A REVIEW OF WOOD SACCHARIFICATION PROCESSES IN THE UNITED STATES PRIOR TO WORLD WAR II

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A REVIEW OF WOOD SACCHARIFICATION PROCESSES IN THE UNITED STATES PRIOR TO WORLD WAR II[1,2]

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The great interest that has once again been focused upon processes for the conversion of wood and waste sulfite liquor into ethyl alcohol because of recent improvements in them makes pertinent a review of their industrial development in this country from their inception until up to the outbreak of the present war. Full and detailed information regarding these early efforts is not available, but enough is at hand to indicate that from the earliest days this interesting development has received the serious consideration of many courageous chemists and chemical engineers.

Sawdust has always been regarded as an outstanding example of waste and, as a consequence, countless investigators have sought to convert it into something new and more useful. Chemical conversion in particular has appeared to offer hope of changing an almost worthless material into products of great value. Since wood is composed of approximately 52 percent cellulose, 21 percent hemicellulose, 23 percent lignin, and about 4 percent extractives, it is obvious that most attention should be given to the cellulosic fraction.

In order to describe properly the work that has been done in this country, it is necessary to review briefly the research of early European experimenters, since they did most of the basic research upon this subject.

Braconnot (1), in 1819, first discovered that cellulose could be converted into fermentable sugar by means of concentrated acid. Since then many investigators have studied this problem in considerable detail. Quite naturally the earliest efforts were directed toward the use of concentrated

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[3]Maintained at Madison, Wis., in cooperation with the University of Wisconsin.

acids at atmospheric pressure. To date all efforts to use concentrated acids, with the exception of those of Bergius in Germany and possibly Giordani in Italy, have failed to meet with success, due largely to the difficulties encountered in the recovery of the large amounts of acid required, or to the inability of the equipment to withstand the corrosive action of strong acids. In spite of several efforts, particularly that of the Ford Motor Company in 1916, in which 40 to 42 percent hydrochloric acid was the dissolving agent, no successful developments using concentrated acid have been reported in the United States.

In 1892 Lindsey and Tollens in England (4) studied the action of dilute acid on wood. Mathaus followed in 1893, but not until the period of 1894-1898 were any important advances made. During this period Simonsen (9) experimented with the use of dilute sulfuric acid under what was then considered high pressures. By cooking chipped wood or sawdust for 15 minutes in the presence of 0.5 percent sulfuric acid at a pressure of approximately 9 atmospheres, he obtained a yield of 26.5 percent sugar. Upon fermentation of the sugars, Simonsen was able to recover 7.6 liters of absolute alcohol from 100 kilograms of dry wood substance. A small experimental plant was erected at Oslo but, unfortunately, Simonsen used too large quantities of water which, with the condensed direct steam, resulted in a great dilution of the resulting sugars and ethyl alcohol. As a result, the plant soon ceased operations. This work of Simonsen's should be considered as classic, since practically all recent work has confirmed his early findings. It is unfortunate that he was unable to industrialize his process in Europe.

In 1899 and 1900 Classen (2) reported that he had developed a process in which sulfurous acid was used as the hydrolyzing agent. He obtained patents in all leading countries, and a great deal of work was done in the attempt to commercialize his process both in the United States and abroad. The American rights to this process were purchased in 1903 by the Classen Lignum Company of Chicago, which erected an experimental plant with a capacity of 2 tons of dry sawdust per day in Highland Park, Illinois.

The research at Highland Park eventually resulted in the erection of a commercial-scale plant at Hattiesburg, Mississippi. This plant, which is reported to have cost $250,000, never operated successfully according to Ruttan (7).

The plant included the following elements:

1. An acid apparatus in which the solution of sulfurous acid was prepared and in which the excess of sulfur dioxide after use could be reabsorbed and saved for further utilization.

2. A revolving cylinder, 30 feet long and about 36 inches in diameter, which formed the converter or digester.

3. An exhausting battery consisting of a series of tanks in which the sugar was washed from the partly converted sawdust by hot water.

4. Neutralizing vats in which the various acids remaining in the saccharine liquid were neutralized by calcium carbonate.

5. Fermentation vats and a still in which the process was completed as in an ordinary distillery.

The wood waste was introduced into the digester (which it nearly, but not completely, filled) made of iron and lined with lead to prevent corrosion by the sulfuric acid, and surrounded by a steam jacket by which it was heated. This revolving cylinder had a capacity of about 2 tons. To the charge of wood waste was added an amount of a nearly saturated solution of sulfur dioxide corresponding to about one-third the weight of the raw material. The drum was closed air-tight and steam turned into the jacket while the whole slowly revolved. The temperature of the interior was thus slowly raised to 290° to 300° F., and the pressure to about 100 pounds. After from 4 to 6 hours, the sulfurous acid and steam were blown off into the absorbing tanks and the sulfur dioxide thus partially recovered. The cover was removed and the contents emptied, looking then very like finely ground coffee. This finely divided, treated wood was conveyed to the exhaustion batteries and the sugar extracted. The liquid obtained contained from 350 to 400 pounds of sugar for each ton of raw material treated. The next steps were to neutralize the acid liquid, allow it to clear by subsidence, pump it into the fermentation vats, ferment it by yeast, and distill the product in the usual way. It was claimed for the process that each ton of wood waste gave about 18 to 20 gallons of absolute alcohol.

The difficulties in the way to success for this process are explained to be: (1) The length of time necessary to convert 1-1/2 to 2 tons of wood, this requiring from 4 to 6 hours; (2) the quantity of acid required; (3) the prolonged action of so much acid and water in the rotating converter, which reduced the wood to a very fine powder and formed much sulfuric acid which, acting on the sugar and other substances, produced gums and caramels and thereby made the complete extraction of the sugar from the residue very tedious and expensive; (4) the buckling and breaking of the lead lining of the converter, which had to be repaired after two or three operations and proved a very great source of delay and expense.

Two chemical engineers, M. F. Ewen and G. H. Tomlinson, who had been associated with Classen in Aachen and at Highland Park, became convinced that the Classen process was not workable and set about modifying it. The results of their further researches indicated that by the use of direct steam the time could be greatly shortened and that the sugar could be much more readily removed. An experimental plant was erected at Chicago Heights, Illinois, by the Wood Waste Products Company, which later became the Standard Alcohol Corporation. Tomlinson and Ewen had obtained patents upon their modification of the Classen process, and these were acquired by the Wood Waste Products Company. Their modified Classen process depended upon the use of direct steam instead of indirect as used in Hattiesburg and by the Compagnie Industrielle des Alcool des l'Ardeche, a concern that attempted unsuccessfully to operate in France in 1904.

The converter in use at Chicago Heights was a revolving steel cylinder 12 feet long by 8 feet in diameter, lined with ceramic tile. It had a capacity of 2 tons of shavings or 3 tons of sawdust. The cylinder was completely filled with wood waste, and gaseous sulfur dioxide was introduced directly into the charge to the extent of 1 percent by weight of the dry wood. Live steam was then introduced, and the material was cooked for 10 to 15 minutes, or until the desired temperature was reached. The steam was then shut off and the digester rotated for 40 to 45 minutes, temperature and pressure being kept constant. At the end of the cook the steam was blown off and the residue removed and extracted with water. This process, however, was never used commercially. It seems that during this period of experimentation Tomlinson and Ewen became convinced that sulfuric acid was a better hydrolyzing agent than sulfurous acid, and they directed their attention toward its use. As a result, the Standard Alcohol Corporation erected a plant at Georgetown, South Carolina. In the meantime, the Classen Chemical Company had interested western capital in the erection of a plant at Port Hadlock, Washington.

The plant at Port Hadlock was equipped with six digesters of the same size and shape as those used in the French plant previously referred to (3). Here again indirect steam was used for heating. Sawdust and enough water were added through a manhole into the space between the tubes to raise the moisture content to about 45 percent. Anhydrous sulfur dioxide was then added and the mixture was cooked at 75 to 100 pounds of pressure. The cost of conversion was excessively high because the digester corroded rapidly. The time necessary to heat the charge was very long, and it was necessary to replace the low-pressure steam with high-pressure steam in the outer jacket in order to prevent sulfurous acid gas from leaking into the digester jacket. The extraction equipment was inefficient, as the modern type of diffusion battery was not used. The plant was well built and much of the equipment was imported from France at high cost.

This plant never operated successfully, in spite of great efforts to utilize the residue as a stock food, and soon passed out of existence.

The plant that was erected at Georgetown was operated successfully by the Standard Alcohol Corporation under the direction of Ewen and Tomlinson. This plant was later acquired by E. I. duPont de Nemours and Company and operated until early 1913, when a fire destroyed the lumber mill from which it received its waste wood. The lumber mill was rebuilt in 1914 and the plant operated continuously until some time after the close of World War I. A complete description of this plant is given by Rudolf von Demuth (11) who acted as a consultant during its early operation. It is interesting to note that the conditions recommended by Simonsen were employed, notably a time of inversion of 15 minutes, an acidity of 0.5 percent sulfuric acid, and a steam pressure of about 9 atmospheres.

After disposing of the Georgetown plant to the duPont Company, the Standard Alcohol Corporation enlisted new capital, mostly foreign, for the erection of a plant at Fullerton, Louisiana. This plant, which did not differ radically from the one at Georgetown, was designed to produce 5,000

gallons of 95 percent alcohol per day. Financial difficulties caused the dissolution of the Standard Alcohol Corporation, and a reorganization was effected under the name of the Standard Lessee Corporation, which operated the plant from July, 1916, to June, 1917. At that time a new company purchased the plant and patent rights under the name of the International Alcohol Corporation. This plant was operated successfully under the management of F. W. Kressman until some time after the close of World War I. The process used both at Georgetown and at Fullerton eventually became known as the American process, although most of the early findings of Simonsen were utilized. Much less water was used in the charge than Simonsen recommended and, as a result, a sugar solution of much greater concentration was obtained, which greatly simplified handling of the moist digested sawdust and also resulted in an alcohol concentration that could be much more efficiently distilled.

The waste wood was taken directly from the sawmill, hogged and shredded, and elevated to a storage bin from which it was taken as required by conveyor belt to bins located above the digesters in the sugar house. Here the chips were conducted by gravity into steel, spherical, tile-lined digesters having a capacity of about 6 tons per charge. The required amount of sulfuric acid and water was introduced at the same time. The digesters were then closed and direct steam introduced as rapidly as possible until a pressure of 115 to 120 pounds was obtained. The material was digested for 15 minutes. The pressure was then reduced to atmospheric by blowing off the steam directly into the air. Attempts were made from time to time to condense the blow-off vapors in order to collect the more valuable products, such as turpentine, but, because of the short time involved and the prevailing high temperature of the water, complete condensation could not be effected without the use of excessively large condensers. As a result, attempts to recover turpentine and other volatile materials were abandoned.

After the steam was blown off, the manhole cover was removed and the contents discharged into a bin by rotating the digester. The amount of water that was introduced and that resulted from some condensation of the direct steam was held to a minimum in order that sugar solution should not be lost during the transportation of the digested wet material to the extraction battery. This transfer was made by conveyor belt and, in spite of efforts to eliminate drip, considerable sugar was lost in this operation. The material was then placed in a diffusion battery consisting of nine cells similar to those used in the beet-sugar industry. Using hot water and countercurrent extraction, a solution was obtained having a Brix of 12° to 13° and containing 6 to 9 percent of total reducing sugar. The resulting sugar liquor was then pumped to a neutralizing tank where milk of lime was added while the liquor was kept in a violent state of agitation by the introduction of air at the bottom of the tank. In order to accomplish this neutralization rapidly and to avoid "burning" of the sugar, a baffle was built into the center of the tank to circulate the liquor up through a central cylinder and cause it to return to the bottom of the tank outside of the cylinder. After neutralizing, this sugar solution was pumped to

settling tanks where it was allowed to settle for about 8 hours. In the meantime, the extracted residue was pressed and the damp material returned to the sawmill, where it was used as fuel. All the power for the operation of the alcohol plant was obtained from the sawmill.

The neutralized liquor, after settling and cooling to 86° F., was ready for fermentation. At Fullerton a fresh inoculum was prepared for each tub to be fermented. This was gradually built up with molasses and wood-sugar solution, together with the required amount of malt sprouts, ammonium sulfate, and calcium phosphate, until a vigorous fermentation was obtained in about 5,000 gallons of the starting liquor. This was then transferred to the large tub and sugar solution gradually added. Fermentation required from 60 to 72 hours. Upon completion of the fermentation the liquor was dumped to a beer well and eventually distilled.

Using this process, a conversion of the wood amounting to about 22 percent sugar was obtained in about 45 minutes. Of this sugar, about 75 percent was fermentable, which should have resulted in about 26 gallons of 95 percent alcohol per ton. Due to loss in handling of the sugar-containing residue and other unavoidable loss in processing, a yield of about 22 gallons was actually obtained. At Fullerton the alcohol was further rectified by passing it through columns of charcoal. The alcohol obtained from this plant was of high purity and was in demand as a cologne spirit.

A sugar solution resulting from the hydrolysis of wood is not an easy material to ferment, and it is surprising that more difficulty was not encountered in the commercial production of ethyl alcohol. Present methods of fermentation have incorporated a number of improvements, so that little difficulty is experienced now in securing a good and complete fermentation of the sugars in a minimum length of time.

The plants at Georgetown and Fullerton operated successfully throughout the last war and for some years afterward. Due to the great demands for lumber and structural timbers placed upon the sawmills during the war, however, they cut over their timber holdings much more rapidly than had been expected, so that, toward the end of their operation, they were transporting timber considerable distances. During the war, the sawmill from which the Fullerton plant obtained its waste was cutting a million board feet a day. The curtailment of mill operations, together with a substantial lowering of the price of blackstrap molasses, eventually resulted in the closing of both plants. Throughout their operation these plants produced from 5,000 to 7,000 proof gallons per day. Both of these concerns used Southern yellow pine as the raw material.

It should be noted here that about 1935 the Cleveland Cliffs Iron Company acquired the American rights to the Scholler process. They erected a pilot plant at Marquette, Michigan, and investigated a modified Scholler process with the result that the conclusion was reached that under the prevailing economic conditions the process was not commercially attractive. As a result they abandoned their rights to the process and discontinued their investigation.

Much the same story holds for the development of the process for the conversion of waste sulfite liquor into ethyl alcohol. Although the process appears to have originated in Scandinavian countries (6), it was not long until the papermills of the United States began to take an active interest in it.

Two experimental plants were installed in Sweden in 1907; one at Koppmanholmen (6), using the Wallin process, and the other at Skutskar, using the Ekstrom process. The processes differed only in minor details, particularly in methods of neutralization. The plant at Koppmanholman closed in 1908. In 1909 the plant at Skutskar was expanded to utilize the mill waste produced at the pulp mill with which it was associated. Two other plants were opened in Sweden before the United States became actively interested in the process.

After a thorough investigation of the Swedish processes, the West Virginia Pulp and Paper Company acquired the American rights to the Ekstrom process and in 1913 erected a plant at Mechanicville, New York. Early in 1914 Dr. Ekstrom, the inventor of the process, came to this country and remained until after the plant was in operation. During this time he had the full cooperation of Dr. Victor Drewson and other members of the company's staff. He brought with him a Race XII culture of Saccharomyces cerevisciae that had been used for the same purpose in Sweden.

The plant was modern in every respect, being constructed of steel and concrete. The fermentation vats, which were of concrete, were later removed and replaced with steel tanks in order to assure more aseptic conditions and also because it was felt that they contributed to the formation of scale in the stills. In the light of recent findings at Thorold, it is now doubtful if the concrete vats were responsible for this difficulty. From 1914 to 1919 two large imported column stills were used. They were of very heavy German construction and were eventually found to be inefficient. One was used as a beer still and the other as a rectifying column. The fermentation house had a capacity of somewhat over 100,000 gallons per day. The liquor was taken directly from the blowpits, together with a small amount of wash water, screened, neutralized with lime sludge from the soda plant, and allowed to settle. The clear, settled liquor was then pumped to 35,000-gallon vats which contained the bottom yeast that remained from the previous fermentation. The required amounts of nutrients, such as autolized yeast extract, ammonium sulfate, phosphates, and a small amount of malt sprouts, had previously been added to the residual yeast before the tub was filled with fresh liquor. The tubs were filled in such a way that a mild agitation was obtained. The tub's contents were allowed to ferment for 48 to 72 hours, after which the beer was pumped directly to the stills. The fermentation was very vigorous and was usually complete at the end of 48 hours.

The yields of alcohol were somewhat variable, due to the fact that the sugar formation varied in winter and summer. In 1919 this variation was from 1.94 to 2.80 percent in winter, while during the summer months it amounted to 1.65 to 2.20 percent. Several theories had been advanced to explain this fluctuation; it appears to be due to different concentrations of free and

combined sulfur dioxide at different temperatures. During 1920 the average sugar concentration was 2.08 percent. Of the sugars produced, about 60 percent were fermentable and were converted to alcohol with an efficiency of about 98 percent.

In 1920 the plant processed approximately 34 million gallons of spent liquor to produce 221,000 gallons of ethyl alcohol. This amounted to about 0.65 percent alcohol actually produced and turned over to the bonded warehouse. The continued reuse of yeast by decantation of the beer and refilling of the tub with fresh liquor eventually resulted in a concentration of short fibers on the surface of the fermenting liquor and caused a rather unsightly appearance of the fermenting liquor. It was thought that infection might be present and that, by the use of freshly developed yeast, the yields might be materially improved. In a plant-sized experiment the two methods were compared, with the result that, while the yields obtained from the yeast reuse method were slightly less than when fresh yeast was used, the difference was not great enough to warrant the additional cost of preparing fresh yeast for each fermentation. It was during this experiment that most of the above figures on sugar and alcohol yields were obtained (8).

This plant was operated over a period of 25 years, although during some years of that period it was closed down. The fact that it operated so long clearly indicates that those in charge were seriously interested in the process and that they did everything possible to make it a success. During part of this time a certain proportion of molasses was used in the operations, and it was found that, unless the market price for alcohol was 50 cents a gallon or higher, the plant could not operate at a profit.

In 1915 Crown-Willamette Paper Company, Oregon City, Oregon, carried on a pilot-plant investigation of the Marchand process. According to Tartar (10), the Marchand process differs from those commercially used in that the combined sulfur in the waste liquor is liberated by treating it with sulfuric acid. The liquor is then evaporated, and the last traces of sulfurous acid remaining are transformed into sulfuric acid by means of an oxidizing agent, such as potassium permanganate. The liquor is then neutralized with calcium hydroxide and is ready for fermentation. After a thorough investigation of the process, the company decided against a commercial development. During the following year the Kimberly-Clark Corporation at Appleton, Wisconsin, again investigated the Marchand process (5). After the investment of a considerable sum in a pilot plant and experimentation, that firm, too, decided against attempting to commercialize the process.

With the advent of a new and apparently more efficient method of reusing yeast, together with a great shortening of the time required to complete the fermentation, the process for the recovery of ethyl alcohol from waste sulfite liquor again becomes of considerable interest. One is forced to the conclusion, however, that the technology involved in the conversion of wood waste and sulfite liquor into ethyl alcohol is fairly complete. Undoubtedly, ways and means will be found to increase slightly the yields now

obtainable, and byproducts will be more efficiently used, but the fact remains that the commercialization of either of the processes will ultimately be decided largely by the prevailing economic situation.

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