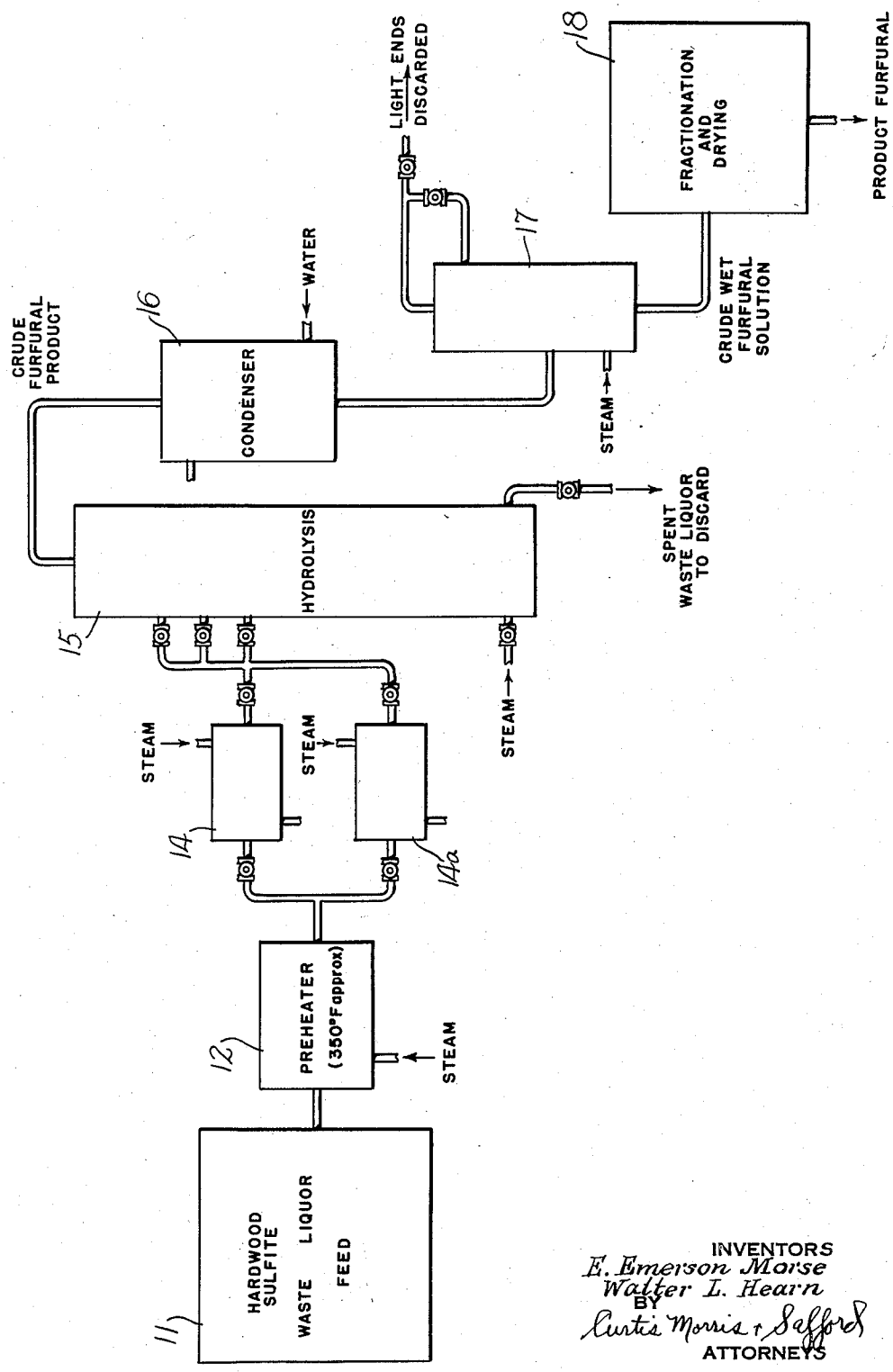
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PROCESSES FOR PRODUCTION OF FURFURAL

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PROCESSES FOR PRODUCTION OF FURFURAL

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This invention relates to methods of producing furfural which is suitable for the manufacture of various chemical materials from waste liquors. More particularly, it relates to producing furfural by the hydrolysis of waste sulfite pulp liquors and especially from hardwood pulp waste liquors.

While it has been recognized for some time that hardwoods contain attractive potential quantities of pentosans which are convertible ultimately to furfural, so far as we are aware no practical or economic processes for recovering furfural from hardwood waste liquors have heretofore been known, despite the several past general, and in some instances specific, suggestions to recover furfural from hardwood waste liquors. Certain prior proposals have not proven to be feasible in attempts at commercial, rather than laboratory, production. Other proposals have been deficient or defective because of low, uneconomic yields, high operating costs, excessive plant costs, operating difficulties or a combination of several of such factors.

Accordingly, it is an object of this invention to produce furfural from acidic hardwood waste liquors and the like by methods which are commercially and technically feasible while minimizing the cost thereof, while maintaining high product yields and while avoiding excessive investment and operating costs. Further objects of the invention will be in part pointed out hereinafter.

In one of its broader aspects the invention may be said to lie in hydrolyzing waste liquors at such temperature and time conditions that substantial destruction of the furfural or furfural-yielding components either by heat, polymerization or combination with other components of the waste liquors is avoided. More particularly, we have found that by maintaining the hydrolysis conditions between about 347° F. and 420° F. (and preferably at 385° F.) for between substantially 40 minutes to 10 minutes, a high proportion of the theoretically recoverable quantity of furfural present in the waste liquor may be obtained while simultaneously avoiding excessive fouling of the equipment used.

Perhaps the features of the invention can best be understood and appreciated by reference to the accompanying drawing which presents a simple flow plan of a particular sequence of processing steps and materials successfully employed.

In the drawing, hardwood sulfite waste pulping liquor **11** is derived from cooking hardwood chips for about 10 hours at 75 p. s. i. pressure; it has a pH of about 1.8 to 2.8 at 25° C. and has a typical solids content of 12–14%. Analyses indicate that such liquor contains about 1.2 to 2.2% potential furfural based on the total liquor. It is to be noted that when the cooking liquor is discharged to the blow pit after the cooking is completed a certain amount of free furfural may be flashed off and lost, thus reducing the potential yield somewhat, although provision may be made for recovery of such flashed furfural as by use of a surface condenser.

The waste liquor **11** after removal from the blow pit is fed into steam heated preheater **12** wherein the temperature of the liquor is raised to about 350° F. Thereafter liquor **11** is conducted to either one of two small (knockout) pots **14** and **14***a* wherein the temperature of the liquor is raised to the preferred hydrolysis point of about 385° F. by steam heating. In knockout pots **14** and **14***a* a certain amount of solids are deposited on the internal surfaces thereof, necessitating occasional cleaning.

In a presently preferred procedure, we next pass the heated liquor **11** to the upper portion of a vertically positioned reaction vessel **15** containing a plurality of sieve plates or other equivalent means of insuring intimate gas-liquid contact. High pressure steam is injected into vessel **15** at a lower portion thereof which serves to maintain the hydrolysis reaction temperature at the needed range of between 347° F. and 420° F. In the particular example now being described the reaction temperature in vessel **15** was held at 410° F. at an operating gauge pressure of 261 p. s. i. The injected steam also serves to provide a current of a stripping gas which sweeps out of the top of vessel **15** the product crude furfural, by-products such as methanol, low-boiling acids and so on as well as any small amounts of entrapped liquid.

It is to be noted that the capacity of vessel **15**, feed point injection points and feed rate are to be selected and adjusted so that the residence time or hold-up of the liquor **11** in the said vessel varies between about 40 minutes at the lower range of reaction temperature and about 10 minutes at the upper temperature ranges; it is also to be noted that the operating pressures range respectively between about 114 to 295 p. s. i. g. at the operating temperatures lying between 347° and 420° F. Lesser times than the ranges indicated result in insufficient conversion to, and recovery of, the desired product furfural. On the other hand greater residence times also cause reduced yields of furfural due apparently to polymerization or degradation of the furfural and perhaps combination with other components of the liquor.

Under the conditions indicated, the effluent spent liquor contains about 0.02% potential furfural and 0.02% actual furfural is conducted to waste discharge. It is to be noted that in describing the flow plan set forth in the drawing, in the interests of simplicity no discussion is made of the particular arrangement of details of heat exchange, equipment characteristics and the like since the present invention is directed to the operating criteria indicated above. Those skilled in the art will appreciate that variations may be made in the specific flow plan shown to meet the requirements of a given mill or plant and to minimize steam consumption, power consumption and so on.

In our studies and research into the problem of producing furfural from waste liquors, we found that, contrary to some indications, it was highly important to maintain the time-temperature conditions in the range indicated. For example, when the hydrolysis temperature exceeded 420° F. we found that tar-like solids were rapidly formed in vessel **15** to an extent which quickly plugged up the vessel and rendered continued operation impractical and, indeed required shut-downs of the plant in order to clean out the equipment. We also noted the formation of undesired coke-like material in the vapor disengaging space in the upper portions of vessel **15**.

On the other hand at temperatures below 347° F. the yield of furfural was quite low and excessive hold-up or residence time in the vessel was necessary even to achieve low yields. This in turn required impractical throughput rates or the use of reaction vessel **15** of excessively large and uneconomic size.

We found that using the practical time-temperature operating conditions we discovered and set forth above, over-all recoveries of the order of 53% of the theoretical furfural present in the feed liquor could be obtained and at low or moderate cost.

Returning now to the description of the specific flow plan shown, the effluent gases from the top of vessel **15** are condensed in condenser **16** and the condensate is next steam distilled in column **17** to remove undesired contaminating volatile components such as methanol and low boiling acids. The bottoms therefrom which is a crude wet dilute furfural is next concentrated and purified in one or more distillation columns **18** at atmospheric or less than atmospheric pressure. Preferably the product furfural, dry and of high purity, is stored under a blanket of inert gas.

From the foregoing it will be understood and particularly by those skilled in the art that the description of the specific embodiment of a process as described above is intended to be illustrative of the principle of the invention and is not intended to unduly limit the invention, the limits of which are set forth more precisely in the appended claims.

Having now particularly described our invention, what we claim is:

1. The process of producing furfural from acidic hardwood waste liquor which comprises establishing and maintaining a hydrolysis-reaction zone, conducting said liquor to said zone, maintaining the liquor in said zone at a temperature between about 347° F. and 420° F. for a period between about 10 and 40 minutes at an operating pressure lying between substantially 114 and 295 p. s. i. g., removing effluent gas and spent liquor from said zone at predetermined areas thereof which are remote from each other, and thereafter separating the product furfural from the effluent gas.

2. The process according to claim 1 where in said acidic hardwood waste liquor has an initial pH of not less than 1.8 nor more than 2.8.

3. The process according to claim 1 wherein said waste liquor is fed to said zone at an upper portion thereof and said spent liquor is removed from said zone at a lower portion thereof.

4. The process of producing and recovering furfural to the extent of at least 45% of the theoretical content thereof in acidic aqueous liquors resulting from the cooking of hardwoods which comprises establishing and maintaining a hydrolysis-reaction zone, conducting said liquor to said zone, maintaining the liquor in said zone at a temperature between about 347° F. and 420° F. for a period between about 10 and 40 minutes at a pressure lying between substantially 114 and 295 p. s. i. g., removing effluent gas and spent liquor from said zone at predetermined areas thereof which are remote from each other, thereafter recovering the product furfural from the effluent gas.

5. The process according to claim 4 wherein stripping steam is injected into said zone to simultaneously maintain said zone temperature and to sweep away volatile reaction products.

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