

THE ROTARY DIGESTER IN WOOD SACCHARIFICATION

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THE ROTARY DIGESTER IN WOOD SACCHARIFICATION^{1,2}

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This investigation into the use of the rotary digester in wood saccharification was begun at the Forest Products Laboratory in the fall of 1943 at the request of the Office of Production Research and Development of the War Production Board. Its purpose was to serve as a collateral program to the study of the Scholler process (3) that was being conducted by members of the Laboratory staff with the Cliffs-Dow Chemical Company.

Apparatus

A schematic diagram of the equipment used in this investigation is shown in figure 1 and two views in actual operation in figures 2 and 3. In figure 1, the digester (A) is a 30-inch diameter sphere constructed of copper silicon alloy sheet of sufficient weight to allow a working pressure of 300 pounds per square inch. It is supported by two hollow trunnions, mounted in babbit bearings and rotated at a speed of 12 revolutions per minute. This was later reduced to 4 revolutions per minute in order to decrease the attrition of the residue. The digester opening is closed by a steel plate (B), faced with heavy copper, fastened down by 10 swing bolts. There are two openings through the plate, one for a 1-inch wort draw-off line (C), closed off by a plug valve (D), and ending in a half union (E₁), the other for a thermometer well (not shown) which extends down into the filter head (F). After two unsuccessful designs, the filter head finally took a form, shown in figure 4, that fits into the neck of the digester with

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about 1/8-inch clearance on all sides. The perforated filtering surface projects into the digester body so that any residue adhering to the head after drawing wort will be swept clear by the charge during subsequent rotation.

Steam, controlled by valve (G), is introduced through one hollow trunnion. Internal pressures and temperature are manually regulated according to the pressure shown on gage (H). Acid solution is injected through the same trunnion by a steam actuated, automatic injector (I), after being mixed to proper concentration in metering tank (J).

To discharge wort, the digester is stopped in an inverted position and the half union (E₁) connected with the other half (E₂) at the end of a length of flexible metal tubing. The wort then passes through the sight glass (K) to the flash tank (L). The vapor flashed from (L) goes through flash condenser (M) and is collected at its base. The wort drops from the bottom of the flash tank to a tared earthenware crock (N) which rests on scale (O). After weighing and sampling, this wort is poured into wooden collecting tank (P). The sample of the composite liquors from each run is taken from this collecting tank after suitable agitation (Q).

After the completion of the run, the pressure in the digester is released through condenser (R). The cover and filter head are removed, the digester inverted, and the drip-free residue dumped on the concrete floor for sampling and weighing.

Wood used for Hydrolysis

Two types of chips were used in this work; one a 3/4-inch pulp chip, the other a chip approximately 1/4 inch in the fiber direction. The only wood used was a Douglas-fir lumber and no bark was present. After chipping, during which mixing of the chips occurred, the chips were sacked. Before each series of runs, the chips were spread out on the floor to a depth of 4 inches. After standing overnight to come to an equilibrium moisture content, the chips were mixed and piled together, a sample taken from the four quarters of the pile, and the wood again sacked. In this way a well-mixed composite material was obtained. The sample was analyzed for potential sugar (6) and for moisture content. The potential sugar content of all the wood used was between 66.5 and 68.5 percent. Samples from individual logs, however, showed much larger variations (6).

Sampling of the Wort

Wort samples were obtained by thoroughly mixing the product of an entire cycle or the composite of all cycles. No samples were taken directly from the wort draw-off line.

Sampling of the Residue

After all free wort had been removed, the residue was mixed in the digester by tumbling, dumped on the floor, further mixed, and shoveled into a pile. A 3-pound sample was taken for analysis. On reaching the laboratory, this sample was again thoroughly mixed in a porcelain dish to insure against any concentration of liquid in the bottom of the sample.

Methods of Analysis

The potential sugar content of the original wood and wood residue was determined by a method described elsewhere (6); the reducing sugar, by the Shaffer and Somogyi method, using reagent No. 50 and a 30-minute heating period (7). The fermentable sugar was determined by measuring the sugar sorbed by yeast in high concentration from a solution of the wood sugar containing 1.5 milligrams of reducing sugar per milliliter (7). Alcohol yields were estimated by multiplying the yield of fermentable sugar by 0.47, a value which represents the weight of alcohol obtained per unit weight of fermentable sugar. This value was established experimentally by comparing the yield of alcohol obtained from 8-liter fermentations with the fermentable-sugar content found by yeast sorption (3).

The reducing sugar content of the wet hydrolyzed-wood residues was determined by mixing a 100-gram sample of the residue and about 400 milliliters of water in a "Waring Blendor" for 10 minutes. The macerated residue was washed on a Buchner funnel until nearly 2 liters had been collected. This was made up to volume in a 2-liter volumetric flask. The well-ground residue remaining was air dried, weighed, and its moisture content determined. It was then analyzed for its potential sugar content. This use of the Waring Blendor saves much time over the older method of washing the intact hydrolyzed chips. A ground sample is obtained at the same time for subsequent analyses.

The Investigation of Wood Hydrolysis in the Rotary Digester

Wood hydrolysis is a complicated study because:

1. Wood is not homogeneous in either its physical or its chemical structure.
2. The physical and chemical character of residual wood changes as hydrolysis progresses.
3. The retention of sugar solution by wood is high; one-half to two-thirds of the sugar produced in each cycle remains with the wood in the digester.

4. Interdependent variables, governing wood hydrolysis, that must be studied both individually and as interrelated functions are: (a) time, (b) temperature, (c) acid concentration, (d) liquid-solid ratio, (e) particle size of charge.

The rotary digester program has included three main lines of investigation:

1. Multistage hydrolysis in which an effort was made to obtain a maximum yield of alcohol. In such operations, yields exceeding 55 gallons per ton were obtained.

2. Single-stage hydrolysis in which an attempt was made to complete the hydrolysis in a minimum of time. Yields of 30 gallons per ton were obtained.

3. Limited multistage hydrolysis giving yields between those obtained in (1) and (2) in the shortest time consistent with economical operation.

I. MULTISTAGE HYDROLYSIS

With the exception of the work begun in 1922 by H. Scholler, and the development of his commercially successful process, the multistage hydrolysis of wood with dilute acids has not been very thoroughly studied. G. Meunier conducted a study at about the same time as Scholler but was unable to commercialize his process successfully. In 1927, when studying the effects of successive hydrolyses on the components of wood, Sherrard and Davidson attained a sugar yield of about 32 percent, calculated as glucose, on a dry-wood basis.

In 1943, Harris and Beglinger made a series of multistage cooks in the spherical rotary digester of the Forest Products Laboratory at Madison, Wisconsin, in which were used the conditions recommended by H. Scholler. In spite of deficiencies in apparatus, alcohol yields of 47.5 gallons per ton of dry softwood chips were obtained.

The present program was authorized:

1. To investigate the advantages and disadvantages, both chemical and mechanical, of the rotary digester as compared with the stationary percolator.

2. To investigate the effects of agitation on sugar yields.

3. As a more flexible piece of equipment, to make basic studies of wood hydrolysis under conditions suggested by work in the stationary equipment.

4. To act as a basic unit for studies of subsequent steps in the process of producing ethyl alcohol from wood, such as neutralization, filtration, and fermentation of wood hydrolysis worts.⁴

The first program for studying multistage hydrolysis involved complete cooks, using constant conditions throughout and varying only one factor in each cook. Such variations were over ranges considered by past experience to be effective. The results of this series were not definitive and will not be included in this paper. This phase of the problem, however, merits further study because of the advantages offered by the simplification of hydrolysis under constant conditions. The program that was finally used involved a cycle-by-cycle study of the conversion of the cellulose to sugar.

Cycle-by-cycle Study

In devising a schedule for the multistage hydrolysis of wood it was considered that, as the cook progressed, it would be necessary to change one or more of the factors affecting the severity of hydrolysis of the succeeding cycles. This was to compensate for the changing chemical nature of the hydrolyzed-wood residue.

Since wood contains hemicellulose, a relatively easily hydrolyzable carbohydrate fraction, the conditions used for the hydrolysis of the first cycle should be less severe than those required for succeeding cycles. This was found to be true by Scholler and other workers.

In order to determine what conditions were sufficiently severe, and yet efficient, for the hydrolysis of the first cycle, samples of finely divided wood together with dilute acid were sealed in glass bombs and hydrolyzed by heating with direct steam in a rotating autoclave according to the methods described in another report (8). This work, as well as some done earlier (3), showed that if the hydrolytic conditions were not sufficiently severe, much of the hemicellulose was rendered soluble but was not hydrolyzed to monosaccharides. This source of potential sugar was therefore lost to the process. Liquors obtained in such inadequately hydrolyzed first cycles can be rehydrolyzed by the addition of more acid and further heating. In commercial operation this would be an undesirable step. In order to reduce the acid, lime, and time consumption to a minimum, however, it is desirable to use no more than the amount of acid required for efficient hydrolysis.

The small-scale study showed that an acid concentration of 0.25 percent and a temperature of 170° C. maintained for 10 minutes is adequate for the satisfactory hydrolysis of the hemicellulose. At a temperature 10° C. lower than this, there is a marked decrease in the ratio of reducing

⁴Much of this work was done with the assistance of the engineering staff of The Vulcan Copper and Supply Company of Cincinnati, Ohio, the designers of the commercial unit under construction.

sugar produced to potential sugar removed from the wood, due to the presence of incompletely hydrolyzed hemicellulose in the wort.

The hydrolysis of wood was then studied in the rotary digester under controlled conditions. The measurement of some of the factors involved require interpretation.

Time of digest is defined as the interval between the time at which the prescribed hydrolysis temperature was reached and the time at which the valve was opened to draw off wort. The hydrolysis of cellulose proceeded during the wort withdrawal period.

Acid concentration is the concentration in the digester during the digest period. The dilution from condensed steam was calculated and checked experimentally. This is in contrast to procedures commonly used in which the acid concentration cited is that of the hydrolysis liquid introduced, thus ignoring the dilution effect of the condensed steam. The amount of hydrolysis solution remaining sorbed by the wood after wort withdrawal was arrived at from the wet residue of the cycle-by-cycle studies and allowed for when computing the amounts of water and acid to be added for the subsequent cycle.

Liquid-solid ratio was calculated on the same basis as the acid concentration. In multistage operation it is desirable to take off as much as possible of the sugar produced in each cycle. The higher the water-wood ratio, the greater will be the amount but as this ratio increases, the acid requirement increases, and the wort concentration decreases. On the basis of earlier experience, it was decided to use a constant liquid-solid ratio of 3 to 1. This represents a satisfactory compromise between steam consumption, acid requirements, sugar yield, and wort concentration.

A series of hydrolyses of 50-pound portions of wood were undertaken in the rotary digester using 0.25 percent sulfuric acid and various temperatures and times. The water-wood ratio was held at 3 to 1 in the digester. The total sugar produced in the hydrolysis was determined by an analysis of the drawn wort and of the wort sorbed in the wet residue. The potential-sugar content of the washed and dried residue was also determined. By subtracting the potential sugar in the residue from that in the original wood, a measure of the gross-sugar production was obtained. The ratio of the net to the gross sugar production was a measure of the efficiency of the hydrolysis. On the basis of such studies it was decided that a temperature of 170° C. with 0.25 percent sulfuric acid for 10 minutes was satisfactory for the first-cycle hydrolysis.⁵

Some of the residue from this first-cycle cook was washed, dried, and ground, and then subjected to a series of experiments using small

⁵Subsequent work has indicated that a temperature of 180° C. with the same acid concentration and time would be even more satisfactory in multistage hydrolysis.

samples, as described previously, to define the conditions required for the second cycle. The residue from the two-cycle cook was used to determine the optimum conditions of hydrolysis for the third cycle and so on.

Operation

The operation of the rotary digester during the hydrolysis proceeded as follows:

Before charging, the digester was heated to the temperature used for the first cycle, the steam condensate removed, and the sampled, weighed charge of chips introduced. The digester and charge were again brought to temperature and the predetermined amount of sulfuric acid solution injected. The cook was timed, the rotation of the digester halted shortly before the digest time elapsed, and the wort discharge line connected through the flexible tubing to the flash tank. At the end of digest period, steam was shut off, the discharge valve was opened, and the discharged wort was collected in a tared crock. It was weighed, sampled, and then dumped into a wooden collecting tank. The flash was collected from the flash condenser, weighed, and sampled. As soon as the sight glass showed the passage of clear vapor, indicating the end of the wort discharge, the discharge valve was shut off, the flexible tubing disconnected, rotation started, and the proper amount of acid solution injected to meet the requirements for the next cycle. The digester was then brought to the proper temperature for this next cycle and the program repeated. At the end of the run, after wort removal, the digester was blown down to atmospheric pressure through the blow-down condenser, the digester cover and filter head removed, and the drip-free contents dumped onto the concrete floor where a representative sample was taken and the residue weighed.

Yields from Interrupted Multistage Hydrolyses

The conditions used for the hydrolysis of wood in the various cycles were as follows:

Time: 10 minutes for the first cycle, 6 minutes for the second, and 4 minutes for subsequent cycles.

Temperature: 170° C. for the first cycle, 180° C. for the second, and 185° C. for subsequent cycles.

Acid concentration: 0.25 percent sulfuric acid for the first cycle and 0.60 percent for all subsequent cycles.

Liquid-solid ratio: 3 to 1 throughout.

Results are shown in table 1 and figure 5.

The experimental errors involved in the determination of the difference in the potential sugar content of the original wood and of the residue made it difficult to determine accurately the change in efficiency with different methods of operation.

After this cycle-by-cycle study was completed and further information was obtained on the theory of wood hydrolysis, it became apparent that wood cellulose does not become more easily hydrolyzed as the length of exposure to hydrolytic conditions increases. This was shown in the following way:

The washed and dried residues from each of the cooks listed in table 1 were hydrolyzed with 0.8 percent sulfuric acid at 180° C. according to the technique described in another paper (8) and the rate of hydrolysis of the residual cellulose in each sample was determined. A sample of the original wood was included for comparison. The results of this experiment are given in table 2 and figure 6. It is seen that there is no significant change in the rate of hydrolysis of the cellulose in the various residues even though the total residue obtained from the 11-cycle cook contained only 12.5 percent of the carbohydrate initially present in the wood. This indicates that after the hydrolysis of the hemicellulose is complete, constant conditions of hydrolysis can be used for the succeeding cycles. This means that the conversion of the cellulose proceeds at a constant rate based on the amount present at any time. If it is desired to complete a hydrolysis in less time when a small amount of cellulose remains, more severe conditions may be used.

To show that the cycle-by-cycle method of investigation was reproducible, a curve was made (fig. 7) of the cumulative sugar production of a complete cook and of interrupted cooks in which identical conditions were used. This figure also shows the cumulative amounts of (a) reducing sugar recovered, (b) reducing sugar sorbed in residue, (c) reducing sugar destroyed, and (d) potential reducing sugar in residual cellulose.

This curve also shows the most important limitation on the yield of sugar obtainable from multistage hydrolysis -- a large percentage of the sugar present in one cycle is retained by the wood to be recooked in the succeeding cycle. This sugar, therefore, is subject to much longer exposure to destructive conditions than if more complete removal was possible.

Completed Multistage Hydrolyses

The first complete cook, No. 72, employed conditions selected from the cycle-by-cycle study that were the same as those used for the cooks in table 1 except that run No. 72 was carried to completion.

The time consumed in this cook and the yields are shown in table 3. The cumulative reducing-sugar production on a time basis is shown in figure 8.

In an endeavor to decrease the total time consumed, cook 74 was made in which the temperature was raised to 190° C. in the fifth cycle and maintained at that point throughout the succeeding cycles. All other conditions remained the same as in No. 72. The time of operation was reduced but the yield remained about the same as in No. 72 as can be seen in table 3 and figure 8.

In another attempt to shorten the time consumed and improve yields, cook 75 was made in which the acid concentration in the digester was increased at the fifth cycle to 0.90 percent and maintained at that level throughout the remainder of the cook. The temperatures used in No. 72 were resumed, however. Yields were substantially improved thereby as is seen in table 3 and figure 8.

This improvement in yield puts the choice on the basis of economics; whether a 10 percent increase in alcohol production plus a 16.5 percent reduction in time consumed per cook outweigh a 30 percent increase in total acid needed plus the increase in the amount of lime necessary for neutralization. This decision can be made only by reviewing local conditions at a proposed plant site.

The amount of sugar destroyed in a solution is in direct ratio to the amount present in the solution at any given period of time (8). In the multistage hydrolysis of wood, a maximum concentration is reached in the first cycle when the hemicelluloses are converted to sugar. It seemed, therefore, that the introduction of a wash cycle between the first and second hydrolysis cycles would decrease the amount of sugar retained in the residue and so reduce the amount decomposed. To accomplish this, 75 pounds of water were injected after the first wort draw-off, the digester was rotated for 6 minutes without any application of heat, and the wash water was drawn off. The amount of liquor withdrawn was weighed, sampled, and dumped into the collecting tank with the other wort. This was done in two cooks, No. 73 and 79, which duplicated in all other respects cooks 72 and 75, respectively. As is seen in table 4, the yields were substantially improved.

The comparative course of the cooks is shown graphically in figure 9.

The reduction in sugar concentration in the wort is an important factor if this method for improving the yields is to be considered for commercial operation.

All the work so far described was done with Douglas-fir chips measuring about 3/4 inch in the fiber direction. To study the effect of particle size, two more cooks were made, one (No. 80) with sawdust and another (No. 83) with chips measuring 1/4 inch in the fiber direction. These cooks were made under the same conditions as cook 75. The yields were as shown in table 5.

Little difference in yield occurred, but an inspection of the comparative-production curves in figure 10 exhibits a somewhat more rapid release of the wood-sugar wort when 1/4-inch chips were used. This may be of importance when selecting the cycle beyond which the financial return is marginal. The advantages which sawdust might show in more rapid diffusion were apparently counteracted by the higher retentive capacity of sawdust in comparison with that of the denser chips.

Discussion and Conclusions

The yields of alcohol attainable from the multistage hydrolysis of Douglas-fir chips in a rotary digester are similar to those obtained in the stationary, vertical percolator. Sugar concentration in the wort, however, is lower and thus requires greater fermentation and distillation capacity and also higher steam consumption for the rectification of the alcohol. The superiority of the percolator arises from the fact that it is an extraction column as well as a digester. Fresh dilute acid pumped in the top washes the sugar toward the bottom and creates a marked vertical concentration gradient. The removal of wort at each cycle, therefore, removes a greater quantity of sugar than would be the case if this concentration gradient did not exist.

Stationary equipment is cheaper both in original cost and upkeep.

There is no danger of plugging of the mass in the rotary digester as sometimes happens in the percolator (3), but the discharge is less convenient than the blow-out system of the percolator.

The data acquired in these studies emphasize that the yields of sugar from multistage hydrolysis with dilute acid in rotary or stationary equipment are limited by the retention of the sugar solution by the hydrolyzed wood. Attempts were made to reduce this limitation in several ways: by the choice of a proper particle size of the wood, by a close study of the hydrolysis efficiency at different points of the hydrolysis, and by the inclusion of one or more extraction cycles. These, however, have brought about little improvement. It is difficult to foresee any positive cure for this inherent characteristic.

The conclusion arrived at by Neumann (5), and repeated by other workers, that 173° to 175° C. is the maximum temperature for the efficient conversion of cellulose to sugars is at variance with the findings of the present investigation. These findings indicate that temperatures up to 190° C. (the limit set by the available steam supply) give equally efficient conversion if the hydrolysis time is sufficiently shortened.

It is impossible to select one optimum set of conditions for the economic conversion of wood to sugar by multistage hydrolysis. In order to use the equipment at maximum efficiency the time should be reduced to a practical minimum. The time required for a complete hydrolysis is almost

exclusively dependent on temperature and acid concentration. These two factors are partially compensating in effect and their manipulation is a matter of relative costs and plant design.

Another factor in multistage hydrolysis which can be established only by economic considerations is the extent to which the hydrolysis can be carried. The sugar yields from the last cycles are low and a thorough review of current alcohol prices, equipment, and operating costs is necessary to determine the exact point at which production costs exceed return.

II. SINGLE-STAGE HYDROLYSIS

During the period extending from 1910 to about 1922, two wood-sugar plants were in operation in this country using the single-stage hydrolysis with dilute acid described by Foth (2), Demuth (1), Tomlinson (9), and Kressman (4). In plant-scale operation, 22 gallons of alcohol⁶ were produced per ton of dry wood containing a maximum of 10 percent bark.

The chief advantage of this process was its simplicity; large variations in operational technique had little effect on the sugar production. The chief disadvantage of the process was the low yield; hence only the largest sawmills could supply enough wood waste to maintain a plant in economical operation.

The process as outlined by Kressman (4) consisted in heating 100 parts of wood, 125 parts of water, and 1.8 to 2.5 parts of sulfuric acid with direct steam in a rotary digester. The time for a complete cook was divided as follows:

Charge.....	5 minutes
Heating.....	15 to 20 minutes
Hydrolysis period.....	15 to 20 minutes
Blowdown.....	5 to 8 minutes
Discharge.....	5 to 7 minutes

The drip-free residue so obtained was washed free of sugars in a diffusion battery.

In the light of present knowledge of wood hydrolysis, this process was open to a number of improvements:

1. The time required for a hydrolysis can be reduced by decreasing the time consumed in coming to temperature. This can be done by injecting the dilute acid at the reaction temperature into the charged digester, thus avoiding the expense of using the digester as a water heater.

⁶Certain plant losses, primarily in distillation, caused this recovery to be low.

2. The time of digestion can be reduced by increasing the acid concentration, the temperature, or both.

3. The yield can be increased. From data presented in another paper from this Laboratory (8) it is apparent that the two factors that increase the speed of hydrolysis also increase the efficiency of conversion of cellulose to sugar.

4. Wood sugars of higher fermentability can be obtained by a proper choice of conditions.

In an effort to complete the digestions in a minimum of time, experiments were first made with the injection of hot dilute acid from an auxiliary autoclave. The experimental difficulties encountered in this type of operation with the available equipment were such that it was considered better to inject cold dilute acid and have better control over the variables involved. The injection of hot dilute acid, while important for efficient plant operation, can be neglected in experimental work, since only 12 minutes are required to raise the pressure from 70 pounds per square inch, below which point attack on the cellulose is relatively slow, to 165 pounds per square inch, the highest pressure used.

The substances in wood-sugar worts that appear as unfermentable sugar include (1) xylose, (2) sugar decomposition products that affect the sugar reagent but are unfermentable, and (3) oligosaccharides of unknown composition in multistage hydrolyses when conditions are not sufficiently severe for the hydrolysis of the hemicellulose.

The changes that occur in the fermentability of wood hydrolyzates from one-stage cooks as a function of time are shown in figure 11. The data for this graph were obtained by the hydrolysis of wood in glass bombs by techniques described elsewhere (8). The fermentability is initially low, for hemicellulose yields about one part of unfermentable sugar to two parts of fermentable sugar. As the unfermentable sugar is destroyed and replaced by fermentable sugar from the resistant portion of the cellulose, the fermentability rises. If there were only two factors involved, the fermentability should approach 100 percent as hydrolysis continues, but due to the accumulation of decomposition products that affect the sugar reagent, the fermentability passes through a maximum and then declines. In multistage hydrolyzates obtained by percolation or from the rotary digester, the fermentability may be 60 percent initially. The sugar produced in the later cycles of the multistage cooks, however, rises to a fermentability of over 95 percent. A smaller amount of decomposition products is formed, and a smaller amount accumulates in such a cook than in the single-stage operations.

In this paper will be described the investigation of the single-stage hydrolysis of Douglas-fir by several methods:

1. The American process, used at the Fullerton plant during World War I under the conditions given at the beginning of this section.

2. A modified American process, in which higher temperatures and acid concentrations are used.

3. Constant temperature wort removal method, in which hydrolysis temperature is maintained during and for a short time after the wort draw-off period.

American Process

The results of the hydrolysis of Douglas-fir hydrolyzed according to the method used commercially in this country 25 years ago are given in table 6, series A. In cooks 121, 123, 124, and 125, 3/4- and 1/4-inch chips were hydrolyzed for 15 and 25 minutes, using the lowest recommended acid-wood ratio and a water-wood ratio only slightly higher than that required to obtain a drip-free residue. In order to obtain a representative sample of the wet residue, it is essential that a minimum of wort be present. Even in those runs that would be considered drip free by industrial standards, any free wort was removed from the residue by the injection of compressed air after the digester had been blown down to atmospheric pressure. This also insured the removal of any free wort that might have been trapped in the filter head. The yields, 22.4 gallons per ton and lower, were less than those reported by Kressman (4). With higher acid-wood ratios, the yield increased to 25.2 gallons per ton (runs 138 and 139). When the water-wood ratio was decreased below that used in runs 138 and 139, and the acid concentration was increased, a further slight improvement in yield occurred (runs 149 and 150). These results are considered a satisfactory confirmation of the earlier work.

Modified American Process

In this method of hydrolysis, higher temperatures and higher acid concentrations were used than those employed in the old American process. The pressure was raised as rapidly as possible and, after completion of the digestion period, was quickly blown down.

In the first experiments, series B, an attempt was made to hold the water-wood ratio at 1.5 to 1 and the acid concentration at 2 percent. The results are given in table 6. Maximum yields of alcohol were obtained with digestion periods ranging from 4 to 8 minutes. The yields, above 27 gallons per ton, were higher than those obtained in series A and by earlier workers (4) for the American process with Douglas-fir wood.

In series C are shown the results of hydrolysis using a 2 to 1 liquid-solid ratio and 1 percent sulfuric acid. The yields were similar to those obtained in series B. The acid requirement was lower, but twice as much time was needed to produce the same yields.

In series D, conditions similar to those used for series C were employed, except that the temperature was increased 5° C. The yield was increased by 1 gallon per ton. The time required was expected to decrease, but the data obtained did not show a time decrease.

In series E and F, the hydrolysis of wood with a 2 to 1 liquid-solid ratio and 2 percent acid is shown. Maximum yields of 28 gallons per ton were obtained in approximately 5 minutes.

Series G shows that when the acid-wood ratio was kept at 4 to 100, as in series E and F, and the water-wood ratio was increased to 3 to 1, the yield of alcohol was essentially the same as that found in series E and F, but the time required was doubled.

In series H, when a 3 to 1 liquid-solid ratio was used with 2 percent acid, the yield rose to 29 gallons per ton with a scarcely significant decrease in time. The acid requirement in this series was 6 percent on the basis of the wood.

It would have been interesting to have continued the study of single-stage hydrolysis, using higher temperatures and correspondingly shorter times, but further work along these lines was limited by the equipment and the steam pressure available.

Constant Temperature Wort Removal Method

By the introduction of a small modification, the yield of sugar in single-stage hydrolysis has been significantly increased. After a digestion period, the free wort is removed from the charge through the digester filter head. The charge with the adherent wort is maintained at digestion temperature for an additional period, and then discharged. This results in a higher total production of reducing sugar than if all the sugar produced in the cook is kept at digester temperature throughout the entire heating period. Sugar production has been raised in this way to more than 31 gallons per ton in 10 minutes. The data for this series of runs are given in series I, table 6.

In runs 106 to 108, inclusive, and 114 to 117, inclusive, the wood was hydrolyzed for 5, 10, and 15 minutes; and the free wort was withdrawn during an additional 5 minutes. The total time of digestion and wort withdrawal is given in table 10. In run 114, the water-wood ratio was too low to take advantage of this type of operation. A maximum yield of 31.2 gallons per ton was obtained in a total time of 10 minutes at reaction temperature.

In runs 180, 181, and 182 the same acid-wood ratio was used as that used in the runs previously described, but 50 percent more water was used. This was expected to give better results because a higher proportion of the

sugar was removed in the hot wort withdrawal. In run 180, the digestion was carried on for 1 minute, and the wort withdrawal occupied 5 minutes. In run 181 a 4-minute digestion period was used, wort withdrawal required 2 minutes, and the residue was held at the digestion temperature for 2 minutes after wort withdrawal. Run 182 was similar to 181 except that the initial digestion period was 8 minutes. The maximum yield found in this series was 31.6 gallons per ton, and the required time was 12 minutes. The residual potential sugar indicated that more severe hydrolysis might have resulted in higher yields.

Indications were obtained in the work on hot wort withdrawal, that larger chips (3/4-inch pulp chips) give lower yields than those obtained from 1/4-inch chips. This fact has not yet been established with certainty.

Discussion and Conclusions

By increasing the acid concentration and the temperature, the yield of fermentable sugar from one-stage cooks was significantly increased.

Alcohol yields above 30 gallons per ton were obtainable from one-stage hydrolyses if the wort was removed at the digester temperature and if the residue was subjected to a small additional holding period.

While the rotary digester was used for this work, there is every reason to believe that stationary equipment would be as satisfactory. The schedule used in this work on single-stage hydrolysis was such that the digestion period occupied a small percentage of the total time required to charge, heat, and discharge available industrial equipment. This indicates the need of new equipment designed for continuous operation.

III. LIMITED MULTISTAGE HYDROLYSIS

Thus far in this paper two general methods of operation for wood hydrolysis have been described: (1) a multistage hydrolysis, giving high yields but requiring an involved operating schedule and a long time, and (2) a single-stage hydrolysis requiring a short time and simpler equipment, and giving much lower yields.

A third general method of operation was studied, which offers a compromise between the techniques previously described. Constant temperature and cycles of equal length are employed. Only one-fourth to one-half as many cycles are required as are commonly used in multistage operation. Yields above 40 gallons of 95 percent alcohol per ton are easily obtained.

In all the runs listed in table 7 a 3 to 1 liquid-solid ratio with 0.25 percent acid was used for the first cycle. In the succeeding cycles the water added, plus the steam condensate, was equal to the original weight of the wood. The acid concentration in this heated water was 1.5 percent. The acid concentration of this solution was lowered in the digester by the residual liquor from the preceding cycle. A total of three or four injections were used. After the last injection and wort draw-off the cooking temperature was maintained for a time equal to the length of the cycle. This resulted in the production of more sugar which, together with that remaining from the last cycle, had to be leached from the residue.

A series of 3-cycle hydrolyses were made: Nos. 183, 184, and 185 at 185° C., and Nos. 186 and 188 at 190° C. The yield varied from 37.7 to 40.4 gallons per ton, always increasing with the severity of the cook as measured by the potential reducing sugar in the residue.

In runs 187 and 189, four 3-minute cycles were used at 190° and 185°, respectively. Yields of 41.5 and 44.0 gallons per ton were obtained. It is considered that such hydrolyses, while not obtaining a maximum yield, make efficient use of the relatively expensive apparatus required for high-pressure wood saccharification. Because this process is essentially a highly abbreviated multistage cook, it is believed that important advantages in yield and wort concentration might be gained by carrying out this operation in a Scholler percolator.

General Conclusions

The yield of alcohol obtainable in single-stage hydrolysis was significantly increased by control of time, temperature, and acid concentrations.

Contrary to the older view, temperatures in excess of 173° C. were proven advantageous.

The use of the rotary digester in multistage wood saccharification has little apparent advantage and certain serious disadvantages over the vertical stationary percolator.

The choice between multistage hydrolysis, either to completion or to a limited degree, and single-stage hydrolysis is governed by economic conditions.

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Table 1.--Reducing sugar from interrupted multistage hydrolyses

Total cycles in cook:	Net-reducing sugar : Dry-wood substance :	Gross reducing sugar : Dry-wood substance :	Efficacy :	Pounds dry residue : Pounds dry-wood substance :
	Percent	Percent	Percent	Percent
1	17.8	15.4	86	76.6
2	22.3	27.2	82	68.4
3	27.1	34.1	80	62.6
4	31.2	38.1	82	58.7
5	34.3	44.0	78	52.2
6	36.7	48.4	76	50.0
7	40.7	51.9	78	47.9
11	47.0	62.4	76	40.8

Table 2.--Residues of cooks of table 1 hydrolyzed with 0.8 percent sulfuric acid

Sample	Potential : reducing sugar :	First order : reaction constant : $k(\text{minutes}^{-1})$:	Half-life of the : resistant portion : of the cellulose :
	Percent		Minutes
Original wood.....	68.0	0.0260	26.6
First-cycle residue....	63.4	.0262	25.4
Second-cycle residue...	57.9	.0265	26.2
Third-cycle residue....	53.6	.0278	24.9
Seventh-cycle residue..	37.6	.0266	26.0
Eleventh-cycle residue..	22.2	.0282	24.6

Table 3.--Yield of alcohol from complete cooks

Cook No.	Total : number of cycles	Total : time	Wort per 100 pounds : dry-wood : substance	Reducing : sugar in wort	Reducing sugar : Dry-wood substance	Ferment- : ability	95 percent alcohol per ton dry-wood substance
		<u>Minutes</u>	<u>Pounds</u>	<u>Grams per</u> <u>100 milli-</u> <u>liters</u>	<u>Percent</u>	<u>Percent</u>	<u>Gallons</u>
72	17	197	1,180	3.79	43.1	81.5	52.8
74	14	150	1,040	4.09	42.8	80.7	51.7
75	15	151	1,090	4.21	45.8	83.0	57.0

Table 4.--Effect of wash cycle on yields

Cook No.	Reducing sugar : Dry-wood substance	Reducing sugar : in composite	95 percent alcohol per ton
	<u>Percent</u>	<u>Grams per 100</u> <u>milliliters</u>	<u>Gallons</u>
72	43.1	3.8	52.8
73	46.4	3.5	56.5
75	45.8	4.2	57.0
79	48.0	3.4	60.0

Table 5.--Effect of particle size on yields

Cook No.	Chip size	Reducing sugar : Dry-wood substance	Ferment- : ability	95 percent alcohol per ton
		<u>Percent</u>	<u>Percent</u>	<u>Gallons</u>
75	3/4 inch	45.8	83.0	57.0
80	Sawdust	45.9	83.0	57.0
83	1/4 inch	47.7	80.5	57.6

Table 6.—Hydrolysis of Douglas-fir by the American process, the modified American process, and the constant-temperature-wort-removal method

Cook No.	Length of chip	Hydrolysis conditions				Wort drawn per 100 pounds dry-wood substance	Reducing sugar in wort	Wet residue in dry-wood substance	Dry residue in dry-wood substance	Reducing sugar in wet residue	Potential reducing sugar in dry-wood substance	Fermentability	Yields		
		Time	Temperature	Acid concentration	Water								Reducing sugar	Fermentable sugar	95 percent alcohol
		Inch	Minutes	%	Percent	Pounds	Percent	Percent	Percent	Percent	Percent	Percent	Percent	Gallons	
Series A -- American Process, 173° C.															
121	3/4	15	173	0.84	2.12	14.7	6.09	229	67.1	7.24	76.3	18.1	13.8	20.5	
123	3/4	25	173	.81	2.21	27.2	11.26	229	66.4	6.18	75.5	17.5	13.4	20.2	
124	1/4	15	173	.80	2.12	9.6	11.98	245	72.8	7.45	78.1	19.3	14.3	21.5	
125	1/4	25	173	.83	2.08	6.4	12.94	245	69.9	7.50	78.8	19.0	15.0	22.4	
138	1/4	15	173	1.12	2.23	29.5	11.50	239	67.0	7.17	77.6	20.2	15.8	23.7	
139	1/4	25	173	1.11	2.26	29.5	11.84	240	68.1	7.33	78.6	20.6	16.8	25.2	
149	1/4	15	173	1.35	1.84	0.0		238	66.2	8.55	79.0	20.2	16.0	24.0	
150	1/4	25	173	1.37	1.82	3.4	15.20	229	70.6	8.78	83.5	20.2	17.2	25.7	
Series B -- Modified American Process, 185° C., 2 Percent Acid, 1.5 to 1 Liquid-solid Ratio															
136	1/4	3	185	1.94	1.66	0.0		218	63.9	10.00	75.3	21.9	17.1	25.7	
151	1/4	5	185	2.02	1.48	14.5	14.10	196	64.2	10.35	77.0	22.1	17.0	25.5	
152	1/4	4	185	2.28	1.30	10.6	15.20	195	64.3	11.34	77.6	23.6	18.3	27.4	
157	1/4	6	185	1.96	1.63	0.0		216	55.0	10.5	83.2	22.7	18.9	28.4	
153	1/4	6	185	2.06	1.45	11.7	16.28	195	59.8	10.84	80.2	22.9	18.4	27.6	
154	1/4	8	185	2.13	1.40	18.2	16.17	193	56.3	10.58	81.8	22.1	18.1	27.3	
162	1/4	15	185	2.03	1.54	0.0		208	53.0	9.48	87.1	19.8	17.3	26.0	
143	1/4	25	185	1.90	1.66	33.4	7.85	176	49.2	8.75	85.0	10.8	9.2	13.8	
Series C -- Modified American Process, 185° C., 1 Percent Acid, 2 to 1 Liquid-solid Ratio															
155	1/4	6	185	1.05	1.86	5.0	11.76	233	67.2	8.74	75.0	20.9	15.5	23.3	
156	1/4	8	185	1.06	1.84	17.7	12.94	224	64.1	8.82	77.2	20.9	16.3	27.1	
161	1/4	10	185	1.08	1.86	21.3	13.75	235	65.0	9.39	80.7	20.9	18.3	27.3	
157	1/4	11	185	1.08	1.79	23.1	8.90	216	61.0	9.3	85.3	21.0	17.8	26.8	
158	1/4	15	185	1.04	1.86	89.3	9.21	212	59.3	9.16	83.6	21.9	18.3	27.5	
Series D -- Modified American Process, 190° C., 1 Percent Acid, 2 to 1 Liquid-solid Ratio															
166	1/4	3	190	.96	2.04	17.8	12.73	230	64.4	8.21	72.8	21.0	15.3	23.1	
167	1/4	5	190	1.01	1.93	16.7	13.66	228	61.7	8.74	76.0	20.9	15.0	25.6	
168	1/4	7	190	1.07	1.83	23.3	14.07	215	59.4	8.98	79.3	22.2	17.6	26.4	
174	1/4	8	190	1.00	1.91	18.4	13.47	208	54.6	9.02	80.7	22.9	18.5	27.8	
169	1/4	9	190	1.07	1.82	26.3	14.20	215	56.0	9.18	80.2	22.5	18.2	27.2	
175	1/4	12	190	1.03	1.91	34.0	13.75	208	56.8	9.02	82.7	23.1	19.1	27.7	
176	1/4	16	190	.98	2.16	54.8	11.53	185	50.1	8.25	85.2	21.1	18.0	27.0	
Series E -- Modified American Process, 185° C., 2 Percent Acid, 2 to 1 Liquid-solid Ratio															
126	3/4	5	185	1.93	2.19	50.0	11.25	210	66.3	6.39	82.4	21.9	19.0	28.4	
127	3/4	10	185	1.97	2.09	20.5	11.90	232	69.2	8.18	87.4	21.5	18.3	27.4	
128	3/4	20	185	2.03	2.00	39.0	8.78	193	51.2	6.00	86.5	18.8	12.8	6.5	
Series F -- Modified American Process, 185° C., 2 Percent Acid, 2 to 1 Liquid-solid Ratio															
132	1/4	2	185	2.13	2.01	8.5	14.44	242	69.0	8.47	77.4	21.6	16.7	25.0	
133	1/4	3	185	2.03	2.12	37.4	12.86	226	61.9	8.25	75.7	21.6	18.5	27.7	
145	1/4	5	185	2.07	1.86	7.2	15.88	228	61.0	8.96	80.0	21.4	17.1	29.7	
144	1/4	4	185	2.15	1.99	28.3	13.23	228	56.9	8.40	80.7	22.7	18.3	27.8	
164	1/4	4	185	2.07	1.85	20.8	13.67	225	59.7	8.60	81.5	22.3	18.2	27.4	
170	1/4	4	185	2.13	1.79	11.9	16.00	219	59.3	9.41	79.3	22.3	17.7	26.6	
171	1/4	4	185	2.13	1.79	4.3	16.00	213	60.7	9.88	77.5	21.7	17.1	25.7	
169	1/4	5	185	1.92	2.04	27.0	12.20	219	56.0	10.07	82.6	22.0	18.2	27.2	
167	1/4	5	185	2.09	1.85	29.4	14.61	209	57.6	9.15	83.0	22.4	18.7	27.0	
148	1/4	6	185	1.94	1.98	46.0	12.83	210	56.2	8.09	82.5	22.7	18.5	27.8	
172	1/4	6	185	2.13	1.79	22.8	14.12	206	59.2	9.45	80.3	22.4	18.4	27.2	
173	1/4	6	185	2.18	1.74	17.3	14.48	213	58.9	9.08	84.7	21.7	18.4	27.6	
130	1/4	10	185	2.07	1.87	37.7	11.21	192	58.9	8.69	87.5	20.5	17.9	26.9	
151	1/4	20	185	2.17	1.87	65.8	7.93	182	49.6	5.99	87.3	14.3	12.5	18.8	
Series G -- Modified American Process, 185° C., 1.5 Percent Acid, 3 to 1 Liquid-solid Ratio															
162-B	1/4	3	185	1.43	2.82	89.5	8.36	229	66.3	6.53	74.0	22.3	16.5	26.8	
163	1/4	5	185	1.48	2.73	84.0	8.90	227	61.3	6.80	75.3	22.3	17.7	26.6	
164	1/4	7	185	1.37	2.97	69.2	7.96	220	58.8	6.28	80.8	20.8	16.7	25.0	
177	1/4	7	185	1.37	2.94	95.2	6.68	227	56.5	6.11	80.0	20.0	17.6	26.3	
165	1/4	9	185	1.23	3.27	102.0	8.26	243	61.0	5.80	80.2	22.1	17.7	26.6	
178	1/4	9-1/2	185	1.49	2.69	87.8	9.50	228	58.0	6.24	83.3	22.8	19.0	26.5	
179	1/4	15	185	1.59	2.58	87.6	9.33	210	58.0	6.55	86.0	21.4	18.4	27.7	
Series H -- Modified American Process, 185° C., 2 Percent Acid, 3 to 1 Liquid-solid Ratio															
160	1/4	3	185	2.12	2.79	84.5	7.94	228	60.6	7.40	86.5	21.8	18.6	27.9	
161	1/4	4	185	2.04	2.90	92.8	7.87	224	58.8	7.37	84.6	21.6	19.8	28.9	
168-A	1/4	5	185	2.19	2.68	85.4	10.10	213	56.3	7.24	83.6	21.5	19.6	29.3	
Series I -- Constant-Temperature-Wort-Removal Method															
106	1/4	10	185	(4)	(2)	106.0	(2)	(5)	55.0	(2)	22.5	22.2	20.6	31.2	
114	1/4	10	185	2.28	2.70	76.2	11.30	121	57.7	9.40	85.7	22.2	19.5	28.8	
115	1/4	10	185	1.89	2.05	98.0	10.70	158	50.0	9.10	86.3	22.1	20.8	35.2	
116	1/4	12	185	1.95	1.98	108.0	(2)	(5)	51.5	(2)	14.3	22.8	19.7	29.6	
117	1/4	15	185	1.96	1.97	118.0	(2)	(2)	49.5	(2)	6.8	22.8	17.8	28.8	
108	1/4	25	185	(4)	(2)	108.0	(2)	(5)	55.0	(2)	22.5	22.2	20.6	31.2	
117	1/4	25	185	1.72	2.74	115.0	7.49	129	52.3	7.75	81.4	22.4	20.0	30.1	
120	1/4	9	185	1.44	2.77	148.0	7.86	143	57.7	7.50	85.0	22.4	20.8	30.1	
121	1/4	15	185	1.44	2.78	145.0	8.15	143	56.6	7.50	85.0	22.4	21.1	31.6	

The water-wood ratio was determined by weighing the flash, wort, and wet residue from each cook. Subtracting the weight of the wood gives the amount of water present.

The determination of the percent reducing sugar by weight requires that a correction be made for the specific gravity of the wort.

By volume.

Figures incomplete.

Not available as wash cycles were introduced after wort was drawn.

Table 7.--Hydrolysis of Douglas-fir by the limited multistage method

Run number	Temperature	Number of injections	Time per cycle	Total time	Wort per 100 pounds wood	Concentration of wort	Wet residue per 100 pounds of wood	Reducing sugar in wet residue	Over-dry washed residue per 100 pounds of wood	Residual potential reducing sugar per 100 pounds of wood	Yield of reducing sugar	Yield of fermentable sugar	Fermentability	Estimated yield of alcohol
	° C.		Minutes	Minutes	Pounds	Grams per 100 milliliters	Pounds	Percent	Pounds	Pounds	Percent	Percent	Percent	Gallons
183	185	3	4	29	357	6.03	175	6.50	47.9	18.1	32.2	25.2	78.3	37.9
184	185	3	6	36	358	6.48	179	6.08	44.9	14.0	32.7	25.9	79.3	38.8
185	185	3	3	26	341	6.26	190	5.89	51.7	21.6	31.7	25.1	79.2	37.7
186	190	3	3	26	354	6.39	178	6.33	47.0	15.7	33.0	26.2	79.4	39.3
187	190	4	3	35	475	6.11	148	5.62	39.2	7.2	36.2	29.3	81.0	44.0
188	190	3	5	36	367	6.60	164	5.95	44.3	13.7	33.1	26.9	81.3	40.4
189	185	4	3	33	467	5.83	149	5.68	42.8	10.1	34.7	26.5	76.4	41.5

Does not include sugar in residue.

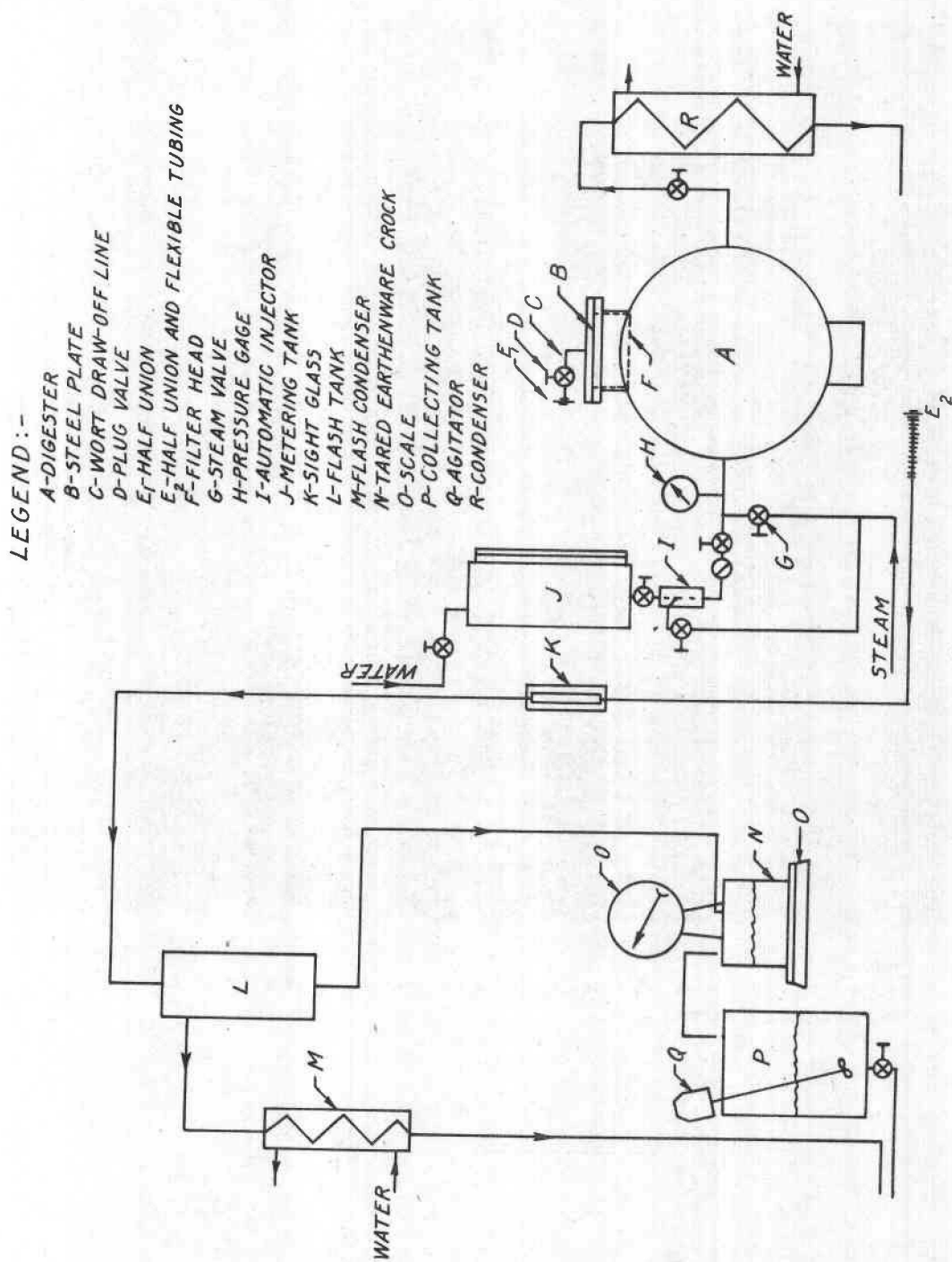


Figure 1.--Flow sheet of wood hydrolysis equipment using rotary digester.

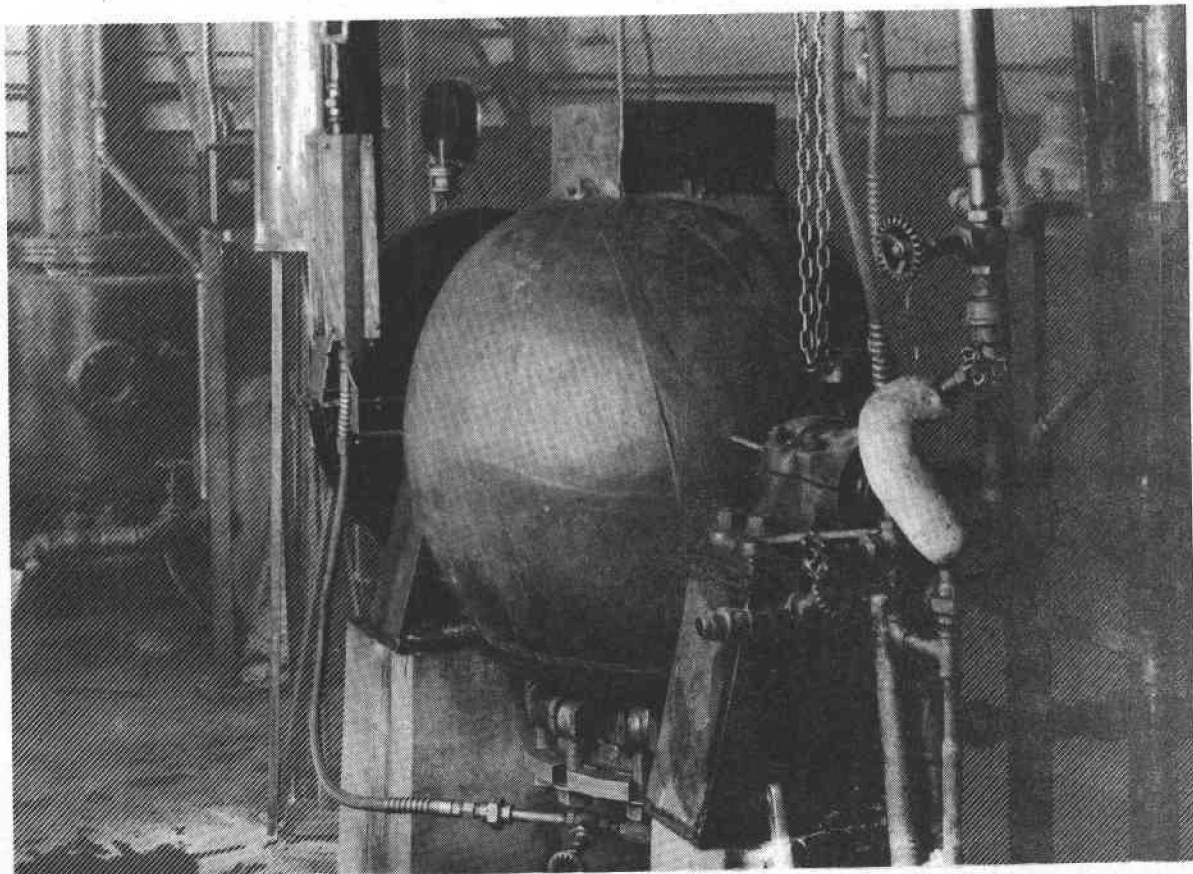


Figure 2.--View of 30-inch rotary digester in position for drawing off wort.

Z M 577Q1 F

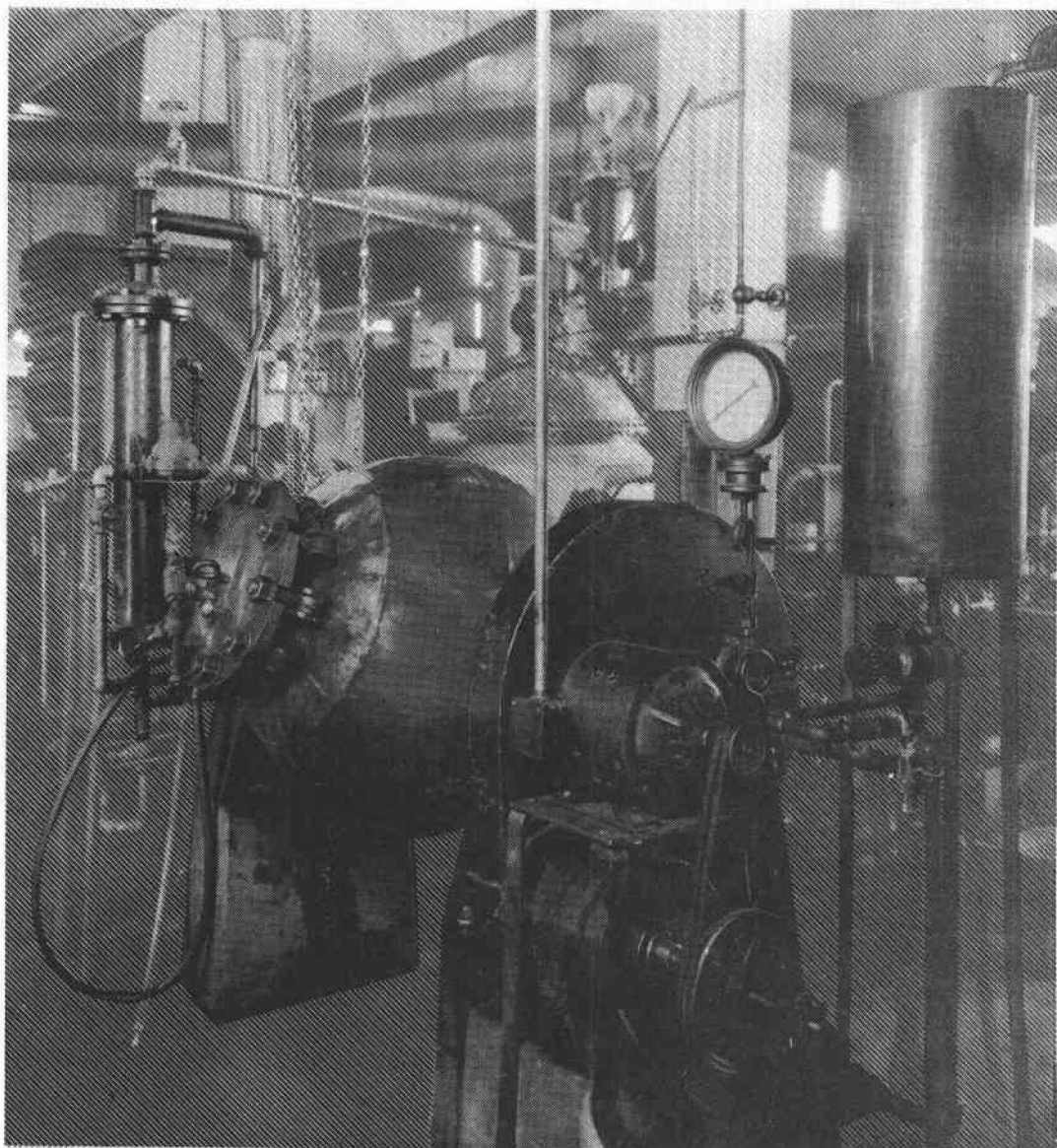


Figure 3.--Rotary digester showing wort draw-off connections,
Z M 57702 F thermometer, motor and drive, and injector system.

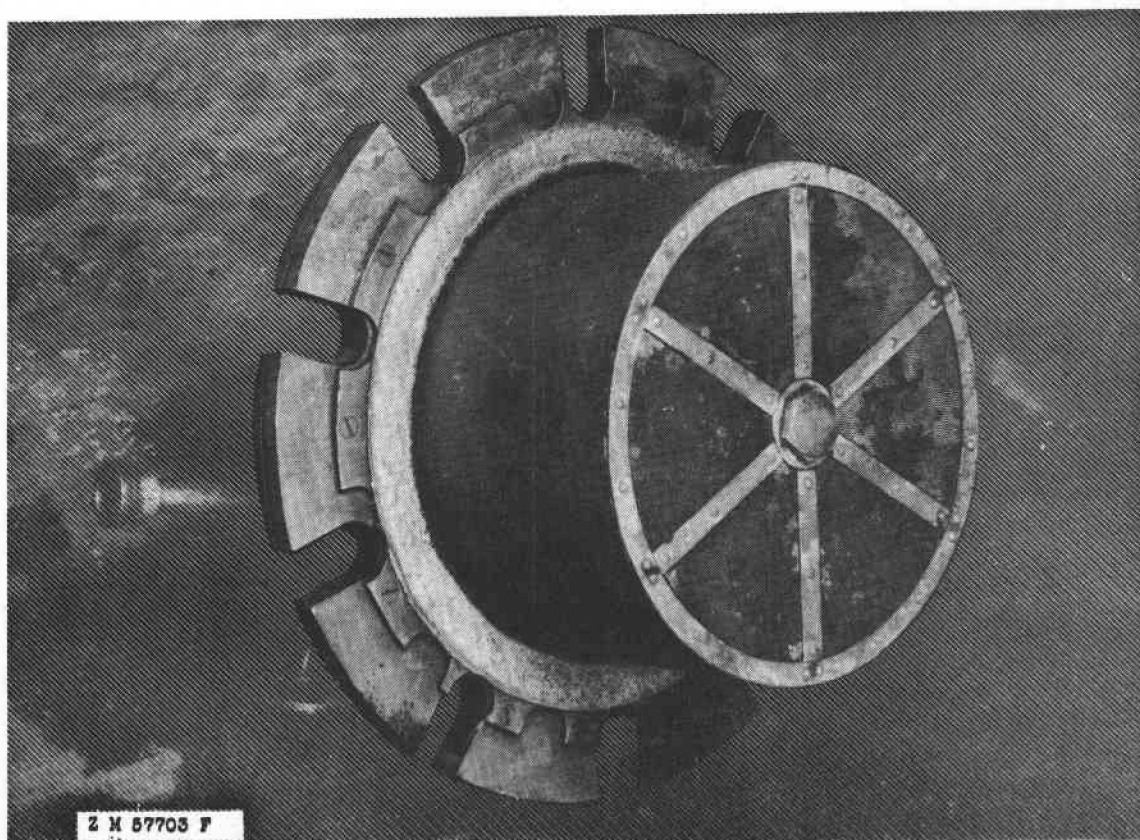


Figure 4.--View of cup-shaped filter head with screen.

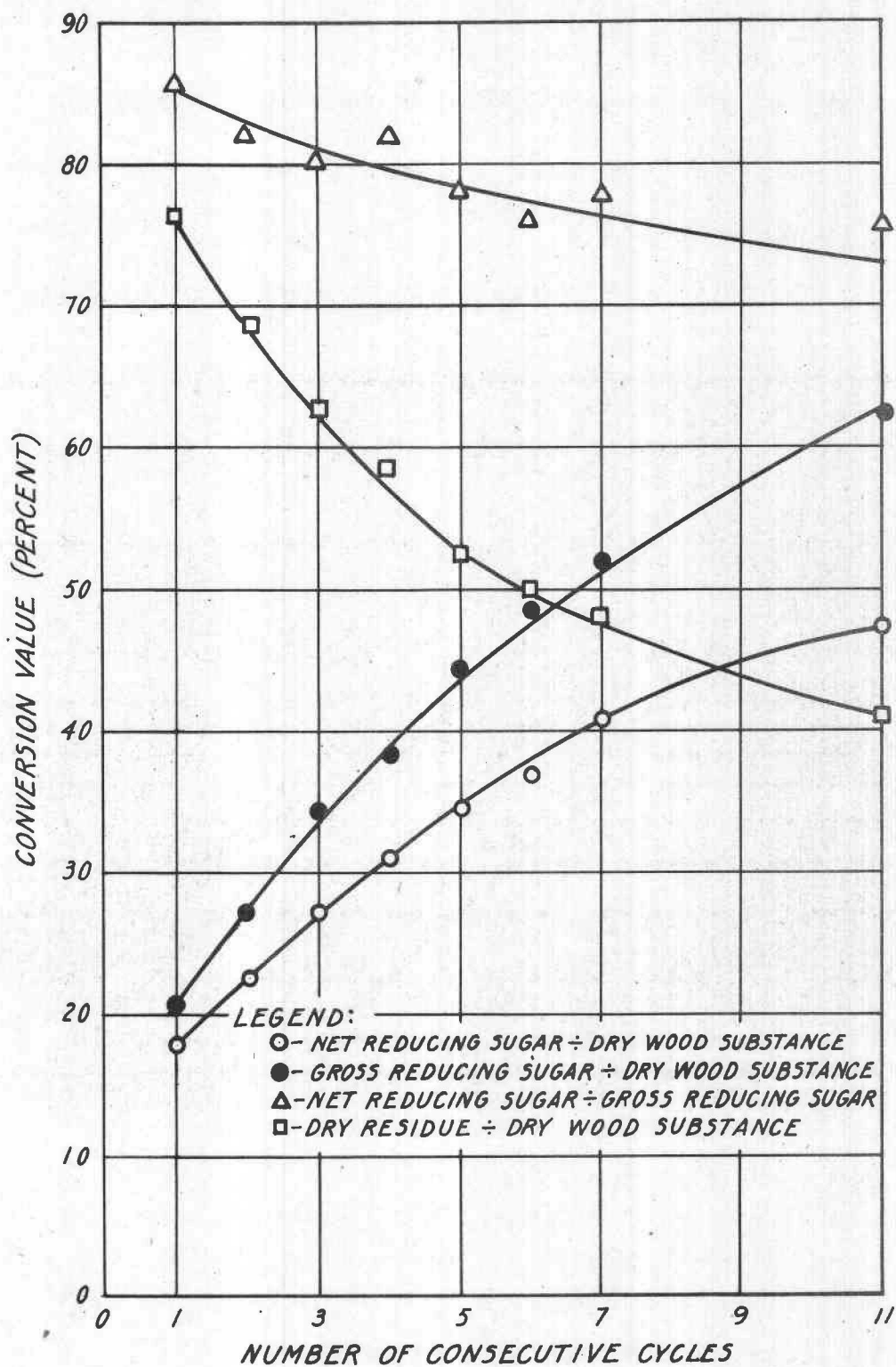


Figure 5.--Yields of sugar and residue found by interrupted multi-stage hydrolyses.

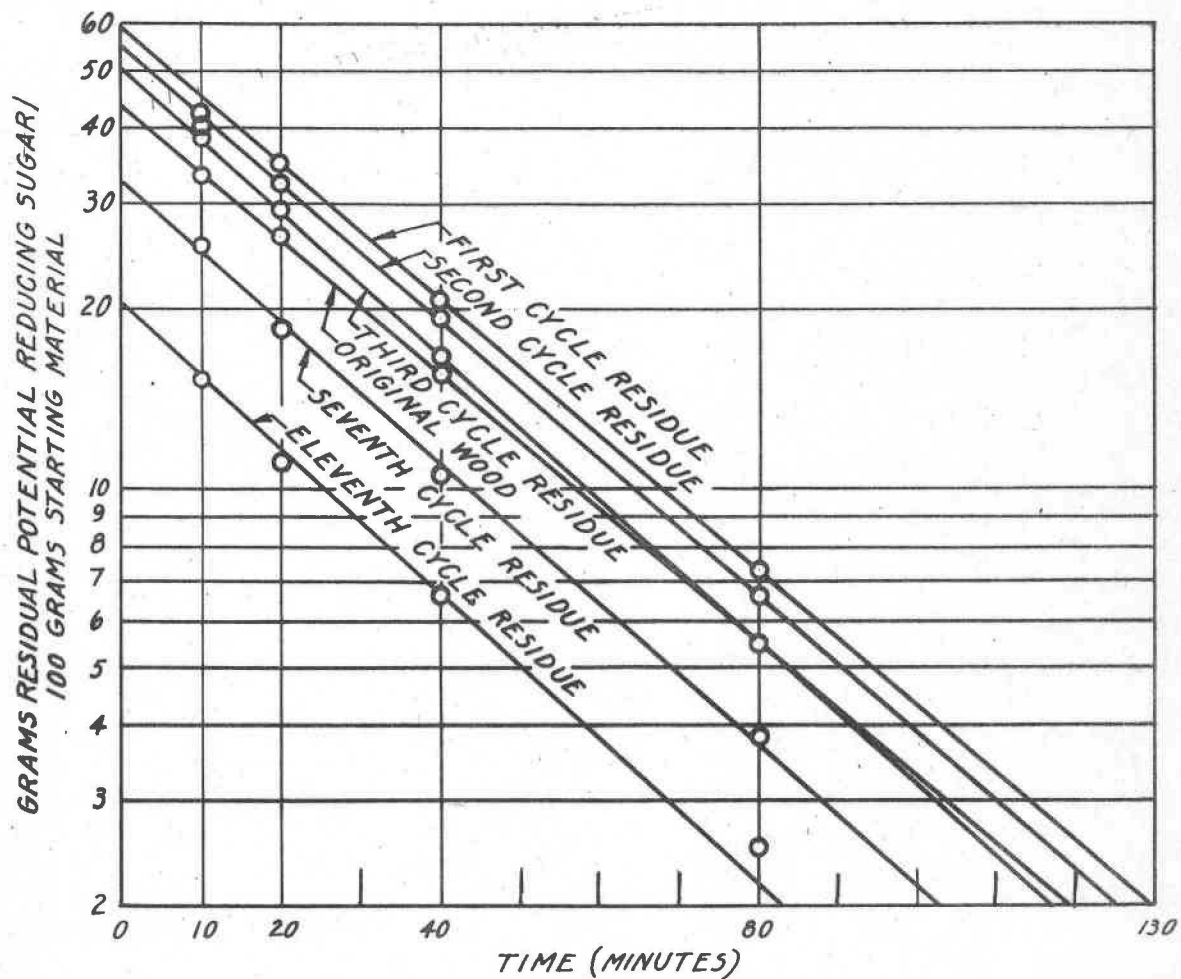


Figure 6.--Hydrolysis of residues.

Z M 56783 1

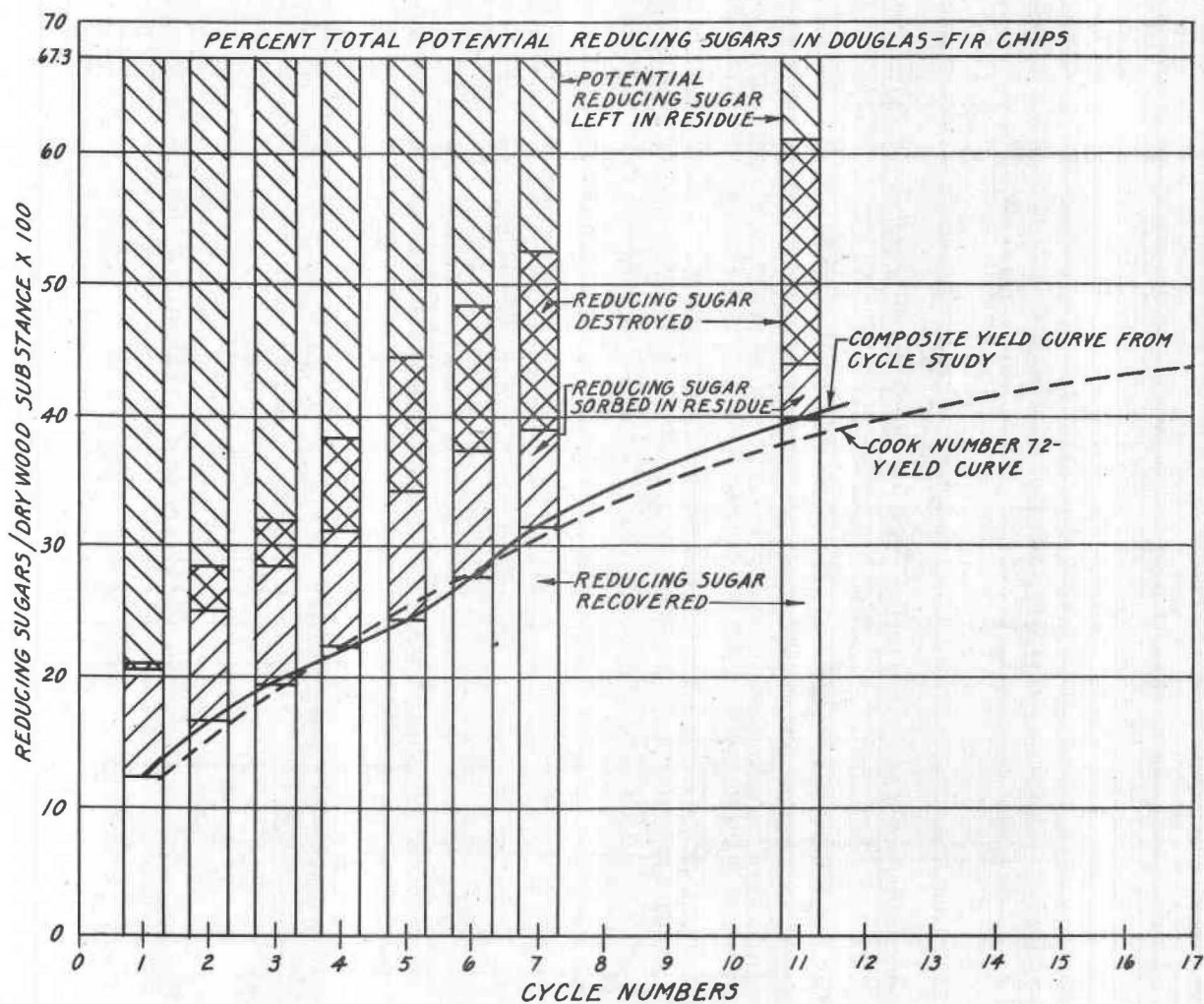


Figure 7.--Progress of interrupted multistage hydrolyses.

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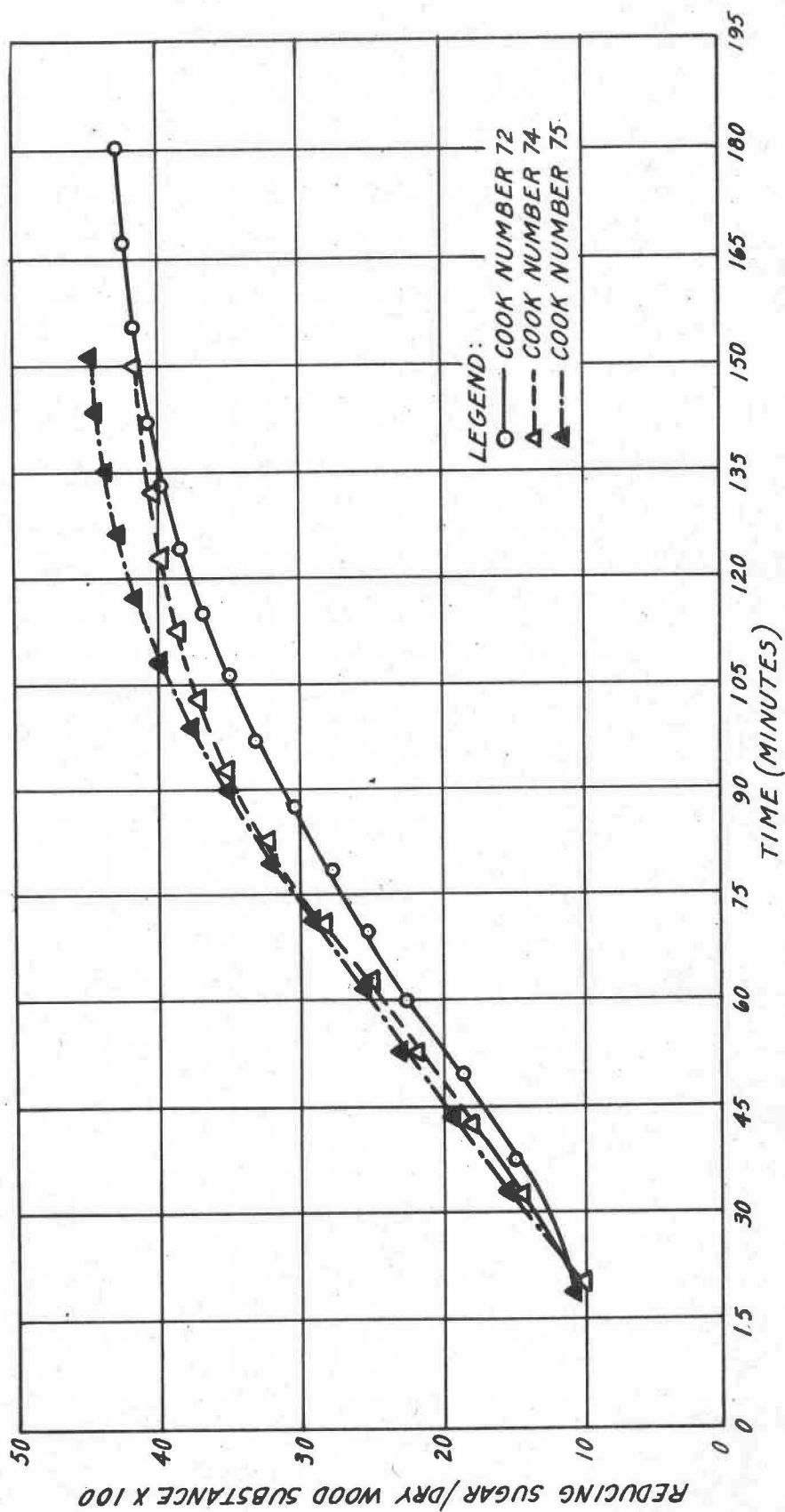


Figure 8.--Effect of acid concentration and temperature on yields and time.

Z M 56785 F

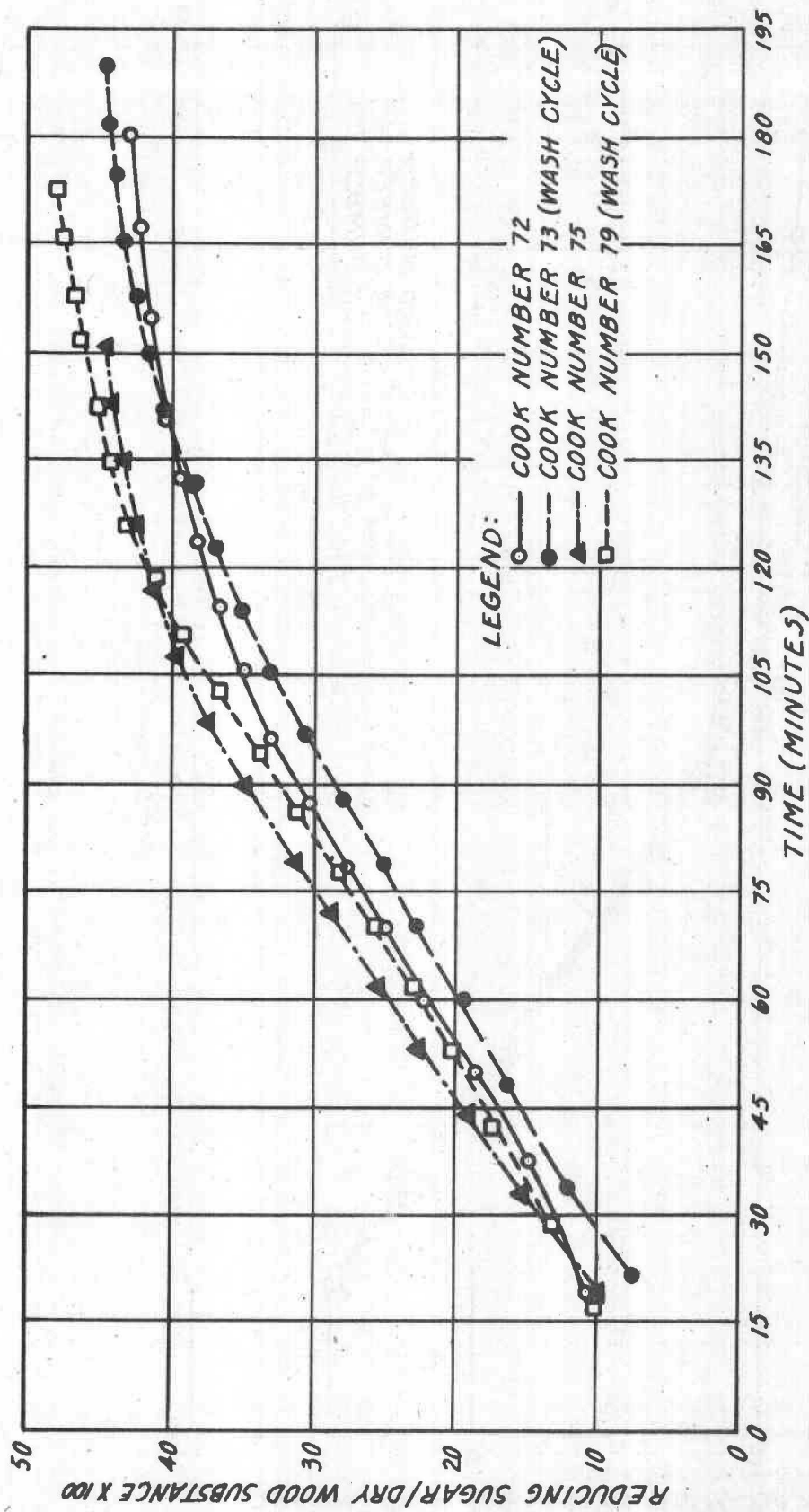


Figure 9.---Effect of wash cycle on yields and time.

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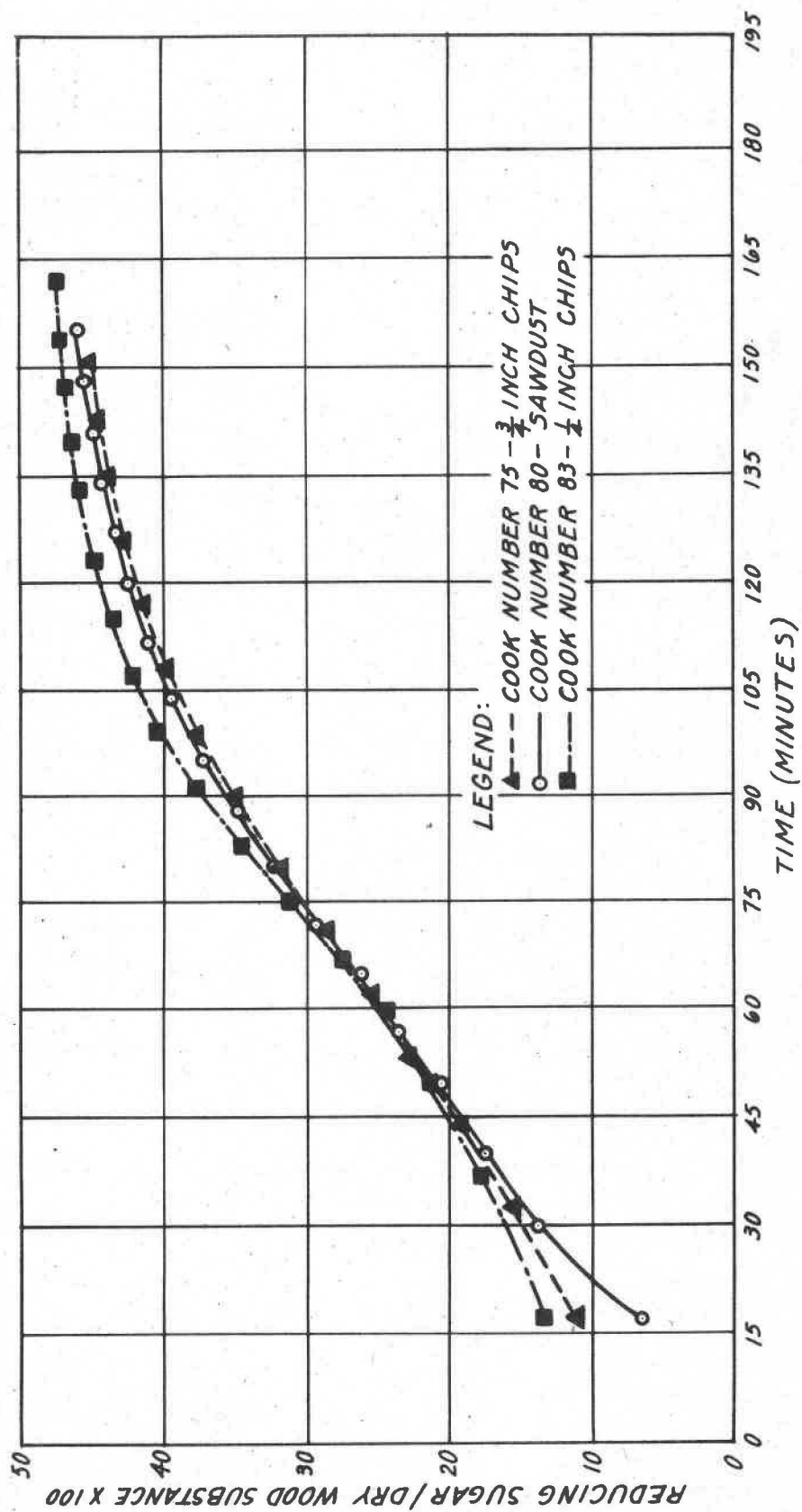


Figure 10.--Effect of particle size on yields.

Z N 56787 F

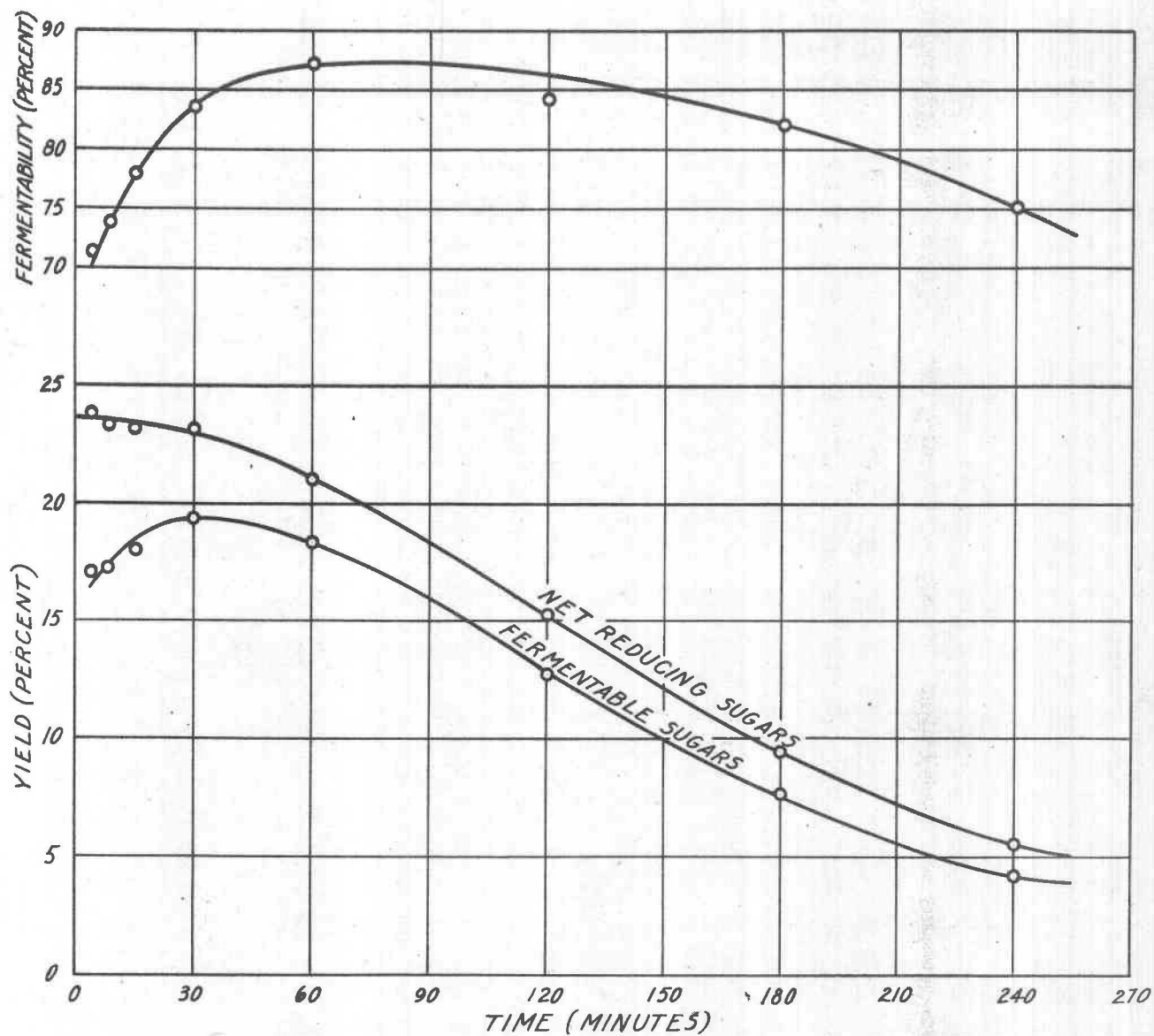


Figure 11.--Hydrolysis of Douglas-fir at 185° C. in 0.5 percent sulfuric acid.
Liquid-solid ratio was 10 to 1.

Z N 56755 F