	10.0	10.0	10.0	30.49	35.56
	20.0	10.0	10.0	20.0	30.49	41.34
	20.0	10.0	10.0	30.0	30.49	45.03
	20.0	10.0	10.0	40.0	30.49	47.81
	20.0	10.0	20.0	10.0	35.78	41.26
	20.0	10.0	20.0	20.0	35.78	45.58
	20.0	10.0	20.0	30.0	35.78	48.91
	20.0	10.0	20.0	40.0	35.78	51.42
	20.0	10.0	30.0	10.0	39.87	44.82
	20.0	10.0	30.0	20.0	39.87	48.71
	20.0	10.0	30.0	30.0	39.87	51.72
	20.0	10.0	30.0	40.0	39.87	53.99
	20.0	10.0	40.0	10.0	42.96	47.42
	20.0	10.0	40.0	20.0	42.96	50.94
	20.0	10.0	40.0	30.0	42.96	53.55
	20.0	10.0	40.0	40.0	42.96	55.70
	20.0	20.0	10.0	10.0	35.70	41.19
	20.0	20.0	10.0	20.0	35.70	45.49
	20.0	20.0	10.0	30.0	35.70	48.33
	20.0	20.0	10.0	40.0	35.70	51.34
	20.0	20.0	20.0	10.0	40.48	45.42
	20.0	20.0	20.0	20.0	40.48	49.32
	20.0	20.0	20.0	30.0	40.48	52.33
	20.0	20.0	20.0	40.0	40.48	54.50
	20.0	20.0	30.0	10.0	44.17	49.64
	20.0	20.0	30.0	20.0	44.17	52.15
	20.0	20.0	30.0	30.0	44.17	54.37
	20.0	20.0	30.0	40.0	44.17	56.32
	20.0	20.0	40.0	10.0	46.95	50.38
	20.0	20.0	40.0	20.0	46.95	54.15
	20.0	20.0	40.0	30.0	46.95	56.61
	20.0	20.0	40.0	40.0	46.95	58.46
	20.0	30.0	10.0	10.0	39.64	44.59
	20.0	30.0	10.0	20.0	39.64	48.48

180	20.0	30.0	10.0	30.0	39.64	51.49
	20.0	30.0	10.0	40.0	39.64	53.76
	20.0	30.0	20.0	10.0	43.95	48.42
	20.0	30.0	20.0	20.0	43.95	51.93
	20.0	30.0	20.0	30.0	43.95	54.65
	20.0	30.0	20.0	40.0	43.95	56.70
	20.0	30.0	30.0	10.0	47.29	51.32
	20.0	30.0	30.0	20.0	47.29	54.49
	20.0	30.0	30.0	30.0	47.29	56.94
	20.0	30.0	30.0	40.0	47.29	58.79
	20.0	30.0	40.0	10.0	49.80	53.44
	20.0	30.0	40.0	20.0	49.80	56.30
	20.0	30.0	40.0	30.0	49.80	58.52
	20.0	30.0	40.0	40.0	49.80	60.19
	20.0	40.0	10.0	10.0	42.52	46.99
	20.0	40.0	10.0	20.0	42.52	50.50
	20.0	40.0	10.0	30.0	42.52	53.22
	20.0	40.0	10.0	40.0	42.52	55.27
	20.0	40.0	20.0	10.0	46.42	50.45
	20.0	40.0	20.0	20.0	46.42	53.62
	20.0	40.0	20.0	30.0	46.42	56.07
	20.0	40.0	20.0	40.0	46.42	57.92
	20.0	40.0	30.0	10.0	49.43	53.07
	20.0	40.0	30.0	20.0	49.43	55.93
	20.0	40.0	30.0	30.0	49.43	58.14
	20.0	40.0	30.0	40.0	49.43	59.81
	20.0	40.0	40.0	10.0	51.69	54.98
	20.0	40.0	40.0	20.0	51.69	57.57
	20.0	40.0	40.0	30.0	51.69	59.57
	20.0	40.0	40.0	40.0	51.69	61.07
	30.0	10.0	10.0	10.0	34.67	40.15
	30.0	10.0	10.0	20.0	34.67	44.47
	30.0	10.0	10.0	30.0	34.67	47.80
	30.0	10.0	10.0	40.0	34.67	50.31
	30.0	10.0	20.0	10.0	39.45	44.40
	30.0	10.0	20.0	20.0	39.45	48.29
	30.0	10.0	20.0	30.0	39.45	51.30
	30.0	10.0	20.0	40.0	39.45	53.57
	30.0	10.0	30.0	10.0	43.14	47.61
	30.0	10.0	30.0	20.0	43.14	51.12
	30.0	10.0	30.0	30.0	43.14	53.84
	30.0	10.0	30.0	40.0	43.14	55.89
	30.0	10.0	40.0	10.0	45.93	49.36
	30.0	10.0	40.0	20.0	45.93	53.13
	30.0	10.0	40.0	30.0	45.93	55.58
	30.0	10.0	40.0	40.0	45.93	57.43
	30.0	20.0	10.0	10.0	39.37	44.32
	30.0	20.0	10.0	20.0	39.37	48.21
	30.0	20.0	10.0	30.0	39.37	51.22
	30.0	20.0	10.0	40.0	39.37	53.49
	30.0	20.0	20.0	10.0	43.69	48.15
	30.0	20.0	20.0	20.0	43.69	51.67
	30.0	20.0	20.0	30.0	43.69	54.38
	30.0	20.0	20.0	40.0	43.69	56.43
	30.0	20.0	30.0	10.0	47.02	51.05
	30.0	20.0	30.0	20.0	47.02	54.23
	30.0	20.0	30.0	30.0	47.02	56.68
	30.0	20.0	30.0	40.0	47.02	58.53
	30.0	20.0	40.0	10.0	49.53	53.17
	30.0	20.0	40.0	20.0	49.53	55.04
	30.0	20.0	40.0	30.0	49.53	58.25
	30.0	20.0	40.0	40.0	49.53	59.92

180	30.0	30.0	10.0	10.0	42.93	47.40
	30.0	30.0	10.0	20.0	42.93	50.91
	30.0	30.0	10.0	30.0	42.93	53.63
	30.0	30.0	10.0	40.0	42.93	55.68
	30.0	30.0	20.0	10.0	46.82	50.86
	30.0	30.0	20.0	20.0	46.82	54.03
	30.0	30.0	20.0	30.0	46.82	56.48
	30.0	30.0	20.0	40.0	46.82	58.33
	30.0	30.0	30.0	10.0	49.83	53.47
	30.0	30.0	30.0	20.0	49.83	56.34
	30.0	30.0	30.0	30.0	49.83	58.55
	30.0	30.0	30.0	40.0	49.83	60.22
	30.0	30.0	40.0	10.0	52.10	55.39
	30.0	30.0	40.0	20.0	52.10	57.98
	30.0	30.0	40.0	30.0	52.10	59.97
	30.0	30.0	40.0	40.0	52.10	61.43
	30.0	40.0	10.0	10.0	45.53	49.57
	30.0	40.0	10.0	20.0	45.53	52.74
	30.0	40.0	10.0	30.0	45.53	55.19
	30.0	40.0	10.0	40.0	45.53	57.04
	30.0	40.0	20.0	10.0	49.05	52.69
	30.0	40.0	20.0	20.0	49.05	55.55
	30.0	40.0	20.0	30.0	49.05	57.77
	30.0	40.0	20.0	40.0	49.05	59.44
	30.0	40.0	30.0	10.0	51.77	55.05
	30.0	40.0	30.0	20.0	51.77	57.64
	30.0	40.0	30.0	30.0	51.77	59.54
	30.0	40.0	30.0	40.0	51.77	61.14
	30.0	40.0	40.0	10.0	53.81	56.78
	30.0	40.0	40.0	20.0	53.81	59.12
	30.0	40.0	40.0	30.0	53.81	60.92
	30.0	40.0	40.0	40.0	53.81	62.28
	40.0	10.0	10.0	10.0	37.62	42.57
	40.0	10.0	10.0	20.0	37.62	46.46
	40.0	10.0	10.0	30.0	37.62	49.47
	40.0	10.0	10.0	40.0	37.62	51.74
	40.0	10.0	20.0	10.0	41.93	46.40
	40.0	10.0	20.0	20.0	41.93	49.91
	40.0	10.0	20.0	30.0	41.93	52.63
	40.0	10.0	20.0	40.0	41.93	54.68
	40.0	10.0	30.0	10.0	45.27	49.30
	40.0	10.0	30.0	20.0	45.27	52.47
	40.0	10.0	30.0	30.0	45.27	54.92
	40.0	10.0	30.0	40.0	45.27	56.77
	40.0	10.0	40.0	10.0	47.78	51.42
	40.0	10.0	40.0	20.0	47.78	54.28
	40.0	10.0	40.0	30.0	47.78	56.50
	40.0	10.0	40.0	40.0	47.78	58.17
	40.0	20.0	10.0	10.0	41.86	46.33
	40.0	20.0	10.0	20.0	41.86	49.85
	40.0	20.0	10.0	30.0	41.86	52.56
	40.0	20.0	10.0	40.0	41.86	54.61
	40.0	20.0	20.0	10.0	45.76	49.79
	40.0	20.0	20.0	20.0	45.76	52.96
	40.0	20.0	20.0	30.0	45.76	55.42
	40.0	20.0	20.0	40.0	45.76	57.27
	40.0	20.0	30.0	10.0	48.77	52.41
	40.0	20.0	30.0	20.0	48.77	55.27
	40.0	20.0	30.0	30.0	48.77	57.49
	40.0	20.0	30.0	40.0	48.77	59.16
	40.0	20.0	40.0	10.0	51.04	54.32
	40.0	20.0	40.0	20.0	51.04	56.91

180	40.0	20.0	40.0	30.0	51.04	56.91
	40.0	20.0	40.0	40.0	51.04	60.42
	40.0	30.0	10.0	10.0	45.08	49.11
	40.0	30.0	10.0	20.0	45.08	52.28
	40.0	30.0	10.0	30.0	45.08	54.73
	40.0	30.0	10.0	40.0	45.08	56.58
	40.0	30.0	20.0	10.0	48.59	52.23
	40.0	30.0	20.0	20.0	48.59	55.10
	40.0	30.0	20.0	30.0	48.59	57.31
	40.0	30.0	20.0	40.0	48.59	58.98
	40.0	30.0	30.0	10.0	51.31	54.59
	40.0	30.0	30.0	20.0	51.31	57.18
	40.0	30.0	30.0	30.0	51.31	59.18
	40.0	30.0	30.0	40.0	51.31	60.69
	40.0	30.0	40.0	10.0	53.36	56.32
	40.0	30.0	40.0	20.0	53.36	58.66
	40.0	30.0	40.0	30.0	53.36	60.46
	40.0	30.0	40.0	40.0	53.36	61.82
	40.0	40.0	10.0	10.0	47.43	51.07
	40.0	40.0	10.0	20.0	47.43	53.93
	40.0	40.0	10.0	30.0	47.43	56.14
	40.0	40.0	10.0	40.0	47.43	57.81
	40.0	40.0	20.0	10.0	50.60	53.89
	40.0	40.0	20.0	20.0	50.60	56.47
	40.0	40.0	20.0	30.0	50.60	58.47
	40.0	40.0	20.0	40.0	50.60	59.98
	40.0	40.0	30.0	10.0	53.05	56.02
	40.0	40.0	30.0	20.0	53.05	58.35
	40.0	40.0	30.0	30.0	53.05	60.16
	40.0	40.0	30.0	40.0	53.05	61.52
	40.0	40.0	40.0	10.0	54.90*	57.58
	40.0	40.0	40.0	20.0	54.90	59.69
	40.0	40.0	40.0	30.0	54.90	61.32
	40.0	40.0	40.0	40.0	54.90	62.55*
	50.0	10.0	10.0	10.0	39.55	44.02
	50.0	10.0	10.0	20.0	39.55	47.53
	50.0	10.0	10.0	30.0	39.55	50.25
	50.0	10.0	10.0	40.0	39.55	52.30
	50.0	10.0	20.0	10.0	43.44	47.48
	50.0	10.0	20.0	20.0	43.44	50.65
	50.0	10.0	20.0	30.0	43.44	53.10
	50.0	10.0	20.0	40.0	43.44	54.95
	50.0	10.0	30.0	10.0	46.45	50.09
	50.0	10.0	30.0	20.0	46.45	52.96
	50.0	10.0	30.0	30.0	46.45	55.17
	50.0	10.0	30.0	40.0	46.45	56.84
	50.0	10.0	40.0	10.0	48.72	52.01
	50.0	10.0	40.0	20.0	48.72	54.59
	50.0	10.0	40.0	30.0	48.72	56.59
	50.0	10.0	40.0	40.0	48.72	58.10
	50.0	20.0	10.0	10.0	43.38	47.41
	50.0	20.0	10.0	20.0	43.38	50.59
	50.0	20.0	10.0	30.0	43.38	53.04
	50.0	20.0	10.0	40.0	43.38	54.89
	50.0	20.0	20.0	10.0	46.90	50.54
	50.0	20.0	20.0	20.0	46.90	53.40
	50.0	20.0	20.0	30.0	46.90	55.62
	50.0	20.0	20.0	40.0	46.90	57.29
	50.0	20.0	30.0	10.0	49.61	52.90
	50.0	20.0	30.0	20.0	49.61	55.49
	50.0	20.0	30.0	30.0	49.61	57.49
	50.0	20.0	30.0	40.0	49.61	58.99

180	50.0	20.0	40.0	10.0	51.66	54.63
	50.0	20.0	40.0	20.0	51.66	56.96
	50.0	20.0	40.0	30.0	51.66	58.77
	50.0	20.0	40.0	40.0	51.66	60.13
	50.0	30.0	10.0	10.0	46.28	49.92
	50.0	30.0	10.0	20.0	46.28	52.79
	50.0	30.0	10.0	30.0	46.28	55.00
	50.0	30.0	10.0	40.0	46.28	56.67
	50.0	30.0	20.0	10.0	49.45	52.74
	50.0	30.0	20.0	20.0	49.45	55.33
	50.0	30.0	20.0	30.0	49.45	57.33
	50.0	30.0	20.0	40.0	49.45	58.83
	50.0	30.0	30.0	10.0	51.91	54.87
	50.0	30.0	30.0	20.0	51.91	57.21
	50.0	30.0	30.0	30.0	51.91	59.01
	50.0	30.0	30.0	40.0	51.91	60.37
	50.0	30.0	40.0	10.0	53.76	56.43
	50.0	30.0	40.0	20.0	53.76	58.54
	50.0	30.0	40.0	30.0	53.76	60.17
	50.0	30.0	40.0	40.0	53.76	61.40
	50.0	40.0	10.0	10.0	48.40	51.69
	50.0	40.0	10.0	20.0	48.40	54.28
	50.0	40.0	10.0	30.0	48.40	56.27
	50.0	40.0	10.0	40.0	48.40	57.78
	50.0	40.0	20.0	10.0	51.27	54.23
	50.0	40.0	20.0	20.0	51.27	56.57
	50.0	40.0	20.0	30.0	51.27	58.37
	50.0	40.0	20.0	40.0	51.27	59.74
	50.0	40.0	30.0	10.0	53.48	56.16
	50.0	40.0	30.0	20.0	53.48	58.27
	50.0	40.0	30.0	30.0	53.48	59.90
	50.0	40.0	30.0	40.0	53.48	61.13
	50.0	40.0	40.0	10.0	55.15	57.57
	50.0	40.0	40.0	20.0	55.15	59.47
	50.0	40.0	40.0	30.0	55.15	60.94
	50.0	40.0	40.0	40.0	55.15	62.05
	60.0	10.0	10.0	10.0	40.65	44.58
	60.0	10.0	10.0	20.0	40.65	47.85
	60.0	10.0	10.0	30.0	40.65	50.30
	60.0	10.0	10.0	40.0	40.65	52.15
	60.0	10.0	20.0	10.0	44.16	47.80
	60.0	10.0	20.0	20.0	44.16	50.67
	60.0	10.0	20.0	30.0	44.16	52.88
	60.0	10.0	20.0	40.0	44.16	54.55
	60.0	10.0	30.0	10.0	46.88	50.16
	60.0	10.0	30.0	20.0	46.88	52.75
	60.0	10.0	30.0	30.0	46.88	54.75
	60.0	10.0	30.0	40.0	46.88	56.26
	60.0	10.0	40.0	10.0	48.93	51.89
	60.0	10.0	40.0	20.0	48.93	54.23
	60.0	10.0	40.0	30.0	48.93	56.03
	60.0	10.0	40.0	40.0	48.93	57.39
	60.0	20.0	10.0	10.0	44.11	47.75
	60.0	20.0	10.0	20.0	44.11	50.61
	60.0	20.0	10.0	30.0	44.11	52.82
	60.0	20.0	10.0	40.0	44.11	54.49
	60.0	20.0	20.0	10.0	47.28	50.57
	60.0	20.0	20.0	20.0	47.28	53.15
	60.0	20.0	20.0	30.0	47.28	55.15
	60.0	20.0	20.0	40.0	47.28	56.66
	60.0	20.0	30.0	10.0	49.73	52.70
	60.0	20.0	30.0	20.0	49.73	55.03

190	10.0	10.0	10.0	10.0	49.55	58.74
	10.0	10.0	10.0	20.0	49.55	63.53
	10.0	10.0	10.0	30.0	49.55	65.49
	10.0	10.0	10.0	40.0	49.55	65.71
	10.0	10.0	20.0	10.0	55.88	62.83
	10.0	10.0	20.0	20.0	55.88	66.45
	10.0	10.0	20.0	30.0	55.88	67.93
	10.0	10.0	20.0	40.0	55.88	68.10
	10.0	10.0	30.0	10.0	58.43	63.73
	10.0	10.0	30.0	20.0	58.48	66.47
	10.0	10.0	30.0	30.0	58.43	67.59
	10.0	10.0	30.0	40.0	58.48	67.71
	10.0	10.0	40.0	10.0	58.77	62.74
	10.0	10.0	40.0	20.0	58.77	64.81
	10.0	10.0	40.0	30.0	58.77	65.65
	10.0	10.0	40.0	40.0	58.77	65.75
	10.0	20.0	10.0	10.0	54.96	61.91
	10.0	20.0	10.0	20.0	54.96	65.52
	10.0	20.0	10.0	30.0	54.96	67.01
	10.0	20.0	10.0	40.0	54.96	67.17
	10.0	20.0	20.0	10.0	59.75	64.99
	10.0	20.0	20.0	20.0	59.75	67.73
	10.0	20.0	20.0	30.0	59.75	68.85
	10.0	20.0	20.0	40.0	59.75	68.98 *
	10.0	20.0	30.0	10.0	61.71	65.68
	10.0	20.0	30.0	20.0	61.71	67.74
	10.0	20.0	30.0	30.0	61.71	68.59
	10.0	20.0	30.0	40.0	61.71	68.68
	10.0	20.0	40.0	10.0	61.93	64.93
	10.0	20.0	40.0	20.0	61.93	66.49
	10.0	20.0	40.0	30.0	61.93	67.13
	10.0	20.0	40.0	40.0	61.93	67.20
	10.0	30.0	10.0	10.0	56.15	61.40
	10.0	30.0	10.0	20.0	56.15	64.14
	10.0	30.0	10.0	30.0	56.15	65.26
	10.0	30.0	10.0	40.0	56.15	65.38
	10.0	30.0	20.0	10.0	59.77	63.74
	10.0	30.0	20.0	20.0	59.77	65.80
	10.0	30.0	20.0	30.0	59.77	66.65
	10.0	30.0	20.0	40.0	59.77	66.75
	10.0	30.0	30.0	10.0	61.25	64.25
	10.0	30.0	30.0	20.0	61.25	65.31
	10.0	30.0	30.0	30.0	61.25	66.45
	10.0	30.0	30.0	40.0	61.25	66.53
	10.0	30.0	40.0	10.0	61.42	63.69
	10.0	30.0	40.0	20.0	61.42	64.87
	10.0	30.0	40.0	30.0	61.42	65.35
	10.0	30.0	40.0	40.0	61.42	65.40
	10.0	40.0	10.0	10.0	54.84	58.81
	10.0	40.0	10.0	20.0	54.84	60.87
	10.0	40.0	10.0	30.0	54.34	61.72
	10.0	40.0	10.0	40.0	54.84	61.82
	10.0	40.0	20.0	10.0	57.58	60.57
	10.0	40.0	20.0	20.0	57.58	62.13
	10.0	40.0	20.0	30.0	57.58	62.77
	10.0	40.0	20.0	40.0	57.58	62.85
	10.0	40.0	30.0	10.0	58.70	60.96
	10.0	40.0	30.0	20.0	58.70	62.14

190	10.0	40.0	30.0	30.0	58.70	62.63
	10.0	40.0	30.0	40.0	58.70	62.68
	10.0	40.0	40.0	10.0	58.82	60.53
	10.0	40.0	40.0	20.0	58.82	61.43
	10.0	40.0	40.0	30.0	58.82	61.79
	10.0	40.0	40.0	40.0	58.82	61.33
	20.0	10.0	10.0	10.0	53.74	60.68
	20.0	10.0	10.0	20.0	53.74	64.30
	20.0	10.0	10.0	30.0	53.74	65.78
	20.0	10.0	10.0	40.0	53.74	65.95
	20.0	10.0	20.0	10.0	58.52	63.77
	20.0	10.0	20.0	20.0	53.52	66.51
	20.0	10.0	20.0	30.0	58.52	67.63
	20.0	10.0	20.0	40.0	58.52	67.75
	20.0	10.0	30.0	10.0	60.49	64.45
	20.0	10.0	30.0	20.0	60.49	66.52
	20.0	10.0	30.0	30.0	60.49	67.37
	20.0	10.0	30.0	40.0	60.49	67.46
	20.0	10.0	40.0	10.0	60.71	63.70
	20.0	10.0	40.0	20.0	60.71	65.27
	20.0	10.0	40.0	30.0	60.71	65.91
	20.0	10.0	40.0	40.0	60.71	65.98
	20.0	20.0	10.0	10.0	57.82	63.07
	20.0	20.0	10.0	20.0	57.82	65.81
	20.0	20.0	10.0	30.0	57.82	66.93
	20.0	20.0	10.0	40.0	57.82	67.05
	20.0	20.0	20.0	10.0	61.44	65.41
	20.0	20.0	20.0	20.0	51.44	67.47
	20.0	20.0	20.0	30.0	61.44	68.32
	20.0	20.0	20.0	40.0	61.44	68.42
	20.0	20.0	30.0	10.0	62.93	65.92
	20.0	20.0	30.0	20.0	62.93	67.48
	20.0	20.0	30.0	30.0	62.93	68.12
	20.0	20.0	30.0	40.0	62.93	68.20
	20.0	20.0	40.0	10.0	63.09*	65.36
	20.0	20.0	40.0	20.0	63.09	66.54
	20.0	20.0	40.0	30.0	63.09	67.02
	20.0	20.0	40.0	40.0	63.09	67.08
	20.0	30.0	10.0	10.0	58.73	62.69
	20.0	30.0	10.0	20.0	58.73	64.76
	20.0	30.0	10.0	30.0	58.73	65.61
	20.0	30.0	10.0	40.0	58.73	65.70
	20.0	30.0	20.0	10.0	61.46	64.46
	20.0	30.0	20.0	20.0	61.46	66.02
	20.0	30.0	20.0	30.0	61.46	66.66
	20.0	30.0	20.0	40.0	61.46	66.73
	20.0	30.0	30.0	10.0	62.58	64.85
	20.0	30.0	30.0	20.0	62.58	66.03
	20.0	30.0	30.0	30.0	62.58	66.51
	20.0	30.0	30.0	40.0	62.58	66.56
	20.0	30.0	40.0	10.0	62.71	64.42
	20.0	30.0	40.0	20.0	62.71	65.31
	20.0	30.0	40.0	30.0	62.71	65.68
	20.0	30.0	40.0	40.0	62.71	65.72
	20.0	40.0	10.0	10.0	57.74	60.73
	20.0	40.0	10.0	20.0	57.74	62.29
	20.0	40.0	10.0	30.0	57.74	62.93
	20.0	40.0	10.0	40.0	57.74	63.01
	20.0	40.0	20.0	10.0	59.80	62.07
	20.0	40.0	20.0	20.0	59.80	63.25
	20.0	40.0	20.0	30.0	59.80	63.73
	20.0	40.0	20.0	40.0	59.80	63.78
	20.0	40.0	30.0	10.0	60.65	62.36
	20.0	40.0	30.0	20.0	60.65	63.25

190	20.0	40.0	30.0	30.0	60.65	63.62
	20.0	40.0	30.0	40.0	60.65	63.66
	20.0	40.0	40.0	10.0	60.74	62.04
	20.0	40.0	40.0	20.0	60.74	62.71
	20.0	40.0	40.0	30.0	60.74	62.99
	20.0	40.0	40.0	40.0	60.74	63.02
	30.0	10.0	10.0	10.0	53.07	58.32
	30.0	10.0	10.0	20.0	53.07	61.05
	30.0	10.0	10.0	30.0	53.07	62.18
	30.0	10.0	10.0	40.0	53.07	62.30
	30.0	10.0	20.0	10.0	56.69	60.66
	30.0	10.0	20.0	20.0	56.69	62.72
	30.0	10.0	20.0	30.0	56.69	63.57
	30.0	10.0	20.0	40.0	56.69	63.66
	30.0	10.0	30.0	10.0	58.17	61.17
	30.0	10.0	30.0	20.0	58.17	62.73
	30.0	10.0	30.0	30.0	58.17	63.37
	30.0	10.0	30.0	40.0	58.17	63.44
	30.0	10.0	40.0	10.0	58.34	60.60
	30.0	10.0	40.0	20.0	58.34	61.78
	30.0	10.0	40.0	30.0	58.34	62.27
	30.0	10.0	40.0	40.0	58.34	62.32
	30.0	20.0	10.0	10.0	56.16	60.13
	30.0	20.0	10.0	20.0	56.16	62.19
	30.0	20.0	10.0	30.0	56.16	63.04
	30.0	20.0	10.0	40.0	56.16	63.14
	30.0	20.0	20.0	10.0	58.89	61.89
	30.0	20.0	20.0	20.0	58.89	63.45
	30.0	20.0	20.0	30.0	58.89	64.09
	30.0	20.0	20.0	40.0	58.89	64.16
	30.0	20.0	30.0	10.0	60.02	62.28
	30.0	20.0	30.0	20.0	60.02	63.46
	30.0	20.0	30.0	30.0	60.02	63.94
	30.0	20.0	30.0	40.0	60.02	64.00
	30.0	20.0	40.0	10.0	60.14	61.85
	30.0	20.0	40.0	20.0	60.14	62.74
	30.0	20.0	40.0	30.0	60.14	63.11
	30.0	20.0	40.0	40.0	60.14	63.15
	30.0	30.0	10.0	10.0	56.84	59.84
	30.0	30.0	10.0	20.0	56.84	61.40
	30.0	30.0	10.0	30.0	56.84	62.04
	30.0	30.0	10.0	40.0	56.84	62.11
	30.0	30.0	20.0	10.0	58.91	61.17
	30.0	30.0	20.0	20.0	58.91	62.35
	30.0	30.0	20.0	30.0	58.91	62.84
	30.0	30.0	20.0	40.0	58.91	62.89
	30.0	30.0	30.0	10.0	59.76	61.47
	30.0	30.0	30.0	20.0	59.76	62.36
	30.0	30.0	30.0	30.0	59.76	62.72
	30.0	30.0	30.0	40.0	59.76	62.77
	30.0	30.0	40.0	10.0	59.85	61.14
	30.0	30.0	40.0	20.0	59.85	61.82
	30.0	30.0	40.0	30.0	59.85	62.09
	30.0	30.0	40.0	40.0	59.85	62.13
	30.0	40.0	10.0	10.0	56.09	58.36
	30.0	40.0	10.0	20.0	56.09	59.54
	30.0	40.0	10.0	30.0	56.09	60.02
	30.0	40.0	10.0	40.0	56.09	60.08
	30.0	40.0	20.0	10.0	57.65	59.37
	30.0	40.0	20.0	20.0	57.65	60.26
	30.0	40.0	20.0	30.0	57.65	60.62
	30.0	40.0	20.0	40.0	57.65	60.66
	30.0	40.0	30.0	10.0	58.29	59.59
	30.0	40.0	30.0	20.0	58.29	60.26

190	30.0	40.0	30.0	30.0	58.29	60.54
	30.0	40.0	30.0	40.0	58.29	60.57
	30.0	40.0	40.0	10.0	58.37	59.34
	30.0	40.0	40.0	20.0	58.37	59.85
	30.0	40.0	40.0	30.0	58.37	60.06
	30.0	40.0	40.0	40.0	58.37	60.09
	40.0	10.0	10.0	10.0	49.64	53.61
	40.0	10.0	10.0	20.0	49.64	55.67
	40.0	10.0	10.0	30.0	49.64	56.52
	40.0	10.0	10.0	40.0	49.64	56.61
	40.0	10.0	20.0	10.0	52.37	55.37
	40.0	10.0	20.0	20.0	52.37	56.93
	40.0	10.0	20.0	30.0	52.37	57.57
	40.0	10.0	20.0	40.0	52.37	57.64
	40.0	10.0	30.0	10.0	53.49	55.76
	40.0	10.0	30.0	20.0	53.49	56.34
	40.0	10.0	30.0	30.0	53.49	57.42
	40.0	10.0	30.0	40.0	53.49	57.48
	40.0	10.0	40.0	10.0	53.62	55.33
	40.0	10.0	40.0	20.0	53.62	56.22
	40.0	10.0	40.0	30.0	53.62	56.59
	40.0	10.0	40.0	40.0	53.62	56.63
	40.0	20.0	10.0	10.0	51.97	54.97
	40.0	20.0	10.0	20.0	51.97	56.53
	40.0	20.0	10.0	30.0	51.97	57.17
	40.0	20.0	10.0	40.0	51.97	57.24
	40.0	20.0	20.0	10.0	54.04	56.30
	40.0	20.0	20.0	20.0	54.04	57.48
	40.0	20.0	20.0	30.0	54.04	57.97
	40.0	20.0	20.0	40.0	54.04	58.02
	40.0	20.0	30.0	10.0	54.89	56.60
	40.0	20.0	30.0	20.0	54.89	57.49
	40.0	20.0	30.0	30.0	54.89	57.86
	40.0	20.0	30.0	40.0	54.89	57.30
	40.0	20.0	40.0	10.0	54.98	56.28
	40.0	20.0	40.0	20.0	54.98	56.95
	40.0	20.0	40.0	30.0	54.98	57.23
	40.0	20.0	40.0	40.0	54.98	57.26
	40.0	30.0	10.0	10.0	52.49	54.75
	40.0	30.0	10.0	20.0	52.49	55.03
	40.0	30.0	10.0	30.0	52.49	56.42
	40.0	30.0	10.0	40.0	52.49	56.47
	40.0	30.0	20.0	10.0	54.05	55.76
	40.0	30.0	20.0	20.0	54.05	56.65
	40.0	30.0	20.0	30.0	54.05	57.02
	40.0	30.0	20.0	40.0	54.05	57.06
	40.0	30.0	30.0	10.0	54.69	55.98
	40.0	30.0	30.0	20.0	54.69	56.66
	40.0	30.0	30.0	30.0	54.69	56.93
	40.0	30.0	30.0	40.0	54.69	56.97
	40.0	30.0	40.0	10.0	54.76	55.74
	40.0	30.0	40.0	20.0	54.76	56.25
	40.0	30.0	40.0	30.0	54.76	55.46
	40.0	30.0	40.0	40.0	54.76	56.48
	40.0	40.0	10.0	10.0	51.92	53.63
	40.0	40.0	10.0	20.0	51.92	54.53
	40.0	40.0	10.0	30.0	51.92	54.89
	40.0	40.0	10.0	40.0	51.92	54.93
	40.0	40.0	20.0	10.0	53.10	54.40
	40.0	40.0	20.0	20.0	53.10	55.07
	40.0	40.0	20.0	30.0	53.10	55.35
	40.0	40.0	20.0	40.0	53.10	55.38
	40.0	40.0	30.0	10.0	53.59	54.55
	40.0	40.0	30.0	20.0	53.59	55.07

200	5.0	5.0	5.0	5.0	57.70	66.52
	5.0	5.0	5.0	10.0	57.70	70.46
	5.0	5.0	5.0	15.0	57.70	71.55
	5.0	5.0	5.0	20.0	57.70	71.07
	5.0	5.0	10.0	5.0	63.39	69.49
	5.0	5.0	10.0	10.0	63.39	72.22
	5.0	5.0	10.0	15.0	63.39	72.97 **
	5.0	5.0	10.0	20.0	63.39	72.64
	5.0	5.0	15.0	5.0	64.96	69.19
	5.0	5.0	15.0	10.0	64.96	71.07
	5.0	5.0	15.0	15.0	64.96	71.60
	5.0	5.0	15.0	20.0	64.96	71.37
	5.0	5.0	20.0	5.0	64.27	67.20
	5.0	5.0	20.0	10.0	64.27	68.50
	5.0	5.0	20.0	15.0	64.27	68.36
	5.0	5.0	20.0	20.0	64.27	68.70
	5.0	10.0	5.0	5.0	62.00	68.10
	5.0	10.0	5.0	10.0	62.00	70.33
	5.0	10.0	5.0	15.0	62.00	71.58
	5.0	10.0	5.0	20.0	62.00	71.25
	5.0	10.0	10.0	5.0	65.93	70.15
	5.0	10.0	10.0	10.0	65.93	72.05
	5.0	10.0	10.0	15.0	65.93	72.57
	5.0	10.0	10.0	20.0	65.93	72.34
	5.0	10.0	15.0	5.0	67.02**	69.95
	5.0	10.0	15.0	10.0	67.02	71.25
	5.0	10.0	15.0	15.0	67.02	71.61
	5.0	10.0	15.0	20.0	67.02	71.46
	5.0	10.0	20.0	5.0	66.54	68.57
	5.0	10.0	20.0	10.0	66.54	69.47
	5.0	10.0	20.0	15.0	56.54	69.72
	5.0	10.0	20.0	20.0	66.54	69.61
	5.0	15.0	5.0	5.0	61.55	65.78
	5.0	15.0	5.0	10.0	61.55	67.67
	5.0	15.0	5.0	15.0	61.55	68.19
	5.0	15.0	5.0	20.0	61.55	67.90
	5.0	15.0	10.0	5.0	64.28	67.21
	5.0	15.0	10.0	10.0	64.28	68.51
	5.0	15.0	10.0	15.0	64.28	68.87
	5.0	15.0	10.0	20.0	54.28	68.71
	5.0	15.0	15.0	5.0	65.03	67.06
	5.0	15.0	15.0	10.0	65.03	67.96
	5.0	15.0	15.0	15.0	65.03	68.21
	5.0	15.0	15.0	20.0	55.03	68.10
	5.0	15.0	20.0	5.0	64.70	66.10
	5.0	15.0	20.0	10.0	54.70	66.73
	5.0	15.0	20.0	15.0	64.70	66.90
	5.0	15.0	20.0	20.0	64.70	66.33
	5.0	20.0	5.0	5.0	58.68	61.60
	5.0	20.0	5.0	10.0	58.68	62.91
	5.0	20.0	5.0	15.0	58.63	63.27
	5.0	20.0	5.0	20.0	53.68	63.11
	5.0	20.0	10.0	5.0	60.56	62.59
	5.0	20.0	10.0	10.0	60.56	63.49
	5.0	20.0	10.0	15.0	60.56	63.74
	5.0	20.0	10.0	20.0	60.56	63.63
	5.0	20.0	15.0	5.0	61.08	62.49
	5.0	20.0	15.0	10.0	61.08	63.11

200	5.0	20.0	15.0	15.0	61.08	63.29
	5.0	20.0	15.0	20.0	61.08	63.21
	5.0	20.0	20.0	5.0	60.85	61.83
	5.0	20.0	20.0	10.0	60.85	62.26
	5.0	20.0	20.0	15.0	60.85	62.38
	5.0	20.0	20.0	20.0	60.85	62.33
	10.0	5.0	5.0	5.0	59.98	66.09
	10.0	5.0	5.0	10.0	59.98	68.81
	10.0	5.0	5.0	15.0	59.98	69.57
	10.0	5.0	5.0	20.0	59.98	69.24
	10.0	5.0	10.0	5.0	63.92	66.15
	10.0	5.0	10.0	10.0	63.92	70.03
	10.0	5.0	10.0	15.0	63.92	70.56
	10.0	5.0	10.0	20.0	63.92	70.33
	10.0	5.0	15.0	5.0	65.01	67.94
	10.0	5.0	15.0	10.0	65.01	69.24
	10.0	5.0	15.0	15.0	65.01	69.50
	10.0	5.0	15.0	20.0	65.01	69.44
	10.0	5.0	20.0	5.0	64.53	66.56
	10.0	5.0	20.0	10.0	64.53	67.46
	10.0	5.0	20.0	15.0	64.53	67.71
	10.0	5.0	20.0	20.0	64.53	67.60
	10.0	10.0	5.0	5.0	62.96	67.18
	10.0	10.0	5.0	10.0	62.96	69.07
	10.0	10.0	5.0	15.0	62.96	69.59
	10.0	10.0	5.0	20.0	62.96	69.36
	10.0	10.0	10.0	5.0	65.68	68.61
	10.0	10.0	10.0	10.0	65.68	69.91
	10.0	10.0	10.0	15.0	65.68	70.27
	10.0	10.0	10.0	20.0	65.68	70.12
	10.0	10.0	15.0	5.0	66.43	68.46
	10.0	10.0	15.0	10.0	66.43	69.36
	10.0	10.0	15.0	15.0	66.43	69.62
	10.0	10.0	15.0	20.0	66.43	69.50
	10.0	10.0	20.0	5.0	66.10	67.51
	10.0	10.0	20.0	10.0	66.10	68.13
	10.0	10.0	20.0	15.0	66.10	68.30
	10.0	10.0	20.0	20.0	66.10	68.23
	10.0	15.0	5.0	5.0	62.65	65.58
	10.0	15.0	5.0	10.0	62.65	66.86
	10.0	15.0	5.0	15.0	62.65	67.24
	10.0	15.0	5.0	20.0	62.65	67.08
	10.0	15.0	10.0	5.0	64.54	66.56
	10.0	15.0	10.0	10.0	64.54	67.47
	10.0	15.0	10.0	15.0	64.54	67.72
	10.0	15.0	10.0	20.0	64.54	67.61
	10.0	15.0	15.0	5.0	65.06	66.46
	10.0	15.0	15.0	10.0	65.06	67.09
	10.0	15.0	15.0	15.0	65.06	67.26
	10.0	15.0	15.0	20.0	65.06	67.18
	10.0	15.0	20.0	5.0	64.83	65.90
	10.0	15.0	20.0	10.0	64.83	66.23
	10.0	15.0	20.0	15.0	64.83	65.35
	10.0	15.0	20.0	20.0	64.83	66.30
	10.0	20.0	5.0	5.0	60.66	62.68
	10.0	20.0	5.0	10.0	60.66	63.59
	10.0	20.0	5.0	15.0	60.66	63.84
	10.0	20.0	5.0	20.0	60.66	63.73
	10.0	20.0	10.0	5.0	61.95	63.37
	10.0	20.0	10.0	10.0	61.96	63.99
	10.0	20.0	10.0	15.0	61.96	64.17
	10.0	20.0	10.0	20.0	61.96	64.09
	10.0	20.0	15.0	5.0	62.32	63.30
	10.0	20.0	15.0	10.0	62.32	63.73

200	10.0	20.0	15.0	15.0	62.32	63.85
	10.0	20.0	15.0	20.0	62.32	63.80
	10.0	20.0	20.0	5.0	62.17	62.84
	10.0	20.0	20.0	10.0	62.17	63.14
	10.0	20.0	20.0	15.0	62.17	63.22
	10.0	20.0	20.0	20.0	62.17	63.18
	15.0	5.0	5.0	5.0	56.63	60.86
	15.0	5.0	5.0	10.0	56.63	62.75
	15.0	5.0	5.0	15.0	56.63	63.27
	15.0	5.0	5.0	20.0	56.63	63.04
	15.0	5.0	10.0	5.0	59.36	62.29
	15.0	5.0	10.0	10.0	59.36	63.59
	15.0	5.0	10.0	15.0	59.36	63.95
	15.0	5.0	10.0	20.0	59.36	63.79
	15.0	5.0	15.0	5.0	60.11	62.14
	15.0	5.0	15.0	10.0	60.11	63.04
	15.0	5.0	15.0	15.0	60.11	63.29
	15.0	5.0	15.0	20.0	60.11	63.18
	15.0	5.0	20.0	5.0	59.78	61.18
	15.0	5.0	20.0	10.0	59.78	61.81
	15.0	5.0	20.0	15.0	59.78	61.98
	15.0	5.0	20.0	20.0	59.78	61.91
	15.0	10.0	5.0	5.0	58.69	61.62
	15.0	10.0	5.0	10.0	58.69	62.92
	15.0	10.0	5.0	15.0	58.69	63.28
	15.0	10.0	5.0	20.0	58.69	63.13
	15.0	10.0	10.0	5.0	60.58	62.60
	15.0	10.0	10.0	10.0	60.58	63.51
	15.0	10.0	10.0	15.0	60.58	63.76
	15.0	10.0	10.0	20.0	60.58	63.65
	15.0	10.0	15.0	5.0	61.10	62.50
	15.0	10.0	15.0	10.0	61.10	63.13
	15.0	10.0	15.0	15.0	61.10	63.30
	15.0	10.0	15.0	20.0	61.10	63.23
	15.0	10.0	20.0	5.0	60.87	61.34
	15.0	10.0	20.0	10.0	60.87	62.27
	15.0	10.0	20.0	15.0	60.87	62.39
	15.0	10.0	20.0	20.0	60.87	62.34
	15.0	15.0	5.0	5.0	58.48	60.51
	15.0	15.0	5.0	10.0	58.48	61.41
	15.0	15.0	5.0	15.0	58.48	61.56
	15.0	15.0	5.0	20.0	58.48	61.55
	15.0	15.0	10.0	5.0	59.79	61.19
	15.0	15.0	10.0	10.0	59.79	61.81
	15.0	15.0	10.0	15.0	59.79	61.99
	15.0	15.0	10.0	20.0	59.79	61.91
	15.0	15.0	15.0	5.0	60.15	61.12
	15.0	15.0	15.0	10.0	60.15	61.55
	15.0	15.0	15.0	15.0	60.15	61.67
	15.0	15.0	15.0	20.0	60.15	61.62
	15.0	15.0	20.0	5.0	59.99	60.66
	15.0	15.0	20.0	10.0	59.99	60.96
	15.0	15.0	20.0	15.0	59.99	61.04
	15.0	15.0	20.0	20.0	59.99	61.01
	15.0	20.0	5.0	5.0	57.10	58.50
	15.0	20.0	5.0	10.0	57.10	59.13
	15.0	20.0	5.0	15.0	57.10	59.30
	15.0	20.0	5.0	20.0	57.10	59.23
	15.0	20.0	10.0	5.0	58.00	58.97
	15.0	20.0	10.0	10.0	58.00	59.41
	15.0	20.0	10.0	15.0	58.00	59.53
	15.0	20.0	10.0	20.0	58.00	59.48
	15.0	20.0	15.0	5.0	58.25	58.93
	15.0	20.0	15.0	10.0	58.25	59.23

200	15.0	20.0	15.0	15.0	58.25	59.31
	15.0	20.0	15.0	20.0	58.25	59.27
	15.0	20.0	20.0	5.0	58.14	58.61
	15.0	20.0	20.0	10.0	58.14	58.32
	15.0	20.0	20.0	15.0	58.14	58.37
	15.0	20.0	20.0	20.0	58.14	58.85
	20.0	5.0	5.0	5.0	50.60	53.52
	20.0	5.0	5.0	10.0	50.60	54.33
	20.0	5.0	5.0	15.0	50.60	55.19
	20.0	5.0	5.0	20.0	50.60	55.03
	20.0	5.0	10.0	5.0	52.48	54.51
	20.0	5.0	10.0	10.0	52.48	55.41
	20.0	5.0	10.0	15.0	52.48	55.66
	20.0	5.0	10.0	20.0	52.48	55.55
	20.0	5.0	15.0	5.0	53.01	54.41
	20.0	5.0	15.0	10.0	53.01	55.03
	20.0	5.0	15.0	15.0	53.01	55.21
	20.0	5.0	15.0	20.0	53.01	55.13
	20.0	5.0	20.0	5.0	52.78	53.75
	20.0	5.0	20.0	10.0	52.78	54.18
	20.0	5.0	20.0	15.0	52.78	54.30
	20.0	5.0	20.0	20.0	52.78	54.25
	20.0	10.0	5.0	5.0	52.02	54.05
	20.0	10.0	5.0	10.0	52.02	54.95
	20.0	10.0	5.0	15.0	52.02	55.20
	20.0	10.0	5.0	20.0	52.02	55.09
	20.0	10.0	10.0	5.0	53.33	54.73
	20.0	10.0	10.0	10.0	53.33	55.36
	20.0	10.0	10.0	15.0	53.33	55.53
	20.0	10.0	10.0	20.0	53.33	55.45
	20.0	10.0	15.0	5.0	53.69	54.66
	20.0	10.0	15.0	10.0	53.69	55.09
	20.0	10.0	15.0	15.0	53.69	55.21
	20.0	10.0	15.0	20.0	53.69	55.16
	20.0	10.0	20.0	5.0	53.53	54.20
	20.0	10.0	20.0	10.0	53.53	54.50
	20.0	10.0	20.0	15.0	53.53	54.59
	20.0	10.0	20.0	20.0	53.53	54.55
	20.0	15.0	5.0	5.0	51.87	53.28
	20.0	15.0	5.0	10.0	51.87	53.90
	20.0	15.0	5.0	15.0	51.87	54.08
	20.0	15.0	5.0	20.0	51.87	54.00
	20.0	15.0	10.0	5.0	52.78	53.75
	20.0	15.0	10.0	10.0	52.78	54.18
	20.0	15.0	10.0	15.0	52.78	54.30
	20.0	15.0	10.0	20.0	52.78	54.25
	20.0	15.0	15.0	5.0	53.03	53.70
	20.0	15.0	15.0	10.0	53.03	54.00
	20.0	15.0	15.0	15.0	53.03	54.08
	20.0	15.0	15.0	20.0	53.03	54.05
	20.0	15.0	20.0	5.0	52.92	53.38
	20.0	15.0	20.0	10.0	52.92	53.59
	20.0	15.0	20.0	15.0	52.92	53.55
	20.0	15.0	20.0	20.0	52.92	53.62
	20.0	20.0	5.0	5.0	50.92	51.89
	20.0	20.0	5.0	10.0	50.92	52.32
	20.0	20.0	5.0	15.0	50.92	52.44
	20.0	20.0	5.0	20.0	50.92	52.39
	20.0	20.0	10.0	5.0	51.55	52.22
	20.0	20.0	10.0	10.0	51.55	52.52
	20.0	20.0	10.0	15.0	51.55	52.60
	20.0	20.0	10.0	20.0	51.55	52.56
	20.0	20.0	15.0	5.0	51.72	52.18
	20.0	20.0	15.0	10.0	51.72	52.39

210	5.0	5.0	5.0	5.0	68.18	70.39
	5.0	5.0	5.0	6.0	68.18	70.99
	5.0	5.0	5.0	7.0	68.18	71.01 *
	5.0	5.0	5.0	8.0	68.18	70.37
	5.0	5.0	6.0	5.0	68.41	70.67
	5.0	5.0	6.0	6.0	68.41	70.75
	5.0	5.0	6.0	7.0	68.41	70.77
	5.0	5.0	6.0	8.0	68.41	70.73
	5.0	5.0	7.0	5.0	68.45 **	70.34
	5.0	5.0	7.0	6.0	68.46	70.40
	5.0	5.0	7.0	7.0	68.46	70.41
	5.0	5.0	7.0	8.0	68.46	70.39
	5.0	5.0	8.0	5.0	68.36	69.92
	5.0	5.0	8.0	6.0	68.36	69.97
	5.0	5.0	8.0	7.0	68.36	69.98
	5.0	5.0	8.0	8.0	68.36	69.96
	5.0	6.0	5.0	5.0	67.61	69.87
	5.0	6.0	5.0	6.0	67.61	69.95
	5.0	6.0	5.0	7.0	67.61	69.97
	5.0	6.0	5.0	8.0	67.61	69.93
	5.0	6.0	6.0	5.0	67.81	69.69
	5.0	6.0	6.0	6.0	67.81	69.75
	5.0	6.0	6.0	7.0	67.81	69.77
	5.0	6.0	6.0	8.0	67.61	69.74
	5.0	6.0	7.0	5.0	67.85	69.41
	5.0	6.0	7.0	6.0	67.85	69.46
	5.0	6.0	7.0	7.0	67.85	69.47
	5.0	6.0	7.0	8.0	67.85	69.45
	5.0	6.0	8.0	5.0	67.77	69.06
	5.0	6.0	8.0	6.0	67.77	69.11
	5.0	6.0	8.0	7.0	67.77	69.12
	5.0	6.0	8.0	8.0	67.77	69.10
	5.0	7.0	5.0	5.0	66.76	68.64
	5.0	7.0	5.0	6.0	66.76	68.70
	5.0	7.0	5.0	7.0	66.76	68.72
	5.0	7.0	5.0	8.0	66.76	68.69
	5.0	7.0	6.0	5.0	66.93	68.48
	5.0	7.0	6.0	6.0	66.93	68.54
	5.0	7.0	6.0	7.0	66.93	68.55
	5.0	7.0	6.0	8.0	66.93	68.53
	5.0	7.0	7.0	5.0	66.96	68.25
	5.0	7.0	7.0	6.0	66.96	68.30
	5.0	7.0	7.0	7.0	66.96	68.31
	5.0	7.0	7.0	8.0	66.96	68.29
	5.0	7.0	8.0	5.0	66.89	67.96
	5.0	7.0	8.0	6.0	66.89	68.00
	5.0	7.0	8.0	7.0	66.89	68.01
	5.0	7.0	8.0	8.0	66.89	67.99
	5.0	8.0	5.0	5.0	65.71	67.27
	5.0	8.0	5.0	6.0	65.71	67.32
	5.0	8.0	5.0	7.0	65.71	67.33
	5.0	8.0	5.0	8.0	65.71	67.31
	5.0	8.0	6.0	5.0	65.85	67.14
	5.0	8.0	6.0	6.0	65.85	67.19
	5.0	8.0	6.0	7.0	65.85	67.19
	5.0	8.0	6.0	8.0	65.85	67.17
	5.0	8.0	7.0	5.0	65.87	66.95
	5.0	8.0	7.0	6.0	65.87	66.98

210	5.0	8.0	7.0	7.0	65.87	66.99
	5.0	8.0	7.0	8.0	65.87	66.98
	5.0	8.0	8.0	5.0	65.81	66.71
	5.0	8.0	8.0	6.0	65.81	66.74
	5.0	8.0	8.0	7.0	65.81	66.74
	5.0	8.0	8.0	8.0	65.81	66.73
	6.0	5.0	5.0	5.0	65.59	67.95
	6.0	5.0	5.0	6.0	65.59	67.93
	6.0	5.0	5.0	7.0	65.59	67.94
	6.0	5.0	5.0	8.0	65.59	67.91
	6.0	5.0	6.0	5.0	65.79	67.67
	6.0	5.0	6.0	6.0	65.79	67.73
	6.0	5.0	6.0	7.0	65.79	67.74
	6.0	5.0	6.0	8.0	65.79	67.72
	6.0	5.0	7.0	5.0	65.83	67.39
	6.0	5.0	7.0	6.0	65.83	67.44
	6.0	5.0	7.0	7.0	65.83	67.45
	6.0	5.0	7.0	8.0	65.83	67.43
	6.0	5.0	8.0	5.0	65.75	67.04
	6.0	5.0	8.0	6.0	65.75	67.09
	6.0	5.0	8.0	7.0	65.75	67.09
	6.0	5.0	8.0	8.0	65.75	67.08
	6.0	6.0	5.0	5.0	65.13	67.00
	6.0	6.0	5.0	6.0	65.13	67.07
	6.0	6.0	5.0	7.0	65.13	67.08
	6.0	6.0	5.0	8.0	65.13	67.05
	6.0	6.0	6.0	5.0	65.29	66.85
	6.0	6.0	6.0	6.0	65.29	66.90
	6.0	6.0	6.0	7.0	65.29	66.91
	6.0	6.0	6.0	8.0	65.29	66.89
	6.0	6.0	7.0	5.0	65.32	66.62
	6.0	6.0	7.0	6.0	65.32	66.66
	6.0	6.0	7.0	7.0	65.32	66.67
	6.0	6.0	7.0	8.0	65.32	66.65
	6.0	6.0	8.0	5.0	65.25	66.33
	6.0	6.0	8.0	6.0	65.25	66.37
	6.0	6.0	8.0	7.0	65.25	66.37
	6.0	6.0	8.0	8.0	65.25	66.36
	6.0	7.0	5.0	5.0	64.42	65.98
	6.0	7.0	5.0	6.0	64.42	66.03
	6.0	7.0	5.0	7.0	64.42	66.04
	6.0	7.0	5.0	8.0	64.42	66.02
	6.0	7.0	6.0	5.0	64.56	65.85
	6.0	7.0	6.0	6.0	64.56	65.89
	6.0	7.0	6.0	7.0	64.56	65.90
	6.0	7.0	6.0	8.0	64.56	65.88
	6.0	7.0	7.0	5.0	64.58	65.66
	6.0	7.0	7.0	6.0	64.58	65.69
	6.0	7.0	7.0	7.0	64.58	65.70
	6.0	7.0	7.0	8.0	64.58	65.59
	6.0	7.0	8.0	5.0	64.52	65.42
	6.0	7.0	8.0	6.0	64.52	65.45
	6.0	7.0	8.0	7.0	64.52	65.45
	6.0	7.0	8.0	8.0	64.52	65.44
	6.0	8.0	5.0	5.0	63.54	64.84
	6.0	8.0	5.0	6.0	63.54	64.88
	6.0	8.0	5.0	7.0	63.54	64.89
	6.0	8.0	5.0	8.0	63.54	64.87
	6.0	8.0	6.0	5.0	63.66	64.73
	6.0	8.0	6.0	6.0	63.66	64.77
	6.0	8.0	6.0	7.0	63.66	64.78
	6.0	8.0	6.0	8.0	63.66	64.76
	6.0	8.0	7.0	5.0	63.68	64.57
	6.0	8.0	7.0	6.0	63.68	64.60

210	6.0	8.0	7.0	7.0	63.68	64.61
	6.0	8.0	7.0	8.0	63.68	64.60
	6.0	8.0	8.0	5.0	63.63	64.37
	6.0	8.0	8.0	6.0	63.63	64.40
	6.0	8.0	8.0	7.0	63.63	64.40
	6.0	8.0	8.0	8.0	63.63	64.39
	7.0	5.0	5.0	5.0	62.47	64.35
	7.0	5.0	5.0	6.0	62.47	64.41
	7.0	5.0	5.0	7.0	62.47	64.42
	7.0	5.0	5.0	8.0	62.47	64.40
	7.0	5.0	6.0	5.0	62.64	64.19
	7.0	5.0	6.0	6.0	62.64	64.25
	7.0	5.0	6.0	7.0	62.64	64.26
	7.0	5.0	6.0	8.0	62.64	64.24
	7.0	5.0	7.0	5.0	62.67	63.96
	7.0	5.0	7.0	6.0	62.67	64.01
	7.0	5.0	7.0	7.0	62.67	64.01
	7.0	5.0	7.0	8.0	62.67	64.00
	7.0	5.0	8.0	5.0	62.60	63.67
	7.0	5.0	8.0	6.0	62.60	63.71
	7.0	5.0	8.0	7.0	62.60	63.72
	7.0	5.0	8.0	8.0	62.60	63.70
	7.0	6.0	5.0	5.0	62.08	63.64
	7.0	6.0	5.0	6.0	62.08	63.70
	7.0	6.0	5.0	7.0	62.08	63.71
	7.0	6.0	5.0	8.0	62.08	63.68
	7.0	6.0	6.0	5.0	62.22	63.51
	7.0	6.0	6.0	6.0	62.22	63.56
	7.0	6.0	6.0	7.0	62.22	63.57
	7.0	6.0	6.0	8.0	62.22	63.55
	7.0	6.0	7.0	5.0	62.25	63.32
	7.0	6.0	7.0	6.0	62.25	63.36
	7.0	6.0	7.0	7.0	62.25	63.37
	7.0	6.0	7.0	8.0	62.25	63.35
	7.0	6.0	8.0	5.0	62.19	63.08
	7.0	6.0	8.0	6.0	62.19	63.11
	7.0	6.0	8.0	7.0	62.19	63.12
	7.0	6.0	8.0	8.0	62.19	63.11
	7.0	7.0	5.0	5.0	61.49	62.79
	7.0	7.0	5.0	6.0	61.49	62.83
	7.0	7.0	5.0	7.0	61.49	62.84
	7.0	7.0	5.0	8.0	61.49	62.82
	7.0	7.0	6.0	5.0	61.61	62.68
	7.0	7.0	6.0	6.0	61.61	62.72
	7.0	7.0	6.0	7.0	61.61	62.73
	7.0	7.0	6.0	8.0	61.61	62.71
	7.0	7.0	7.0	5.0	61.63	62.52
	7.0	7.0	7.0	6.0	61.63	62.55
	7.0	7.0	7.0	7.0	61.63	62.56
	7.0	7.0	7.0	8.0	61.63	62.55
	7.0	7.0	8.0	5.0	61.58	62.32
	7.0	7.0	8.0	6.0	61.58	62.35
	7.0	7.0	8.0	7.0	61.58	62.36
	7.0	7.0	8.0	8.0	61.58	62.34
	7.0	8.0	5.0	5.0	60.77	61.84
	7.0	8.0	5.0	6.0	60.77	61.88
	7.0	8.0	5.0	7.0	60.77	61.89
	7.0	8.0	5.0	8.0	60.77	61.87
	7.0	8.0	6.0	5.0	60.86	61.76
	7.0	8.0	6.0	6.0	60.86	61.79
	7.0	8.0	6.0	7.0	60.86	61.79
	7.0	8.0	6.0	8.0	60.86	61.78
	7.0	8.0	7.0	5.0	60.88	61.62
	7.0	8.0	7.0	6.0	60.88	61.65

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