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PRODUCTION OF FURFURAL FROM
PENTOSE LIQUORS

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This application is made under the act of March 3, 1883, as amended by the act of April 30, 1928, and the invention herein described and claimed if patented in any country, may be manufactured and used by or for the Government of the United States of America throughout the world for governmental purposes without the payment to us of any royalty thereon.

This invention relates to the production of furfural by the conversion of pentoses by means of acids. It has among its objects the production of furfural from aqueous solutions of pentoses, particularly xylose.

Another object of the invention is the provision of a continuous process whereby pentose-containing solutions, such as pentosan hydrolysates, are converted by acid to produce furfural in yields greatly exceeding those heretofore obtainable.

The source of pentoses or pentosan hydrolysates is usually from a particular class of cellulosic compounds, for example, corncobs, oat hulls, cottonseed hull bran and rice hulls. The yield of furfural presently obtained by known methods averages about 10 percent of the processed raw material. This amounts to 50 to 60 percent theoretical yields of furfural based on the disappearance of pentosans from the saccharified raw material.

In general, the commercial process for the preparation of furfural consists in heating the cellulosic material with a small amount of dilute sulfuric acid at superatmospheric pressure. The procedure is necessarily batch-wise. Once the raw materials have attained reaction temperature, live steam is blown through the material to remove the furfural as a vapor mixed with steam. The process from a practical standpoint is a one-step procedure. However, chemically speaking, the overall reaction is composed of a plurality of intermediate stages. The first involves the acid hydrolysis of the pentosan to pentose. The acid then serves to convert the pentoses to furfural. Prior workers have attempted to increase the yield of furfural by rapid steam distillation, to remove the furfural as rapidly as it is formed. This procedure was based on the theory that furfural tends to decompose in the presence of hot aqueous acid. It has been the general belief that pentosan is transformed to pentose quite readily by acid hydrolysis and the transformation of the pentose to furfural proceeds through a series of intermediates. These intermediates tend to react with furfural itself to form resinous byproducts, thus reducing the overall yield.

It has been shown recently that the stability of

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furfural to hot aqueous acid and to thermal decomposition is much greater than might have been supposed by earlier investigators in this field. Furfural is relatively stable to dilute aqueous acids at normal temperatures. In fact, rather drastic conditions seem to be required to produce extensive destruction of furfural by acids either aqueous or non-aqueous. Moreover, furfural evidences no appreciable decomposition when heated to 180° C. in a sealed glass tube for several days.

According to prior conceptions, the instability of furfural has been overestimated considerably. It is not possible to account for the decreased yields of furfural in present commercial processes solely on the ground of decomposition of furfural.

According to our investigations, there is still another factor which affects the overall yield of furfural. We have discovered that this factor is much more significant in controlling the overall yields than is the instability of the furfural, especially under the dynamic conditions prevailing in the conversion zone.

Pentoses appear to enter into side reactions other than those directly involved in the conversion to furfural, and these side reactions materially reduce the yields of furfural independent of any side reaction entered into by furfural itself. As a consequence, we believe that the conversion to furfural actually competes with parallel reactions originating from the effect of acid on pentoses. We have discovered that the presence of furfural in the acid medium not only slows down the reaction and suppresses the further formation of furfural but actually drives the side reactions toward completion. We have further discovered that the efficient removal of furfural from the acid medium, if carried out so as to maintain a certain minimum concentration in the acid medium, results in suppression of the side reactions and consequent greatly increased overall yield of furfural.

Prior workers have recommended prompt removal of furfural from the conversion zone by such expedients as steam distillation or continuous removal of the furfural-containing vapors. In every prior instance known to us, processes suitable for commercial production of furfural result in low yields, for example, 50 to 60 percent based on the disappearance of pentose. The low yields thus encountered are brought about by the residual amount of furfural remaining in the reaction medium, not removed by the usual methods of steam distillation or vapor removal. Although this concentration may be small in actual

amount, nevertheless it is considerably in excess of the critical maximum for our improved yields.

According to our invention, furfural can be produced in a continuous manner from pentose-containing liquids in yields which compare favorably with the actual analytical method for determination of pentoses. We have discovered that if the concentration of furfural in the reaction medium is maintained at 0.6 percent or lower the overall yield of furfural is increased to a remarkable degree. According to our invention, we are able to obtain yields of about 80 percent or higher by a process readily adaptable to commercial scale operation. This compares favorably with the 88-90 percent yield obtainable by the analytical method involving the conversion of pure xylose to furfural.

We prefer to employ a pentosan hydrolysate as a source of pentoses, but the advantages of our invention may be realized with any of the reaction masses containing pentose, as now known in the art for the production of furfural. We prefer to employ a solution of 1½ to 10 percent xylose and 1½ to 5 percent acid as the conversion medium. We employ conversion temperatures within the range of 140° C. to 165° C., since under these conditions furfural is formed fairly rapidly. The conditions of reaction may be varied considerably, however, and the yield of furfural attained will approximate those of our preferred procedure so long as the concentration of furfural in the conversion zone is kept below 0.7 percent.

The conversion of pentoses to furfural in a hot aqueous acid medium proceeds readily, and it is necessary to employ efficient means for removal of furfural in order to maintain the concentration of furfural in the conversion medium at the desired minimum. The removal may be accomplished by any of a number of different methods.

From the sole standpoint of efficiency of removal, we prefer to maintain the concentration of the medium below 0.7 percent furfural by means of an extraction solvent, such as toluene. This may be accomplished by pumping a pentose-acid solution through a heat exchanger into a soaking drum providing 4 to 10 minutes hold-up time. The pentose-acid solution from the soaking drum is then passed through a cooler to an extracting column where the furfural is continuously removed with toluene countercurrently. The pentose-acid solution is then recycled until the sugar content is practically used up. This method is referred to below as method I. The apparatus may be a single unit of a continuous process in which the sugar solution, instead of being recycled through the same tower, is pumped to an additional unit operating in a similar manner. The effluent sugar solution from the second unit may be sent to a third and the operations repeated until the sugar content is reduced to the desired minimum.

Another somewhat similar method, preferably with dilute solutions of pentose, consists of pumping the pentose-acid conversion medium through a heat exchanger to a steam-heated reaction column. In this method II the pentose-acid solution enters at the top of the column, the solvent being introduced at the bottom. The solvent, for example, toluene, carries away the furfural by countercurrent extraction. The solution of furfural in toluene leaves the tower at the top and the spent pentose medium leaves the tower at the bottom.

For most efficient operation method II requires the use of a pentose solution of not to exceed 5 percent when the extraction is carried out at temperatures of approximately 150° C.

The procedure of method I, however, permits the use of more concentrated solutions of xylose, for example, up to 10 percent, since the extraction is carried out after cooling the conversion medium.

Still another method III that may be employed according to the principles of our invention involves the continuous removal of furfural by means of superheated steam. According to this method, the pentose-acid solution is pumped to a reaction column. The column consists of a series of plates through which the superheated steam continuously strips furfural from each plate. When employing this method, as well as those described above, it is desirable that the columns be maintained as nearly as possible under adiabatic conditions with respect to the steam. The cost of the steam is a major factor, and steam economies should be applied throughout, such as use of the effluent steam in heating jackets of the column or for preheating the pentose-acid solution to reaction temperature. Under these conditions, continuous production of furfural is readily attained, but the yields of furfural are slightly lower than those when employing a solvent for removing the furfural. The process must be conducted with careful consideration for the efficient contact of steam through the spargers and efficient removal of the furfural-laden vapors in order to maintain the concentration of furfural in the conversion medium at the desired minimum.

Example 1

A solution containing 3.24 percent xylose and 2 percent sulfuric acid was converted in an apparatus according to method I. The solution was heated to 150° C. in a heat exchanger and the residence in the soaking drum was approximately 10 minutes. After passing through the cooler, the temperature of the conversion medium was less than 50° C. at which temperature it was extracted with toluene in the extraction column. The effluent xylose acid was recycled through the heat exchanger. After the heating, cooling, and extraction was carried through 6 cycles, about 50 percent of the xylose added disappeared and 84.7 percent yield of furfural was obtained, based on the xylose that had disappeared. The concentration of the furfural in the conversion medium did not rise above 0.6 percent at any time during the process.

Example 2

An aqueous solution containing 9 percent xylose and 2 percent sulfuric acid was heated to 150° C. while toluene was being pumped through the reaction medium in an apparatus according to method II. A series of experiments were carried out in which the concentration of the furfural in the reaction medium was varied by rate of furfural extraction. As long as the furfural concentration in the reaction medium was maintained below approximately 0.55 percent, a yield of 85 percent furfural was obtained. When the concentration rose to 0.66 percent, the yield of furfural was reduced to 76 percent, based on the disappearance of xylose.

Example 3

A solution containing 5 percent xylose and 4 percent sulfuric acid was converted in an ap-

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paratus according to method I. The solution was heated to 150° C. in a heat exchanger, and the residence time in the soaking drum was approximately 12 minutes. After passing through the cooler, the temperature of the conversion medium was less than 50° C. at which temperature it was extracted with toluene in the extraction column. The effluent xylose-acid was recycled through the heat exchanger. After the heating, cooling, and extraction was carried through three cycles, about 36 percent of the xylose added disappeared and 85.4 percent yield of furfural was obtained, based on the xylose that had disappeared. In this and other similar experiments, approximately 12 percent of the xylose disappears in each cycle. The concentration of the furfural in the conversion medium was maintained below 0.6 percent during the reaction time.

It is apparent from the above examples that pentose sugars dissolved in a dilute acid solution may be continuously converted to furfural in high yields by any of a number of different methods, provided the furfural is removed from the reaction medium sufficiently rapidly and completely so as to attain a concentration of less than 0.7 percent. According to our invention, the acid used may be any of the mineral acids known in the art for the conversion of pentoses or pentosans to furfural.

Having thus described our invention, we claim:

1. A process for the production of furfural which comprises heating a solution containing 1½ to 10 percent xylose and 1½ to 5 percent sulfuric acid to a temperature of 140° to 165° C. to convert the xylose to furfural, maintaining the concentration of furfural in the conversion below 0.7 percent by continuously removing aqueous xylose-acid solution from the conversion, cooling the removed solution below about 50° C., extracting the cooled solution countercurrently with toluene to remove furfural, removing the toluene-furfural solution, re-heating the effluent xylose-acid solution and recycling it to the xylose conversion heating step.

2. A process for the production of furfural which comprises heating a solution containing 1½

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to 10 percent xylose and 1½ to 5 percent mineral acid to a temperature of 140° to 165° C. to convert the xylose to furfural, maintaining the concentration of furfural in the conversion below 0.7 percent by continuously removing aqueous xylose-acid solution from the conversion, cooling the removed solution below about 50° C., extracting the cooled solution countercurrently with toluene to remove furfural, removing the toluene-furfural solution, re-heating the effluent xylose-acid solution and recycling it to the xylose conversion heating step.

3. In a continuous process for the production of furfural from pentosan hydrolysate, in which pentosan hydrolysate is heated with acid in aqueous medium at not lower than about 140° C. to convert it to furfural, the improvement comprising maintaining the concentration of furfural in the conversion below 0.7 percent by continuously removing aqueous pentosan hydrolysate-acid solution from the conversion, cooling the removed solution below about 50° C., extracting the so cooled removed solution with toluene to remove furfural, removing the toluene-furfural solution, and continuously recycling the effluent pentosan hydrolysate-acid solution to the conversion.

4. The process of claim 3 in which the acid is 1½ to 5 percent sulfuric acid.

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