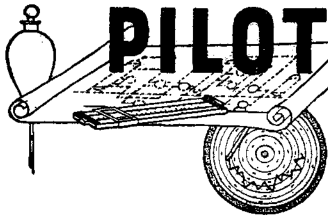

HYDROLYSIS OF WOOD

Using Dilute Sulfuric Acid

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THE interest of the Tennessee Valley Authority in wood hydrolysis processes was predicated on the availability of large amounts of nontimber grades of wood and of waste from woodworking industries in the Tennessee Valley area. It was considered that development of a technically and economically feasible process for wood hydrolysis would contribute to fuller utilization of the forest resources of the valley and of other sections of the United States.

Hydrolysis of wood with dilute sulfuric acid at elevated temperatures and pressures has been studied both in this country and abroad. The earlier research of European experimenters has been reviewed by Sherrard and Kressman (*16*), the work of Scholler and his co-workers in Germany that resulted in a commercial process bearing his name was described by Collins (*2*) and by Faith (*4*), and the field of wood saccharification has been reviewed comprehensively by Harris (*6*). Hydrolysis with dilute sulfuric acid was studied by the Forest Products Laboratory (*7*, *8*, *12*, *13*) and resulted in a process described in detail by Harris and Beglinger (*7*). The process, known as the Madison wood sugar process, was deemed superior to the German practice, in that comparable yields of reducing sugars were obtainable in approximately one fifth the time required by the Scholler process and with the possibility of considerably reduced labor and maintenance requirements.

The procedure formulated by the Forest Products Laboratory was used as the basis for a plant designed and built by the Vulcan Copper and Supply Co. in 1944–47 at Springfield, Ore., to process approximately 220 tons of Douglas fir sawmill waste into 11,500 gallons of 95% ethyl alcohol per day. The hydrolysis section of this plant consisted of five digesters, each of 2100-cubic foot capacity, which represented a 76-fold expansion from the 27-cubic foot digester used in the Forest Products Laboratory studies. Trial operation of the plant disclosed engineering problems and operating difficulties (*11*) and indicated the desirability of pilot plant studies on a scale intermediate between those of the Forest Products Laboratory and the Springfield plant.

Consequently, the Tennessee Valley Authority undertook a pilot plant study of the process, in close cooperation with the Forest Products Laboratory. The objectives were to identify the causes and correct certain operating difficulties, to test a number of simplifying departures from the Madison wood sugar process, and to produce a quantity of molasses for feeding tests.

Objectives of TVA Plant Were Simpler Equipment and More Concentrated Sugar Solutions

This paper describes the pilot plant built at Wilson Dam and the experimental work, the results of which were used to formulate a modification of the Madison wood sugar process that is believed to be economically preferable because it (1) uses somewhat simpler equipment and (2) produces solutions of higher concentration. Results of cost estimates made to gage the economic feasibility of this method for the utilization of nontimber grades of wood and of waste from woodworking industries are presented also.

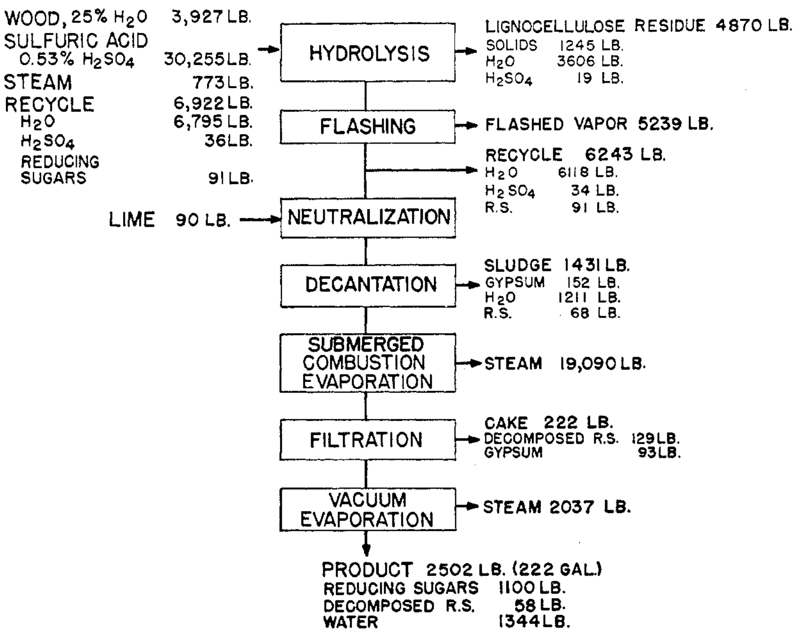

Figure 1. Flow Sheet of Typical Pilot Plant Test

Departures from Madison Wood Sugar Process. The procedure formulated by the Forest Products Laboratory consists of the following sequence:

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1. Wood chips are charged into a digester.
2. The charge of wood is submerged rapidly in hot, dilute sulfuric acid (0.5% H_2SO_4) and the contents are "held" for a time at 250° to 300° F.; the pressure is the equilibrium pressure of saturated steam (15 to 50 pounds per square inch gage).
3. More acid is percolated continuously through the digester until the concentration of reducing sugar in the solution leaving the digester drops to 1%. During the percolation the temperature in the digester is raised to 365° to 380° F., and the pressure is the equilibrium pressure of saturated steam (145 to 185 pounds per square inch gage).
4. The hydrolyzate is flashed to 30 pounds per square inch and then neutralized and filtered continuously under this pressure; it is then processed to either ethyl alcohol, molasses, or yeast.

In the Madison wood sugar process the level of the solution in the digester was allowed to decrease slowly as the percolation cycle proceeded by withdrawing the hydrolyzate at a rate higher than that of incoming acid. In the Oregon plant the level controller, which regulated the flow of hydrolyzate, was found to be troublesome. To ensure complete submergence of the charge and to simplify the control of the hydrolyzate removal, the flow in the Wilson Dam pilot plant was regulated by a pressure-actuated valve. This valve was operated at a hydraulic pressure higher than the equilibrium steam pressure that corresponded to the temperature of the contents of the digester.

In the pilot plant the hydrolyzates were neutralized and the resultant slurries were settled at atmospheric pressure in contradistinction to the Madison wood sugar process where neutralization and filtration were at 30 pounds per square inch; the change permitted the use of simpler equipment and operating controls. The higher pressure and the corresponding temperature (275° F.) were used by the Forest Products Laboratory in the filtration step to decrease the concentration of calcium sulfate, which is more soluble in cold than in hot water. The presence in the filtrate of larger amounts of calcium sulfate than corresponded to its solubility at 275° F. caused serious scaling in the vacuum evaporating equipment used to process the sugar solutions to either molasses or to alcohol. The change to neutralization and filtration at atmospheric pressure was made together with a change that involved concentration to 25% reducing sugars by submerged combustion evaporation, filtration, and subsequent concentration to 50% reducing sugars by vacuum evaporation to prevent excessive loss of reducing sugars.

In the continuous percolation process the concentration of reducing sugars in the hydrolyzate decreases with the progress of the percolation cycle, because of the depletion of the cellulose content of the charge. Kinetic data obtained by Saeman (*13*) suggested that the six-carbon sugars that result from the hydrolysis of resistant cellulose would not be decomposed to any appreciable extent if they were recycled to the digester containing a charge of fresh chips at a temperature below 300° F. Exploratory tests made at the Forest Products Laboratory (*18*) and in the TVA laboratories confirmed the above and indicated that recycling of dilute hydrolyzates was feasible and might result in a more economical process because of the increase in the concentration of reducing sugars in the hydrolyzate and the consequent decrease in the cost of concentrating these solutions to molasses.

Pilot Plant Centered around a High Temperature-Pressure, Monel Digester

The process that was studied in the pilot plant is shown in the flow sheet of Figure 1; the quantities given are for a typical single batch of wood chips. The pilot plant layout is illustrated by a scale model of the plant (Figure 2). Use of the model, which was constructed of transparent plastic sheet and rods, facilitated the rational layout of the pilot plant and its construction.

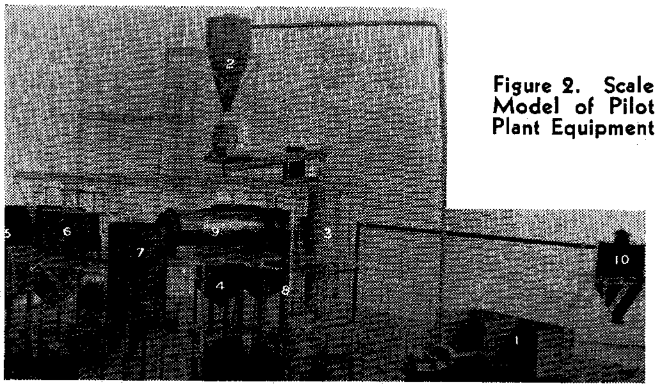

Figure 2. Scale Model of Pilot Plant Equipment

Charge Preparation. Wood logs, 3 to 8 inches in diameter and 52 inches long, were fed manually into a sawmill hog, which had a rated capacity of 5 tons of chips per hour at a shaft speed of 1200 r.p.m. and required a 50-hp. motor. The chips were transported to a 250-cubic foot cyclone-type chip storage bin through a 10-inch diameter, sheet metal duct using an air blower that had a capacity of 3000 cubic feet per minute of free air. The chips

Table I. Data Sheet A—Charge, Time, Temperature, and Hydrolyzate Volumes for Typical Pilot Plant Test

(Charge: 3927 pounds mixed hardwood chips; moisture = 25%)

Time (1/26/51)			Temp., ° F.		Digester Pressure, Lb./Sq. Inch Gage	Solution Levels, Inches				Operating Conditions
	Elapsed, minutes						Hydrolyzer			
Clock	Total	Percolation	Inlet solution	Exit hydrolyzate		Recycle feed tank[a]	Receiver I[b]	Receiver II[b]	Recycle receiver[a]	
10:00	0	...	...	...	42	49	..	..	..	Charging:
10:10	10	...	275	...	40	39	..	..	..	Shock to 65 lb./sq. inch gage
10:20	20	...	275	...	45	28	..	..	..	Steam to 275° F.
10:30	30	...	274	...	45	18	..	..	..	Recycling and holding:
10:40	40	...	280	...	55	8	..	..	..	Recycle rate, 18 gal./min.
10:48	48	...	280	...	70	0	..	..	..	Temp., 275° F.
11:03	63	0	...	275	70	..	..	..	..	Acid rate, 1.8 lb./min. for 5 min.
11:18	78	15	350	275	200	..	7	..	..	
11:33	93	30	376	285	205	..	22	..	..	Time, 63 min.
11:48	108	45	378	322	210	..	39	..	..	Percolation:
12:18	138	75	375	368	210	..	77	..	..	Water rate, 18 gal./min.
12:48	168	105	375	372	215	..	91	17	..	Acid rate, 0.88 lb./min. for all min.
1:18	198	135	376	374	215	..	..	46	..	
1:48	228	165	377	375	215	..	..	75	0	....
2:19	259	196	377	375	215	..	..	..	30	....
	Draining			...	...	..	..	..	46	Temperature schedule,
	Solution levels after cooling			...	...	..	89	74	44	375° F. in 20 min.

[a] One-inch level change corresponds to 17.5 gallons.

[b] At zero level tanks I and II hold 95 and 75 gallons, respectively; 1-inch level change corresponds to 17.6 gallons (average).

were discharged from the bin into a weigh-bucket through a slide gate and then were charged to the digester. After the digester was filled, the charge was compressed by application of high pressure steam (135 pounds per square inch gage) to the top of the charge through a quick-opening valve, which was kept open until the pressure in the digester reached about 35 pounds per square inch. An additional quantity of chips was then charged to the digester to fill it. A single steam shock sufficed to give a packing density of about 16 pounds of dry-wood substance per cubic foot of digester volume. Repeated steam shocks had very little further effect on the charge density.

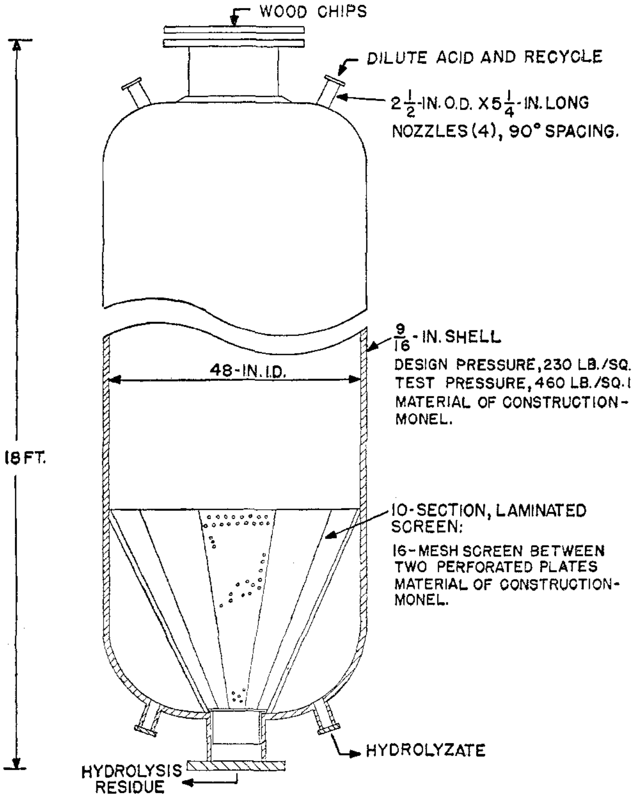

Figure 3. Pilot Plant Digester for Hydrolysis of Wood

Hydrolysis of Chips. The pilot plant digester is shown in Figure 3. It was a Monel vessel, 48 inches inside diameter and 18 feet in over-all height, and was equipped with a conical screen bottom, which supported the wood chips and served to separate the solution from the hydrolysis residue. The digester volume was 200 cubic feet. The digester was operated at a pressure of approximately 60 pounds per square inch during the filling and holding periods and at a hydraulic pressure of 200 to 225 pounds per square inch during percolation. These pressures were higher than the equilibrium steam pressures.

In operation, air was displaced from the charge with steam and the charge then was heated to 275° to 300° F. by means of live steam. In tests without recycling of dilute hydrolyzate, hot water (275° to 300° F.) and concentrated sulfuric acid in an amount required to result in 0.5% H_2SO_4 in the charge were pumped to the digester until it was filled. The contents were held for 15 to 30 minutes, and then acid solution at selected conditions of flow, acid concentration, and time-temperature schedule was percolated through the charge until the concentration of reducing sugars in the hydrolyzate leaving the digester decreased to about 1%.

Water for percolation was pumped with a cast-iron, two-stage centrifugal pump, and the flow was metered and regulated by a pneumatic recorder-controller. The water was heated to a maximum of 300° F. through use of a steam-water, bayonet-type heat exchanger and then heated further to a maximum of 385° F. by passing it through a carbon monoxide-fired, radiation-type heater, which was designed by the method of Lobo and Evans (*9*). The temperature of the hot water immediately before it was mixed with the acid was measured with an iron-constantan thermocouple that was shielded with copper. Rapid response of the thermocouple to temperature changes was ensured by imbedding the bead in a copper block, which was part of the shield. The thermoelectric voltage developed by this thermocouple was amplified electronically and was used to operate a regulating valve that controlled the flow of fuel gas to the combustion chamber of the water heater; by these means the temperature of hydrolysis was controlled automatically at a predetermined value. A similar thermocouple, protected by a Monel shield with the bead welded to the shield bottom, was used to measure the temperature of the solution at the top of the digester where the temperatures agreed within 2° F. with those measured in the hot water line.

In the initial pilot plant installation the concentrated acid was mixed with hot water under pressure in a 2-inch Monel tee that was connected to one of the nozzles in the digester. The thermocouple used for measuring the temperature of acid solution was located in a 1-inch Monel tee, through which the acid solution entered the digester. However, after frequent failures because of corrosion of the Monel pipe, valves, and thermocouple shield and failures of substitute A.I.S.I. Type 316 stainless steel fittings, the system was revised so that the concentrated acid was injected into the hot water stream within the digester. A readily replaceable Monel nipple was used to protect the digester nozzle (Figure 4). Hastelloy B was found to be the best material for the acid injection pipe, and either Monel or stainless steels (A.I.S.I. Type 316 and Carpenter 20) were found to be suitable for valves, fittings, and line immediately adjacent to the digester. The best service was obtained from a renewable-seat, bolted bonnet, Teflon-packed globe valve, manufactured by Aloyco Steel Products Co. from Carpenter 20-type stainless steel. This valve was used for digester closure during the holding period and after the percolation was completed; a check valve made of

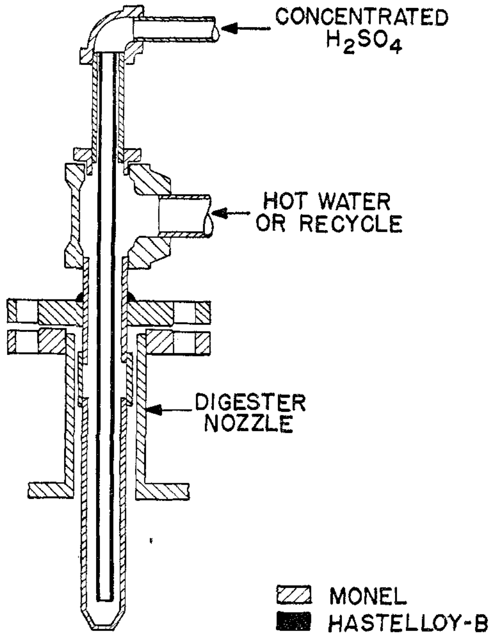

Figure 4. Acid Injection System

the same material was used to protect the hot water line from digester contents during percolation.

The concentrated sulfuric acid (93% H_2SO_4) was pumped with a positive displacement piston pump, which was fed from a small weight-tank that was mounted on platform scales and connected to piping with a flexible metal hose (black iron). Concentrated sulfuric acid was handled successfully in a black iron line; a stainless steel check valve and a globe valve, similar to ones used in the hot water line, were used to close off the acid line from the digester contents.

The progress of hydrolysis was followed by sampling the hydrolyzate at regular intervals during the percolation period. After cooling, the densities of the hydrolyzate samples were measured by means of spindles calibrated in degrees Brix. A graph relating the degrees Brix of a solution with its reducing sugar content was prepared from determinations of both the densities and the reducing sugar contents of a large number of samples from an early test.

The product, as a solution of reducing sugars, left the digester through a 1-inch pipe, and the flow of the solution was controlled by means of $^1/_2$-inch diaphragm valve, which was regulated indirectly by the pressure in the digester. This pressure was transmitted through a corrugated, pressure-sensitive, Monel diaphragm to a pressure controller-recorder and thence to a hydrolyzate discharge valve. The solution then was flashed to atmospheric pressure in a Monel vessel, 3 feet in diameter and 4 feet high, placed immediately downstream of the hydrolyzate discharge valve.

Solutions of reducing sugars were handled successfully in brass lines with brass or bronze valves; apparently, the presence of sugars greatly inhibited the corrosive effect of the sulfuric acid.

In early pilot plant operation considerable difficulty was experienced from deposition of resinous sludges in the bottom of the flash tank, in the line that connected the flash tank to the neutralizer tanks, and in the neutralizer tanks. This sludge, which was formed during hydrolysis, appeared to be fluid at the temperatures of the hydrolyzate before flashing, but it solidified to a brittle solid at temperatures in the neighborhood of 200° F. The sludge in the pilot plant was controlled by insulating the flash tank to keep the sludge fluid and by installing a trap in which most of the sludge was collected. Subsequently, operating conditions were identified that decreased the formation of sludge.

At the end of the percolation period the remaining solution was drained to the neutralization tanks and the lignocellulose residue from hydrolysis was blown out through a motor-operated process valve, of a type commonly used for discharge of pulp in the manufacture of paper, to a collecting cyclone. An 8-inch iron pipe with sweeping elbow turns was used to connect the valve to the cyclone collector. The cyclone discharged into a portable bin that was serviced periodically by a pickup truck.

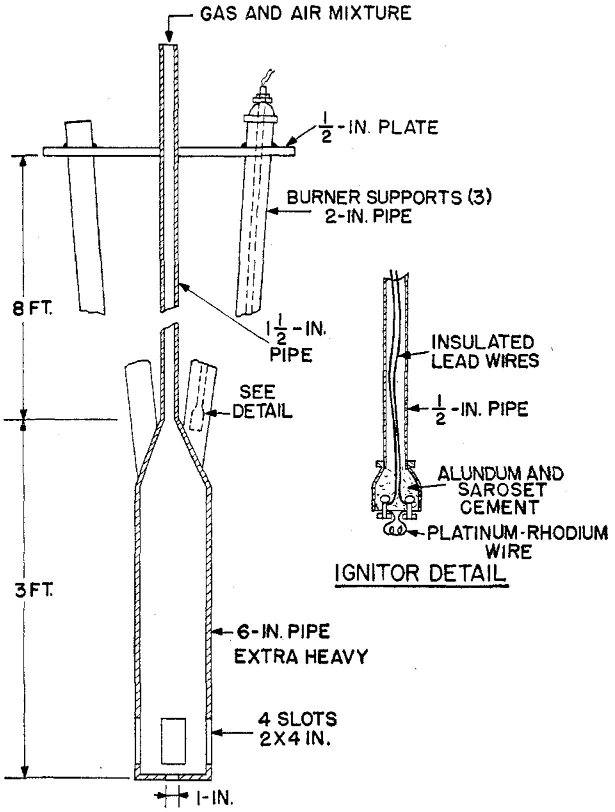

Figure 5. Submerged Combustion Burner

In recycle tests the dilute sugar solution obtained during the last portion of a test was stored in a steel tank lined with an acid-proof material. This solution was heated to about 275° F. through injection of steam and was used for submerging a charge of fresh chips in a successive test. A bronze pump and brass line handled the recycle solution satisfactorily.

Neutralization of Hydrolyzate. The hot sugar solutions (about 200° F.) were neutralized to a pH of 3.7 to 3.9 with lime or limestone (−100 mesh) in open steel tanks, 6 feet in diameter and 10 feet high. The contents were agitated by means of air spargers, and a vibrating feeder was used to introduce the lime or limestone. When limestone was used some foaming of the contents was observed. However, the foaming was not serious as long as the limestone was added gradually and a freeboard of about 2 feet in the neutralization tanks was adequate. The slurries settled rapidly, and laboratory tests showed that they could be centrifuged easily. A rotary, vacuum filter gave satisfactory filtering rates

Table II. Data Sheet B—Acid and Water Consumption, pH, and Reducing Sugar Concentration of Hydrolyzate for Typical Pilot Plant Test

Time (1/26/51)	Acid Used, Lb.		Water Used, Gal.		Hydrolyzate Samples			
	Reading	Difference	Reading	Difference	Time	pH	° B./° C.	Reducing sugar, %
10:00	262.0	..	.....	..	11:08	1.32	7.8/23.3	5.5
10:05	254.5	7.5	.....	..	11:18	1.53	9.4/22.6	6.9
11:03	310	..	436,625	..	11:28	1.75	9.2/22.8	6.7
11:08	306	4	436,710	85	11:38	1.78	8.3/22.9	5.9
11:23	293	13	.....	..	11:48	1.55	7.7/23.4	5.4
11:38	279	14	.....	..	11:58	1.37	7.7/23.3	5.4
11:53	266	13	.....	..	12:08	1.28	8.0/23.7	5.7
12:08	252	14	437,820	1110	12:18	1.37	8.5/23.7	6.1
12:23	239	13	.....	..	12:28	1.46	7.6/23.6	5.4
12:38	225	14	.....	..	12:38	1.44	7.2/24.0	5.0
12:53	212	13	.....	..	1:08	1.26	5.9/24.3	3.9
1:08	198	14	438,930	2220	1:38	1.18	4.8/24.9	3.0
1:23	185	13	.....	..	2:08	1.13	3.0/25.2	1.4
1:38	171	14	.....	..	...	..	......	...
1:53	168	13	.....	..	Tank I	3.8	8.7/25.8	6.4
2:08	144	14	439,035	3325	Tank II	3.8	6.0/25.9	4.1
2:19	133.5	10.5	440,250	3625	Recycle	1.13	3.1/24.4	1.5

with hot slurries, but cold slurries filtered slowly. The slurries were settled for about 8 hours, the supernatant was pumped off, and the sludge, which contained 3 to 4% of the reducing sugars produced, was discarded to the sewer. In a commercial plant sludge would be centrifuged and the loss at this point would be negligible.

50% Molasses Was Produced by Submerged Combustion and Vacuum Evaporation

In the early part of the pilot plant study, dilute sugar solutions were concentrated to molasses by submerged-combustion evaporation alone. Although this method utilized the fuel efficiently and caused no scaling difficulties, the recovery of reducing sugars averaged only about 60% when producing molasses containing 40 to 42% reducing sugars, and losses increased rapidly if further evaporation was attempted. Most of the sugar losses occurred after the solution in the evaporator reached a concentration of about 25% reducing sugars. Further losses were incurred in filtering the 40 to 42% molasses.

In an effort to produce molasses containing a higher percentage of reducing sugars and to realize greater recoveries, a two-stage evaporation procedure was devised. In this procedure submerged-combustion evaporation was used to increase the sugar concentration to 20 to 25%, the resultant solution was cooled, settled, and then filtered through 8-ounce duck cloth on a plate-and-frame filter. The filtrate then was concentrated to 45 to 50% reducing sugars by means of vacuum evaporation. Further filtration of molasses obtained in this manner was found to be unnecessary. This procedure permitted the evaporation of 80% of the water to be removed by a relatively inexpensive method and the completion of the evaporation by a method that was not destructive to the sugars. Also, filtration of the 25% solution was much faster than that of the more concentrated molasses. About 85% of the reducing sugars produced by hydrolysis was recovered in the molasses product.

The submerged-combustion evaporator consisted of a tank, 6 feet in diameter and 10 feet high, and had a conical bottom. By-product carbon monoxide gas was mixed with 5 to 10% of excess air and was burned under the surface of the solution in a 3-foot section of 6-inch standard iron pipe, which constituted the burner. Ignition of the fuel was accomplished through the use of an electrically heated platinum-rhodium glow coil. The dimensions of the burner, shown in Figure 5, were calculated using the average of volume, heat-release, and linear-velocity factors quoted by Walthall, Miller, and Striplin (*20*) for a number of pilot plant and commercial units. Dilute sugar solution was supplied to the evaporator at a constant rate by means of a constant-head feeding device.

The vacuum evaporator, a long-tube, natural circulation type, was designed and built at Wilson Dam. It had a heat exchange surface of 32 square feet and an evaporative capacity of 250 pounds of water per hour. Auxiliary equipment included a foam separator and spray-type condenser. Vacuum (20 to 22 inches of mercury) was provided by a steam-actuated, two-element, tube-jet air pump, and a barometric leg and a hot well were used to seal both the condenser and the vacuum tube jet. Product molasses was withdrawn by means of a rubber-impeller rotary pump that was driven by a variable speed air motor.

Analytical Methods. The reducing sugar content of hydrolyzate samples and of product molasses was determined by the method of Schaffer and Somogyi (*15*). The potential reducing sugar content of wood chips and the residual cellulose in the residues from hydrolysis were determined by first subjecting

Table III. Effect of Operating Conditions on Time of Hydrolysis and Yield and Concentration of Reducing Sugars in Hydrolyzate

			Holding		Percolation					Experimental Results		
Group	Reducing Sugar Content of Recycle, %	Packing Density, Lb./Cu. Ft.	Temp., ° F.	Duration[a], min.	Temp. rise, ° F./min.	Maximum temp., ° F.	Rate, gal./min./cu. ft.	Acid concentration, % H_2SO_4	Total Water Used, Lb./Lb. Dry-Wood Substance	Time of percolation, min.	Yield[b], % of potential reducing sugars	Concentration, % reducing sugars
					Comparison with Forest Products Laboratory Tests							
A[c]	0	14.7	302	10[d]	1	365	0.075	0.55	10.2	180	74.2	5.2
B	0	15.7	300	30	1	365	0.077	0.53	13.7	200	70.3	3.6
					Effect of Recycling							
C	0	15.3	275	30	3	374	0.091	0.56	12.4	170	76.3	4.3
D	1.8	16.1	275	30	3	375	0.091	0.54	10.1	191	75.6	5.0
					Effect of Temperature and Duration of Holding Period							
E	0	15.7	275	15	1	365	0.076	0.54	13.6	218	70.5	3.6
F	0	15.4	275	30	1.2	365	0.084	0.53	13.8	206	71.9	3.7
B	0	15.7	300	30	1	365	0.077	0.53	13.7	200	70.3	3.6
					Effect of Rate of Percolation							
G	0	14.5	275	30	1.5	365	0.065	0.55	12.3	215	66.7	3.7
H	0	14.0	275	30	1.5	365	0.081	0.53	14.3	195	72.2	3.8
I	0	15.0	275	30	1.5	365	0.092	0.54	14.0	190	73.3	3.9
D	1.3	16.1	275	30	3.0	375	0.091	0.55	10.1	191	75.6	5.0
J	1.4	15.6	275	30	3.0	375	0.108	0.53	10.0	155	74.8	5.2
					Effect of Rate of Temperature Rise							
F	0	15.4	275	30	1.2	365	0.084	0.53	13.8	206	71.9	3.7
H	0	14.0	275	30	1.5	365	0.081	0.51	14.3	195	72.2	3.8
K	0	14.8	275	30	3.0	365	0.089	0.53	13.9	190	72.3	3.9
D	1.8	16.1	275	30	3.0	375	0.091	0.55	11.1	191	75.6	5.0
L	1.6	16.6	275	30	4.9	375	0.092	0.54	9.7	179	77.7	5.7
					Effect of Maximum Temperature of Percolation							
K	0	14.8	275	30	3.0	365	0.089	0.53	13.8	206	71.9	3.7
C	0	15.3	275	30	3.0	374	0.091	0.56	12.4	170	76.3	4.3
L	1.6	16.6	275	30	4.9	375	0.092	0.54	9.7	179	77.7	5.7
M	0.9	16.1	275	30	5.0	385	0.090	0.53	7.9	148	77.3	7.0
					Effect of Acid Concentration							
N	0	14.1	275	30	3.0	367	0.091	0.43	13.8	212	64.0	3.1
K	0	14.8	275	30	3.0	365	0.089	0.53	13.9	190	72.3	3.9
D	1.8	16.1	275	30	3.0	375	0.091	0.55	10.1	191	75.6	5.0
O	1.7	16.1	275	30	3.0	375	0.089	0.81	10.1	166	73.9	5.6

[a] In TVA tests, 33 minutes were required for filling digester; temperature during filling period was same as shown for holding period.
[b] Basis: dry-wood charge, including bark.
[c] Average of data for 33 tests made at Forest Products Laboratory using oak mill waste (*17*).
[d] Time required for filling digester and for holding was 30 minutes of which about 20 minutes were needed for filling (*17*).

these materials to quantitative saccharification (*14*) and analyzing the resultant solutions for reducing sugars by the method of Schaffer and Somogyi.

Moisture determinations were made on samples of chips as charged to the digester; the standard toluene distillation method was used.

After the initial operating problems were resolved, the pilot plant was operated 8 hours per day and 5 days per week. Because of the limitations in the capacity of evaporative equipment and in the number of operators and laborers that could be assigned to the project, it was possible to process only three batches of wood chips per week to solutions containing 25% reducing sugars. After approximately 2000 gallons of 25% solution was accumulated, only the evaporative section of the pilot plant was operated to concentrate this solution to 50% molasses. During hydrolysis tests the pilot plant personnel consisted of a chemical engineer, two nonprofessional operators, and one laborer. The engineer was responsible for the general adherence to the desired conditions of operation and for the analyses that controlled the operation. The nonprofessional operators and laborer hogged the wood, charged the digester, operated the equipment, recorded the data, and were responsible for housekeeping in the pilot plant. One nonprofessional operator was required for carrying out the concentration step.

The data collected in the pilot plant are illustrated in Tables I and II for a typical test.

Recycling and Rate and Temperature of Percolation Were Important Process Variables•

When wood chips are treated with dilute sulfuric acid at elevated temperatures and pressures, the wood celluloses are hydrolyzed into simple five- and six-carbon sugars. These sugars decompose to humic substances of indefinite composition (*16*) so that the net yield of reducing sugars is the difference between the quantity produced by hydrolysis and the quantity decomposed. The rates of cellulose hydrolysis and of sugar decomposition were redetermined a few years ago by Saeman (*13*) who showed that the rates of both reactions increased with increase in temperature and acid concentration. Because hydrolysis increased faster than sugar decomposition, net yields of sugar could be increased by treating the wood with acid of higher concentrations at higher temperatures, provided the sugars could be removed from the reaction zone rapidly. Although the rates of hydrolysis and decomposition are known for a wide range of temperatures and concentrations, the yields and concentrations of reducing sugar obtainable when dilute acid is percolated through a digester filled with wood chips cannot be calculated. They are subject to experimental determination, because of the complexity of the system and of the effect of diffusion in the process.

As a result of extensive experimental work, Harris and his coworkers formulated conditions that represented a close approach to the best practical conditions for hydrolysis of Douglas fir (*7*). The pilot plant tests reported in this paper were made to determine the yield and concentration of reducing sugars obtainable under the conditions of the Madison wood sugar process from hardwood chips and to explore the effect of changes in operating conditions on (*a*) the time required to exhaust the cellulose content of the charge, (*b*) the yield and concentration of reducing sugars, and (*c*) the operability of the plant.

In most of the pilot plant tests the charge was comprised of chips from cordwood. The wood used was cut at three locations in Tennessee and was characterized by the following approximate distribution of species: oak, predominantly black and red, 85%; hickory, 10%; and miscellaneous hardwoods, including black gum, dogwood, sourwood, and maple, 5%. Tests showed that hydrolysis of wood from the different locations gave comparable results. The chips contained on the average 57.7% of potential reducing sugars. This value was calculated from the potential reducing sugar content of bark-free, dry-wood substance and of bark, 63.6 and 37.5%, respectively (*15*), and from the average bark content of the charge, 22.8% (dry basis). Hydrolysis yields given in this paper are on the basis of dry-wood charge, including bark.

The effects of the recycling of dilute solutions and of experimental variables—temperature and duration of the holding period, rate of percolation, rate of temperature rise, maximum temperature of percolation, and acid concentration—are shown by the data in Table III. The data for 50 hydrolysis tests, in which desired conditions of operation were maintained, are arranged into 15 groups, according to the conditions used. The values given are averages of those for individual tests. Average results of 33 tests made at the Forest Products Laboratory using oak mill waste (*17*) are included for comparison as group A. Although efforts were made to stop the percolations when the concentration of reducing sugars in the hydrolyzate reached 1%, the terminal concentration deviated somewhat from that value in a number of tests. To permit direct comparison of the data, all the results presented in Table III were adjusted to a terminal concentration of 1%.

Comparison with Forest Products Laboratory Results. The results of the Forest Products Laboratory tests reported by Harris for oak mill waste (group A in Table III) were compared with the results of pilot plant tests made under closely similar conditions, group B. The comparison shows that the hydrolysis of hardwood chips in the pilot plant resulted in lower yield of reducing sugars, 70.3% compared with 74.2%, and that longer percolation was required to exhaust the cellulose content of the charge —namely, 200 and 180 minutes, respectively. The extended percolation caused the use of a larger amount of water and resulted in lower concentration of reducing sugars (3.6 and 5.2%) for the pilot plant tests and for the Forest Products Laboratory tests, respectively.

Recycling of Dilute Solutions. In an effort to increase the concentration of solutions obtainable by hydrolysis of hardwood chips, dilute sugar solutions produced in the latter portions of percolation were recycled to a charge of fresh chips in a subsequent test. The data of groups C and D show that recycling increased the concentration of reducing sugars by about 15%; there was no apparent effect on yield.

Effect of Holding. The desirability of preceding percolation with a holding period was indicated by the experience of Forest Products Laboratory (*7*). The holding period permits the hydrolysis of the hemicellulosic portion of the charge to take place under mild conditions, which are not destructive to the sugars produced. Inadequate extraction of hemicellulose sugars in some of the early tests made in our pilot plant without a holding period resulted in excessive formation of sludge and caused difficulties in operation. In some of these tests, in which the charge was preheated with steam to 250° to 265° F. and then submerged and held at these temperatures, the concentration of sugars in the hydrolyzate issuing from the digester immediately following the holding period was below 2%, indicating that the hydrolysis of hemicellulose was slow at those temperatures. Variation of the temperature of holding between 275° and 300° F. and the duration of the holding period between 15 and 30 minutes in groups E, F, and B showed that under these conditions the yields and concentrations of reducing sugars were comparable. Therefore, a holding period of 30 minutes at 275° F. was selected for use in most of the pilot plant tests reported.

Effect of Rate of Percolation. The effect of rate of percolation, which determines the retention of sugars in the digester, on yield and concentration of reducing sugars is shown by the data of groups G, H, and I (without recycle) and of groups D and J (with recycle). Increase in percolation rate from 0.065 to 0.081 gallon per minute per cubic foot of digester volume, corresponding to retentions of approximately 90 to 70 minutes, respectively, resulted in (*a*) increased yield of reducing sugars, (*b*) a reduction of time necessary to exhaust the cellulose content of the charge by attaining the maximum temperature in less time, and (*c*) a slight increase in the concentration. Further increase in percolation rate to 0.108 gallon per minute per cubic foot, corresponding to a retention of about 50 minutes, further decreased the time of percolation but had only a slight effect on yield and concentration. In the range of percolation rates tested, considerably less sludge was formed at higher rates, and sludge was carried through the lines and deposited in the sludge trap provided for that purpose.

Effect of Rate of Temperature Rise. As shown by the data of groups F, H, and K (without recycle) and of groups D and L (with recycle), increase in the rate of approach to the maximum temperature of percolation decreased the time required for the percolation and effected a slight increase in yield and in concentration. With the use of a holding step, in which the easily hydrolyzable hemicellulose and the resultant sugars were removed from the charge before the temperature was raised, there appeared to be no reason for limiting the rate of temperature rise for any other reason than the physical limitations of the heat transfer equipment.

Effect of Maximum Temperature of Percolation. As expected from the kinetic data, increase in the temperature of percolation, groups K and C (without recycle) and groups L and M (with recycle), caused a decrease in the time required to exhaust the cellulose content of the charge and an increase in the concentration and yield of reducing sugars. In test group M an average yield of 77.3% of reducing sugars was obtained in 148 minutes at a concentration of 7.0% when a percolation temperature of 385° F. was reached at a rate of 5° F. per minute.

The use of temperatures above 385° F. for hydrolysis of hardwood chips was not feasible, because it was impossible to separate the hydrolysis residue from the solution by means of the screens with which the digester was equipped (16-mesh). It appeared that at the higher temperatures the hydrolysis proceeded so far that even the bottom portion of the charge lost its fibrous structure and the lignin was carried with the solution. The rapid rate of water flow necessary to remove the sugars produced at this higher temperature was perhaps also a factor.

Effect of Acid Concentration. Increase in acid concentration had a similar, though lesser effect than the increase in temperature. Data of groups N and K (without recycle) and of groups D and O (with recycle) showed that an increase in acid concentration from 0.43 to 0.53% H_2SO_4 increased both the yield and concentration and decreased the time of percolation. Further increase up to about 0.8% H_2SO_4 decreased the time of percolation and resulted in further increase in concentration but was attended by a slight decrease in yield.

In another group of tests (not included in the table) the wood chips were extracted with hot water at 225° to 250° F. for about 30 minutes prior to hydrolysis in an attempt to improve the quality of molasses by pre-extraction of tannin. This procedure failed to extract enough tannin to affect the quality of molasses but resulted in a reduced yield of reducing sugars due to the hydrolysis of some hemicellulose during the attempted extraction in the presence of wood organic acids.

Conditions for Highest Yield and Concentration Also Minimized Formation of Sludge

Formation and deposition of sludges in the various parts of the equipment were the principal difficulties encountered. The formation of sludge was especially pronounced when accidental in-

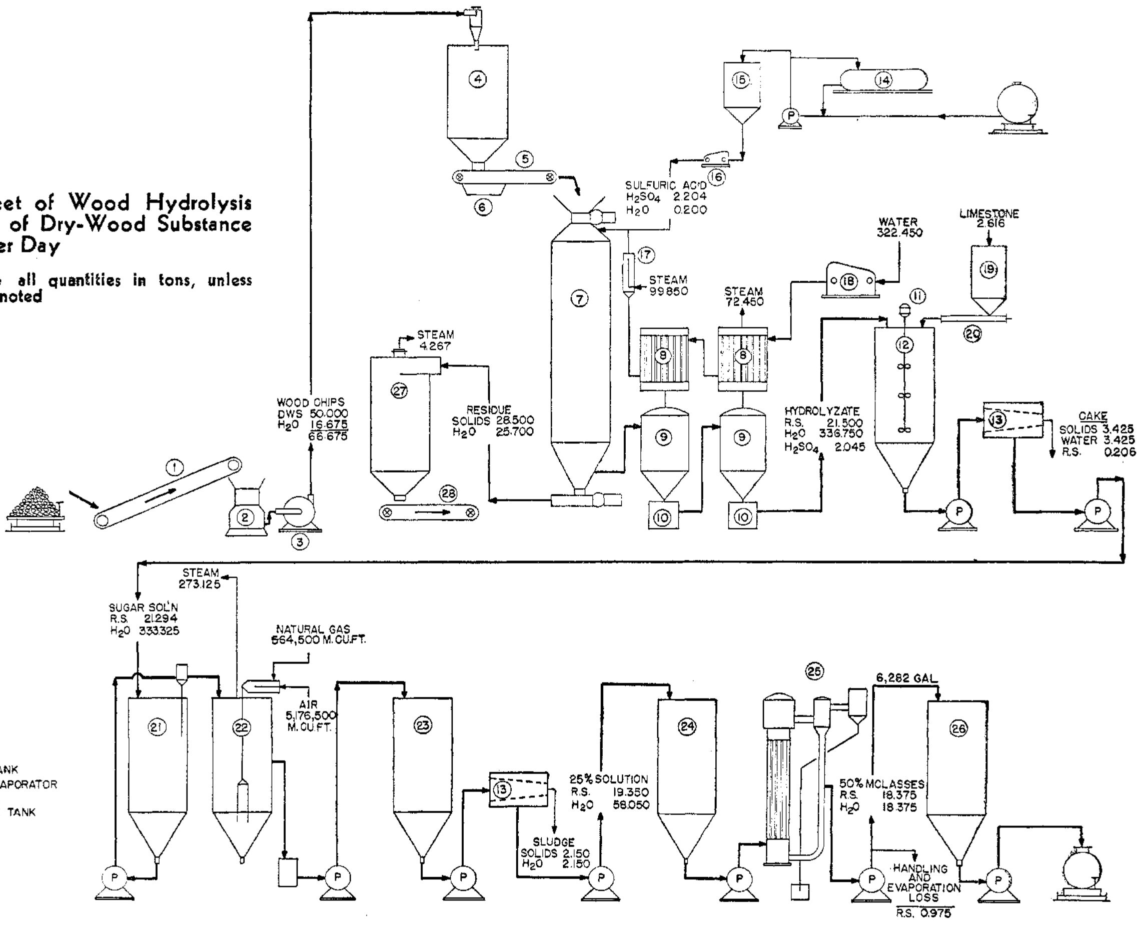

Figure 6. Flow Sheet of Wood Hydrolysis Plant Using 50 Tons of Dry-Wood Substance per Day

Basis: 24-hour operation; all quantities in tons, unless noted

EQUIPMENT ITEMS

1	CORDWOOD CONVEYOR
2	WOOD HOG
3	CHIP BLOWER
4	CHIP STORAGE BIN
5	CHIP CONVEYOR
6	FEEDOWEIGHT
7	DIGESTER
8	FLASH TANKS
9	HEAT EXCHANGERS
10	SLUDGE SEPARATORS
11	AGITATOR
12	NEUTRALIZER
13	CENTRIFUGE
14	ACID STORAGE TANK
15	ACID FEED TANK
16	ACID FEED PUMP
17	STEAM INJECTION HEATER
18	WATER FEED PUMP
19	LIMESTONE STORAGE TANK
20	LIMESTONE FEEDER
21	DILUTE SOLUTION STORAGE TANK
22	SUBMERGED COMBUSTION EVAPORATOR
23	25% SOLUTION STORAGE TANK
24	CLARIFIED SOLUTION STORAGE TANK
25	VACUUM EVAPORATOR
26	MOLASSES STORAGE
27	LIGNIN RECEIVER
28	LIGNIN LOADER
P	TRANSFER PUMP

terruption of normal percolation procedure would cause excessively long retention of sugar solutions in the digester. Fortunately, the conditions that minimized sludge formation also gave highest yield and concentration of sugars.

Table IV. Estimated Investment Cost for Wood Molasses Plant

(Capacity: 50 tons dry-wood substance per day)

Wood storage and charge preparation	$ 48,400	
Hydrolysis	114,200	
Neutralization and evaporation	105,600	
Total cost of installed process equipment	$268,200	(A)
Process piping, 20%[a] of A	$ 53,600	
Instrumentation, 7%[a] of A	18,800	
Building, 10%[a] of A	26,800	
Auxiliary facilities, 25%[a] of A	67,000	
Outside lines, 5%[a] of A	13,400	
Total physical plant cost	$447,800	(B)
Engineering and construction overhead, 20%[a] of B	$ 89,500	
Contingencies, 20%[a] of B	89,500	
Total plant cost	$626,800 or $627,000	

[a] Percentage used was taken from Chilton (*1*).

As a result of experience in the operation of the pilot plant, it is believed that sludge formation can be tolerated in the process provided that the digester outlet is connected to the flash tank with a short line, that the regulating valve can open wide to permit occasional purging of sludge accumulation, and that a trap is used for sludge removal immediately after flashing. It is believed that availability of steam at a pressure higher than that maintained in the digester would be helpful in plant operation because this would facilitate periodic purging of the hydrolyzate line.

In general, the pilot plant operated satisfactorily. The steam-water heater used to heat water for percolation to about 300° F. was found to operate with an over-all heat transfer coefficient of 210 to 360 B.t.u. per hour per square foot per ° F. of mean temperature difference for linear velocities of 1.5 to 2.2 feet per second, respectively.

The radiation-type carbon monoxide–fired heater was designed to heat the water to 385° F. on assumption that 44% of the heat would be absorbed by the water. It was found that 42.8% of the heat of combustion of carbon monoxide was actually utilized in the heating of the water.

In the submerged combustion evaporator almost 100% of the heat of combustion of the fuel (by-product carbon monoxide) was utilized in heating the solution to the boiling point (180° to 185° F.) and in evaporating the water. The unit evaporated 1650 pounds of water per hour and used 100 cubic feet per minute of 290 B.t.u. per cubic foot gas. The vacuum evaporator was of conventional design and operated with a close approach to its design capacity, 250 pounds of water evaporated per hour.

Separation of hydrolysis residues from the sugar solution in the pilot plant digester was accomplished by means of the conical screen that supported the charge. This screen required cleaning after about 50 tests. The cleaning procedure involved dismantling and removal of the screen and was time-consuming. In several tests the screen was removed from the digester and the hydrolyzate was withdrawn through two screened nozzles inserted into the digester. This arrangement increased the space available for the chips and was an effective means of removing the solution.

On the basis of experimental results and observations discussed here, the following procedure is believed to give the maximum yield of reducing sugars concomitant with highest concentration and shortest percolation in an operable plant when using mixed hardwood chips:

1. Pack the digester to a charge density of about 16 pounds per cubic foot and submerge the chips by filling the digester with a hot (275° to 300° F.), dilute acid and sugar solution containing about 0.5% sulfuric acid and 1% of reducing sugars from a previous percolation cycle. (In a plant installation at least two and preferably three digesters should be used, the dilute hydrolyzate drained at the end of the cycle from one flowing to another digester.)
2. Hold the contents for about 30 minutes and then percolate with 0.5% sulfuric acid at a rate of about 0.1 gallon per minute per cubic foot of digester volume.
3. Increase the temperature of the acid entering the digester at a rate of about 5° F. per minute to a maximum of 375° to 380° F. and hold temperature at that level until the end of the percolation, 150 to 180 minutes.
4. Recycle the solution remaining in the digester to fresh charge of chips in another digester.

Under these conditions a yield of about 75% of the potential reducing sugars and a concentration of about 6% can be expected.

Molasses Could Be Produced Commercially for 20 to 25 Cents per Gallon

An economic evaluation was made of the process for production of molasses by wood hydrolysis formulated on the basis of pilot plant results. The evaluation comprised estimates of investment cost, production cost, and sale price of molasses and a comparison of that price to current market prices of competitive materials.

Estimate of Investment Cost. In these estimates, which are summarized in Table IV, it was assumed that the plant would process 50 tons of dry-wood substance per day to a molasses containing 50% of reducing sugars. This capacity approaches closely the quantity of wood waste believed to be available in several manufacturing centers in the Tennessee Valley and elsewhere in the United States. Equipment requirements are illustrated diagrammatically in the flow sheet of Figure 6, which includes the quantities of materials in process for 24 hours.

The installed costs of equipment items were obtained from recent cost data in TVA files and from correlations published by Chilton (*1*) and have been corrected to an *Engineering News-Record* index of 542, as of July 1951 (*3*). The percentages of total installed equipment cost used in estimating the cost of process piping, instrumentation, building, auxiliary facilities, and outside lines are those recommended by Chilton (*1*) and are applicable to a mixed processing plant having an average amount of automatic controls and comprising a closely integrated major addition to an existing manufacturing facility. Outdoor construction was assumed and an engineering and construction overhead and a contingency of 20% of total physical cost, each, were used. These percentages relate to a plant characterized by an average labor/materials ratio and a design subject to minor changes only.

Estimate of Production Cost. It is not possible to formulate a rigid estimate of production cost that would apply generally because unit costs vary in different locations and organizations. Nevertheless, an estimate of production cost for a Memphis, Tenn., location was made for purpose of illustration and to permit comparison with market prices of competitive commodities. The Memphis location was selected because it is both a major center of wood-using industries and a commerical center that serves a large agricultural area that may be considered to be a potential market for wood molasses.

The production cost estimate, summarized in Table V, showed that wood molasses could be produced at a cost of 20.4 to 23.8 cents per gallon for the two assumptions as to the cost of wood used in the process: $4.47 per cord (equivalent to coal at $5.50 per ton) and $12 per cord delivered to plant site.

Comparison with Blackstrap Molasses and with Corn. For the purposes of this comparison the sale price of wood molasses has been estimated by adding to the production cost (Table V) sales expense (5% of production cost), administrative expense (1.5% of capital investment), federal corporate tax (at the applicable schedule), and return on investment after payment of taxes. The capital investment was taken as the sum of total plant cost, the cost of 2 weeks' supply of raw materials, and of cash equivalent to 1 month's production cost, exclusive of raw materials cost. The resultant sale price of 50% wood molasses (in tank cars), calculated for a range of assumed rates of net return on investment, has been plotted in Figure 7, for the two assumptions as to the cost of wood.

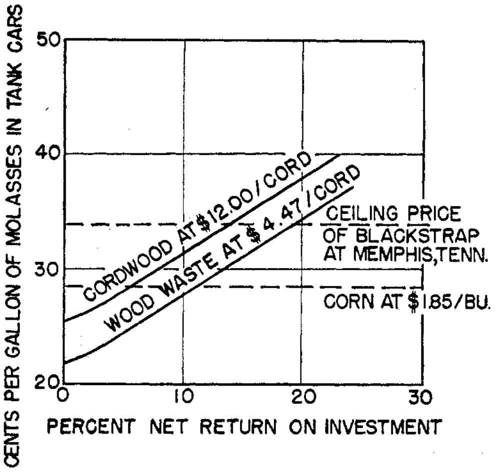

Figure 7. Estimated Sales Price for Wood Molasses *vs.* Rate of Net Return on Investment

Because wood molasses can be used for production of mixed feeds and in ensilage, just as blackstrap molasses is used, a comparison with the market price of blackstrap molasses is indicated. The October 1951 ceiling price of blackstrap at Memphis, Tenn., adjusted for transportation cost from port of entry is 33.86 cents per gallon (*5*) and is shown in Figure 7. This comparison indicates that a 14% net return on investment could be realized even with wood at the higher value. However, the price of blackstrap during the past decade has fluctuated between 8.6 and 41.0 cents per gallon at Memphis. The price was controlled at about 20.5 cents per gallon during World War II. Any guess as to the future price would be extremely hazardous.

An alternative basis of comparison is indicated by the use of molasses for cattle feeding, a use that is expanding rapidly and permits equating the price of molasses to an equivalent amount of corn, which it can replace in mixed feeds at a rate of 6.5 gallons for 1 bushel of shelled corn (*19*). Accordingly, the cost of the equivalent amount of corn, using the July 1951 price of $1.85 per bushel, is shown in Figure 7 also.

The use of corn for reference appears reasonable, because under the parity system, the price of corn would reflect the current prices and costs in industry, which, in turn, would determine the production costs of wood molasses. The comparison with corn, at $1.85 per bushel, indicates that production of wood molasses from cordwood at $12 per cord would permit a return of approximately 5%. Production of wood molasses from wastes available at a cost equivalent to that of coal may be expected to give a return of approximately 11%.

Acknowledgment

The authors wish to acknowledge the advice and guidance of T. P. Hignett, who was in the administrative charge of the project. A. B. Phillips assisted in the design and supervised the construction of the pilot plant, and W. D. Sandberg assisted in the preparation of the cost estimates used in the economic evaluation. R. C. Mullins and Inez J. Murphy performed the analytical work.

Table V. Estimated Production Cost[a] of Wood Molasses at Memphis, Tenn.

Capacity: 50 tons dry-wood substance per day (2,041,666 gallons of 50% molasses per year, 325 operating days); estimated total plant cost, $627,000

		Cost per Gallon of 50% Molasses in Tank Cars, Cents
Direct production costs		
A. Raw materials		
Sulfuric acid (66° Bé.), lb.	0.753	0.94
Limestone (53% CaO), lb.	0.833	0.25
Wood (basis A[b]), cords	0.004522	2.02
Wood (basis B[c]), cords	0.004522	5.43
B. Utilities		
Steam, lb.	49.23	3.30
Air, cu. ft.	824	0.82
Natural gas, cu. ft.	89.9	1.46
Water, gal.	16.8	0.02
Electricity, kw.-hr.	0.57	0.36
C. Operating labor[d], man-hr.	0.0153	2.45
D. Supervision	10% of operating labor	0.25
E. Payroll overhead	20% of labor and supervision	0.54
F. Maintenance	5% of plant cost	1.51
G. Supplies	15% of maintenance	0.23
Indirect production costs		
Technical and analytical services, transportation, medical services, etc.	60% of labor, supervision, and maintenance charges	2.54
Fixed costs		
A. Depreciation	10% of investment	3.07
B. Local taxes	1% of investment	0.31
C. Insurance	1% of investment	0.31
Total production cost	Basis A	20.4
	Basis B	23.8

[a] Procedure outlined by Newton and Aries (*10*) was followed.

[b] Based on use of wood waste at a cost derived from price of coal (wood waste at $4.47 per cord, equivalent to coal at $5.50 per ton).

[c] Based on use of cordwood at $12 per cord, delivered.

[d] Based on an operating labor force of three men per shift and two additional men during the day shift, when chips for 24 hours of operation would be prepared.

E. E. Harris of the Forest Products Laboratory closely followed the work reported in this paper and made many helpful suggestions, which are gratefully acknowledged.

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Received for review April 23, 1952. Accepted May 15, 1952.