Furfural from Corncobs[1,2]

IV—Economic Aspect of Furfural Production

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In this, the concluding article of the series dealing with the work of the Bureau of Chemistry on furfural production, the factors of importance in connection with the commercial utilization of the process are discussed. Consideration is given the supply of raw material, the possible market for furfural, the plant equipment required, and the operating conditions peculiar to the process. Itemized estimates are given for the cost of production in a plant capable of handling 50 tons of cobs per day, equivalent to 9000 pounds of furfural. The estimated total cost of production is 6.15 cents per pound of furfural.

The annual production of corn in the United States has ranged from 2.5 to 3 billion bushels for the past ten years. For each bushel of shelled corn produced there results about one bushel of cobs weighing from one-fourth to one-third as much as the grain, or a yearly total of 15 to 20 million tons of cobs. By far the greater part of the corn crop is raised in the valleys of the Mississippi, Missouri, and the Ohio rivers, the section of the Middle West known as the Corn Belt.

Methods of harvesting differ somewhat in different localities, but in all cases the ears are gathered and shelled either on the farm or at central shellers. Although at the present time the tendency is toward farm shelling, there are many districts where the custom of central shelling prevails. This is especially the case in the very fertile section of Kentucky and Indiana along the Ohio river and in certain parts of Iowa. The sizes of the central shellers vary considerably, and most of them are too small to supply sufficient cobs to serve as raw material for manufacturing. In a number of localities, however, shelling is done on a considerable scale with a production of cobs large enough to supply the needs of a good sized furfural plant for 6 or 7 months in the year. Some of the larger shellers produce as much as 25 to 50 tons of cobs per day during the shelling season from November 1 to May 1. Most of these larger plants are located close to other towns where shelling is done or are in a position to influence large amounts of ear corn to the plants should there be a market for the cobs. Thus it seems probable that in certain centers as much as 100 tons of cobs per day could be provided for the entire year within an assembling radius of 20 to 30 miles. Under such conditions the price of cobs need not exceed $2.00 or $3.00 per ton.

While storage for part of the year would be necessary in any case, a portion of the cobs could be held at subsidiary shellers until the local supply was exhausted before being shipped to the plant.

Possible Market for Furfural

One of the most important considerations in the production of a comparatively new material is the possible market for the product, which will necessarily limit plant size, location, etc. The market and price of product are largely interdependent. Whereas a comparatively large market must be assured in order to warrant large-scale production, the low cost thus brought about will lead to the opening up of new fields of utilization and will further enlarge the market.

In 1920, when furfural was quoted as high as $30 per pound, it is doubtful if more than 50 pounds were used in the United States during the year, and that chiefly as a reagent and standard in organic analysis and research. Through material supplied by the Color Laboratory of this bureau to various individuals and manufacturers for coöperative research, a start was made on commercial furfural utilization, and several promising fields have been opened. During the past year and a half the Miner Laboratories, of Chicago, have by their own and coöperative research aided considerably in extending the field of use, until now it is reported that several thousand pounds of furfural per month are being sold at a price of 25 cents per pound.

In France and Germany, where some furfural is being produced as a by-product in the manufacture of alcohol from wood waste, there has also been considerable interest in commercial utilization. As evidence of the possibilities in this field it may be mentioned that over sixty patents dealing with various phases of the production and utilization of furfural have been granted in this and other countries, for the most part during the past five years.

The chief fields of utilization so far developed are in the production of synthetic resins, as a fungicide and preservative, as a solvent, and as a fuel. The phenol-furfural resin has been developed to a stage where it is a commercial success. With furfural even now selling below formaldehyde, the market of some 3,000,000 pounds per year of the phenol-formaldehyde resin lies open to invasion. The low price of the furfural resin also opens up possibilities of invading the field of molded articles made from shellac, of which from 10 to 20 million pounds are used annually in phonograph records alone, to say nothing of numerous other molded devices. Resins of the soluble type produced by the reaction of furfural with various amines and ketones offer possibilities in replacing some of the varnish resins now used. There is a considerable field for the use of furfural as a cheap and effective repellent for certain insects and as a fungicide. It can also replace formaldehyde in a number of instances as a preservative. Its property of dissolving varnish resins and the cellulose esters makes it of importance as a solvent in industries dealing with those materials. Furfural burns slowly with a luminous flame, and as a very low price might compete with some of the accepted fuels for specific purposes. A market, then, of several million pounds of furfural per year in the near future is not at all inconceivable.

The Plant and Process

Plant Location and Size—The large quantities of cheap raw material and of fuel needed for the process make it desirable to locate the plant where these may be obtained without long rail transportation. Water for condensing purposes must also be at hand. In order to produce furfural most economically, manufacture on a considerable scale is necessary; that is to say, a plant should be able to handle at least 40 to 50 tons of cobs per 24 hour day, equivalent to 3.5 to 4.5 tons of furfural. It would, however, be feasible to operate

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[2] Previous articles in this series: This Journal, 15, 499, 823, 1057 (1923).

such a plant initially for 8 hours per day if required by market conditions. The plant should be located in contact with a large sheller in a region of high concentration of corn. A number of places in the Ohio and Mississippi valleys might fulfil the foregoing requirements. As typical favorable locations the towns of Henderson, Kentucky, and Keokuk, Iowa, may be mentioned.

EQUIPMENT REQUIRED—In the process of furfural production, as first developed in the Bureau of Chemistry experimental plant, high pressure steam alone was the digestive agent. It was later found that by the addition to the charge of a small quantity of sulfuric acid equivalent to the natural base of the cobs the furfural yield obtained was 9 per cent of the weight of the cobs as compared with 6 per cent obtained without the catalyst.

The catalytic process will naturally be the one employed in the commercial plant. Full details of the process are given to the second and third papers of this series. In brief, it consists in digesting the cobs with steam at about 135 pounds pressure for approximately 2 hours, while distilling off slowly the furfural formed and collecting it as a dilute aqueous solution. The latter is then put through a column still provided with continuous decantation, in order to separate the furfural in the form of a 95 per cent solution. Just enough sulfuric acid (about 0.75 per cent of the weight of cobs) is added with the charge to neutralize the bases present, and water is added in such quantity that with condensed steam the cob-water ratio 30 minutes after digestion begins will be about 4:1. At the end of the digestion the digester contents are discharged, drained, washed, and pressed to separate the cellulosic residue and liquor. The liquor contains some furfural, which is recovered as a weak solution to be used in subsequent digester charges. The total yield of furfural (100 per cent basis) is about 9 per cent of the air-dry weight of cobs. A flow diagram for the process is shown in Fig. 1.

In general, the steam digestion stage of the process for the production of furfural from corncobs follows very closely the operation commonly used in garbage reduction. In the garbage reduction process the material is digested for several hours by high pressure steam in stationary cookers. The pressure is then relieved by blowing off through a condenser, and the contents of the digester are discharged by means of a valve into a hopper, from which they are fed to a specially constructed, continuous acting, rotary press. The liquid which is removed falls into a tank while the press cake is carried off for further treatment. The digesters used are cylindrical in shape, tile lined, and generally have an available capacity of about 400 cubic feet each. They are grouped in batteries of four units supported over the hopper and press.

This type of equipment is well suited to the digestion of the cobs. A 400-cubic foot digester will hold 1.5 to 2 tons of cobs, so that the battery just described would easily take care of 50 tons per 24-hour day, allowing 3 hours for each digestion period including charging and discharging. Since the steam will be on each digester about 2 hours and 15 minutes, by using four units three will be under steam at all times, thus insuring a uniform load on the boilers.

In addition to the digester equipment, a column still is necessary for the separation of the furfural from the dilute digester distillate. Two stills would probably be advisable for the battery of four digesters. To recover the small amount of furfural from the discharged liquor obtained by draining and pressing the cellulosic residue, either a single-effect evaporator or a special exhausting column could be used. A small still is also needed to separate the constituents of the heads accumulated from the main stills.

Suitable boiler equipment for the generation of the steam necessary to the process would be required; also a small turbine generator for electrical power unless such power is available at very low rates.

Besides these main items, the equipment would include machinery for the piling of the cobs in open storage sheds and their automatic transfer to the digesters, and for the handling of the cellulosic residue. Storage tanks for sulfuric acid, hot water, and furfural solutions are also necessary. Other items include pumps, meters, regulators, and piping. If, in addition to technical furfural, a C. P. product is to be manufactured, a vacuum still for the purification of the crude material should be included.

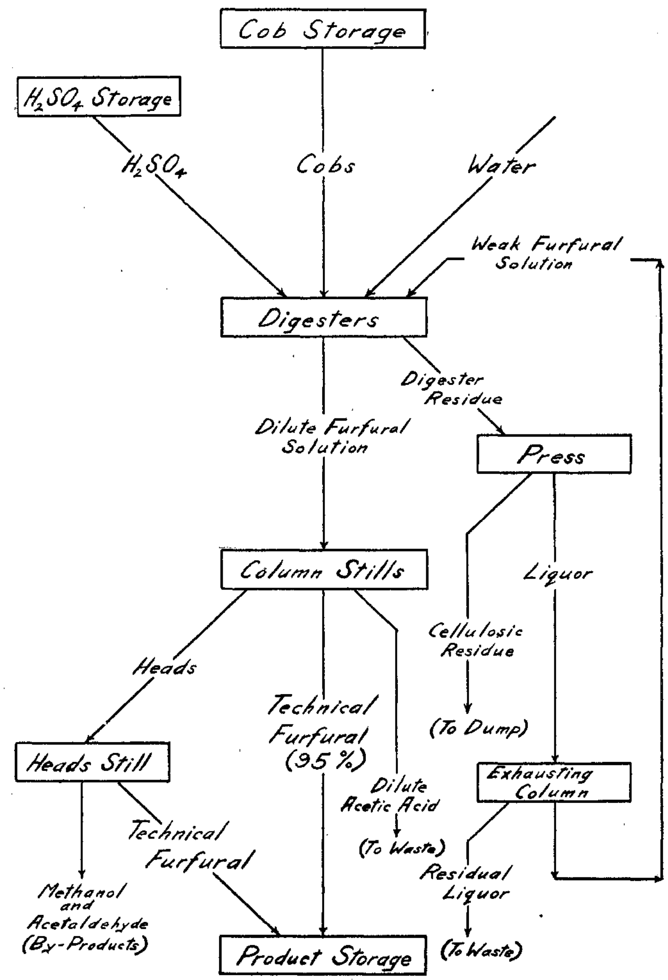

FIG. 1—FLOW DIAGRAM FOR FURFURAL PRODUCTION

POWER AND FUEL REQUIREMENTS—The steam consumption required for the digestion of the cobs as determined in the semicommercial plant is approximately 5550 B. t. u. per pound of cobs, or 61,500 B. t. u. per pound of furfural produced. This includes the recovery of dilute furfural from the discharge liquor and assumes no saving of heat except that the charge liquor is heated by waste steam. For the separation of the crude furfural from the dilute solution (3 to 4 per cent furfural) 15,000 B. t. u. per pound of furfural allows for a very low efficiency of operation. Another 1000 B. t. u. is more than ample for the treatment of the heads and production of C. P. furfural. These items, totaling 77,500 B. t. u. per pound of furfural, constitute the main steam, and consequent power, requirements of the process, although there must be added to them the power for the operation of conveyors, press, pumps, etc. These requirements, however, are small in comparison with those necessary for digestion and distillation, and 10 per cent added to the main power requirement would be a liberal allowance. A total of 85,000 B. t. u. per pound of furfural or 7650 B. t. u. per pound of cobs would cover all steam requirements. For a 50-ton plant this would correspond to 32,000,000 B. t. u. per hour, necessitating a boiler capacity of approximately 1000 b. h. p. Provision should be made for an operating boiler pressure of 150 pounds.

To furnish the 32,000,000 B. t. u. per hour, assuming 14,000 B. t. u. coal and 60 per cent boiler efficiency, would require 3800 pounds of coal per hour or about 46 tons per day, a little over 10 pounds of coal per pound of furfural produced.

LABOR FACTOR—The labor item, which is the most important in determining operating cost in a small-scale plant, decreases in importance with increase in size of plant and accompanying possibility of automatic machinery installation. Operating on a 24-hour basis, three shifts of practically all the men employed will be required. The technical men required would consist of the chemical engineer in charge of the plant, two plant control engineers for the other shifts, and two mechanical engineers in charge of the power plant. There are also needed for each shift digester operators and column still operators, firemen and laborers for the boilers, mechanics and helpers for general repairs, laborers to attend the conveyors and to assist at the digesters, press, stills, etc., and clerks for the office.

CHEMICALS REQUIRED—The only chemical required by the process as outlined here is a comparatively small quantity of sulfuric acid as a catalyst. The quantity used, 0.75 per cent of the weight of cobs, would amount to about 750 pounds per day for a 50-ton plant. Where the by-products are to be recovered, other chemicals would, of course, be needed.

PRODUCT AND BY-PRODUCTS—The product of the column still contains about 5 per cent of water, small amounts of acetaldehyde and methanol, and traces of acetic acid and other substances as impurities. This material is known as "technical" furfural and is entirely suitable for the manufacture of resins and fungicides. For solvent purposes it is generally desirable to remove by redistillation the methanol and acetaldehyde and traces of other impurities. For purposes where C. P. furfural may be needed, the technical material is redistilled under partial vacuum and the water eliminated with the first fraction of the distillate.

The by-products have been fully discussed in the previous articles. Of the volatile by-products, the organic acids (acetic and formic), amounting to about 3 and 1 per cent of the weight of the cobs, respectively, are obtained in such dilute solutions as to make economical recovery by the ordinary methods questionable. Comparatively small quantities of acetaldehyde and methanol are concentrated in the heads from the column still. Since they must be separated in recovering the furfural from the heads, they might form an additional small source of income.

The cellulosic residue makes up in dry weight about 65 per cent of the original weight of cobs, and as fuel with proper utilization methods might furnish a substantial portion of the heat required in the process. It may also be used as a wood flour substitute, or even as a humus adding material to be applied to the soil. While the cellulosic residue has no very objectionable properties and may be temporarily sent to the dump, its value would soon demand its utilization in one or more of the suggested ways.

COST OF PRODUCTION

BASIS FOR ESTIMATES—The estimates for cost of production of furfural are based on the data obtained in the operation of the bureau experimental plant, on extended estimates made on a somewhat similar type of plant for the production of adhesive from corncobs, and on general engineering practice. The estimates are conservative in that (1) the yield adopted for the calculations is that obtained in semicommercial runs and can be somewhat improved with the equipment described here, (2) possible income from the by-products, including the fuel value of the cellulosic residue, is neglected, and (3) the allowances for the various items are for the most part liberal.

The costs are figured for the process using the sulfuric acid catalyst, the yield being taken as 9 per cent of the air-dry weight of the cobs. The plant is considered as handling 50 tons of cobs per day equivalent to 9000 pounds of furfural and as operating 300 days of 24 hours each per year. Costs apply to the location of the plant at a town which is situated at the mine mouth and is at the same time a shelling center, and will vary considerably with other locations. The estimated cost of production includes interest on the investment, but does not include selling costs.

The product of the plant, technical furfural, will vary in composition between the limits of 94 and 96 per cent furfural or perhaps wider limits, according to the atmospheric temperature prevailing or to the specifications to be met by the product. The yield, calculations made from it, and cost of production are all figured in this article in terms of the quantity of 100 per cent furfural contained in the technical product.

TABLE I—ESTIMATED LABOR REQUIREMENTS FOR FURFURAL PLANT HANDLING 50 TONS OF COBS PER 3-SHIFT 24-HOUR DAY

TYPE OF LABOR	Number of Men	Daily Wage	Cost per Day
Plant manager or chemical engineer	1	$15	$ 15
Plant control chemists	2	10	20
Mechanical engineers	2	10	20
Digester operators	3	6	18
Column still operators	3	6	18
Firemen	3	6	18
Mechanics	3	6	18
Laborers	24	3	72
Clerks	2	4.50	9
TOTAL	43		$208

FIXED CHARGES—The entire cost of the plant is set at $150,000 with the main items as follows: building and site, $40,000; power plant, $40,000; digester unit, $25,000; stills, $12,000; storage and conveying facilities, $10,000. No attempt has been made to obtain competitive bids on minor details, but from figures obtained on the main items it is believed that the total allowed is liberal.

Standard practice is followed in allowing charges of 9 per cent for depreciation, 6 per cent for interest on the investment, and 2 per cent for taxes and insurance, or a total annual fixed charge of 17 per cent of the cost of the plant.

TABLE II—ESTIMATED COST OF PRODUCTION OF FURFURAL FROM CORNCOBS USING THE STEAM DIGESTION PROCESS WITH SULFURIC ACID CATALYST

(Calculated on three-hundred 24-hour working days per year with 9 per cent yield of furfural on the weight of cobs. Plant to handle 50 tons of cobs equivalent to 9000 pounds of furfural per day)

				Cost per Day		Cost per Pound of Furfural Produced
FIXED CHARGES:						
(Investment $150,000)						
Depreciation	9 per cent	17 per cent		$85.00		$0.944
Interest on investment	6 per cent					
Taxes and insurance	2 per cent					
INVENTORY CHARGES:						
(1 month coal and 2 months' cob supply—$2300 + $6250 = $8550)						
Charge = 8 per cent of inventory				2.28		0.025
OPERATING CHARGES:						
Labor (see labor sheet)			$208.00		2.311	
Employees' compensation insurance ($20 per $1000)			4.16		0.046	
Fuel (46 tons per day at $2.00)			92.00		1.022	
Boiler water (81,000 gallons per day at $5.35 per 100,000 gallons)			4.33		0.048	
Condensing water (650,000 gallons per day. No charge—under fixed charges, fuel, labor)			...		...	
Oil, supplies, etc. (2 per cent of operating charges)			6.71		0.075	
Maintenance (6 per cent of operating charges)			20.12		0.224	
Total operating charges:				335.32		3.726
CHEMICALS USED:						
(750 pounds sulfuric acid per day at $16.00 per ton)				6.00		0.067
RAW MATERIAL:						
(50 tons cobs at $2.50 per ton)				125.00		1.398
TOTAL COST OF PRODUCTION				$553.60		6.15

Inventory Charge—In order to insure continuous operation, an average of 1 month's coal supply and 2 months' supply of cobs must be maintained the year around. Allowing 25 working days per month, 1150 tons of coal and 2500 tons of cobs will be needed for this reserve. An inventory charge of 8 per cent, including interest on investment, taxes, and insurance is allowed for this item.

Operating Charges—The estimated labor requirements are given in Table I, which shows a total labor charge of $208 per day. An item of $20 per $1000 of wage paid is included for employees' compensation insurance.

Under the item of fuel, the unit price of $2.00 per ton may seem low, but is within the average price which has prevailed in normal years at the mine mouth in the section for which this plant is planned.

Since the main consumption of steam is in the digestion and rectification process, only a relatively small amount of condensed steam can be returned to the boiler. At 85,000 B. t. u. per pound of furfural, 74 pounds, or approximately 9 gallons, of boiler feed water will be required per pound of furfural, or 81,000 gallons per day. A standard charge of $5.35 per 100,000 gallons is allowed for this item. During the process a quantity of solution equivalent (at the maximum) to about 50 times the weight of furfural formed must be condensed. Assuming a 50° C. heat rise in the condensing water, about six hundred times the weight of furfural would be necessary as condensing water, a total of 650,000 gallons per day. For a plant located on a river, the condensing water could be pumped directly from and discharged into the river. The charge for condensing water will then be distributed over the items of fixed charges, labor, fuel, and maintenance.

As customary in estimates for plants of about this size, an allowance of 2 per cent of the total operating charges for oil and supplies and of 6 per cent for maintenance is made.

Raw Material—The unit price set for the cobs is $2.50 per ton, although in certain localities adequate supplies have been offered as low as $2.00 per ton.

Total Production Cost—The various items entering into the cost of production are assembled in Table II. The total estimated cost of production for the plant handling 50 tons of cobs per day is 6.15 cents per pound of furfural produced.

The Influence of Certain Compounding Ingredients in Hard Rubber[1]

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Hard vulcanized rubber has been a common, everyday material nearly as long as has soft vulcanized rubber, for it was back in 1851 that a patent was granted to Nelson Goodyear, a brother of Charles Goodyear, as a result of his investigation on the vulcanization of rubber. Yet, although one new use after another has developed for this material, the volume of business is still only a matter of a few millions of dollars a year, or only a small fraction of the amount that is spent for soft rubber goods.

This means that there are relatively few companies interested in hard rubber and a correspondingly small number of technical men who have devoted much time to the subject. From time to time articles have appeared in the journals dealing with certain phases of hard rubber manufacture; yet almost nothing has appeared which might be considered a discussion of hard rubber compounding.

Two years ago North[2] contributed an exceedingly comprehensive and thorough paper dealing with the effect of certain compounding ingredients upon the physical properties of soft rubber. One could certainly visualize a rubber stock if data on all the properties of the mix as considered by North could be obtained. In the case of hard rubber, however, some of the physical properties usually given, such as permanent set, resiliency, etc., may be neglected. The purchaser may require certain standards of electrical and acid resistance, as well as finish and type of fracture, depending upon the use of the material in question. Often, however, he will only ask: "Is it of proper hardness; what is the proportion of filling materials; is the tensile strength satisfactory; is it properly vulcanized?" It is the writer's purpose to make a beginning in this field by showing the effect of certain compounding ingredients upon the physical properties of hard rubber. The data obtained consist of only the breaking strength and ultimate elongation of various hard rubber stocks, and while the data are not so complete as North's, nevertheless, they do give some conception of the action of the materials in question, as properties such as hardness and ductility seem to change with the breaking strength and ultimate elongation.

Investigators who have attempted to obtain reliable data when testing soft rubber goods know that it is difficult to get consistent, trustworthy results. The same applies to hard rubber testing, but more so. It is known that when a piece of hard rubber is dropped into hot water it becomes soft and pliable. If it is tested under these conditions, the ultimate elongation and breaking strength are found to be vastly changed. These differences, to a lesser extent, occur with smaller differences of temperature. Likewise, the rate of separation of the clamps on the testing machine has a considerable influence. Other factors, such as milling conditions, age of stock, type of test piece, etc., have their influence.

Experimental

The results of the tests discussed herein were obtained under conditions as nearly identical as possible. A standardized method of handling all mixings was followed, and the tests were carried out at 21° C. on a horizontal Scott tester, the clamps separating at the rate of 0.5 cm. per minute. (These conditions, as well as the shape of the test piece, are as recommended by the Hard Rubber Division of the War Service Committee in its report of August, 1918.) In order to eliminate the cutting and grinding of each test piece down to accurate dimensions, a three-cavity mold was constructed, so that the only cutting necessary was that of separating the thin overflow from the test piece. Results recorded are the average of at least three tests. They do not represent

[1] Presented before the Division of Rubber Chemistry at the 64th Meeting of the American Chemical Society, Pittsburgh, Pa., September 4 to 8, 1922. Received October 24, 1923.

[2] *India Rubber World*, **63**, 98 (1920).