

Recovery of Furfural from Aqueous Solutions

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IN GENERAL there are two methods for separating the components of a solution: distillation and extraction. The former method as described by Mains (4) has found extensive use commercially for the recovery of furfural from aqueous solutions. To the authors' knowledge no solvent extraction method has ever been proposed for this particular separation. In this paper an extraction procedure is described, and to give a comparison of the two methods the steam requirement for each has been calculated.

Materials and Procedure

The furfural was prepared by fractionating technical furfural three times through a 180-cm. (6-foot) Hempel column packed with 6-mm. glass Raschig rings. The pressure was maintained at 15 mm. of mercury, and discards of 15 per cent of the total volume were made at the beginning and end of fractionation.

The ethyl acetate used was Baker's c. p. absolute.

The solubility data were obtained by titration in the following manner: Solutions of known concentration of two of the components were prepared and then titrated slowly with the third component until the cloud point was reached. This point was assumed to be the saturation point of the system, and inasmuch as comparatively large volumes of furfural, ethyl acetate, and water were employed a rather high degree of accuracy and reproducibility was attained. During the entire procedure the tem-

perature was maintained at 25° C. in a constant-temperature bath.

The mutual solubility of furfural and water and of ethyl acetate and water at 25° C. was obtained from International Critical Tables (3).

TABLE I. SYSTEM FURFURAL-ETHYL ACETATE-WATER AT 25° C.

Furfural %	Ethyl Acetate %	Water %
2.7	5.8	91.5
5.8	3.3	90.9
11.0	85.2	3.8
19.8	76.1	4.1
26.8	69.0	4.2
37.6	57.9	4.5
45.4	49.9	4.7
51.3	43.9	4.8
55.9	39.2	4.9
56.2	39.0	4.8
61.8	33.3	4.9
68.5	26.4	5.1
77.1	17.8	5.1
82.3	12.6	5.1
88.0	6.8	5.2

The data in Table I are presented in graphical form in Figure 1, the shaded areas denoting the region of complete miscibility and the blank region indicating compositions of the three components which separate into two liquid phases.

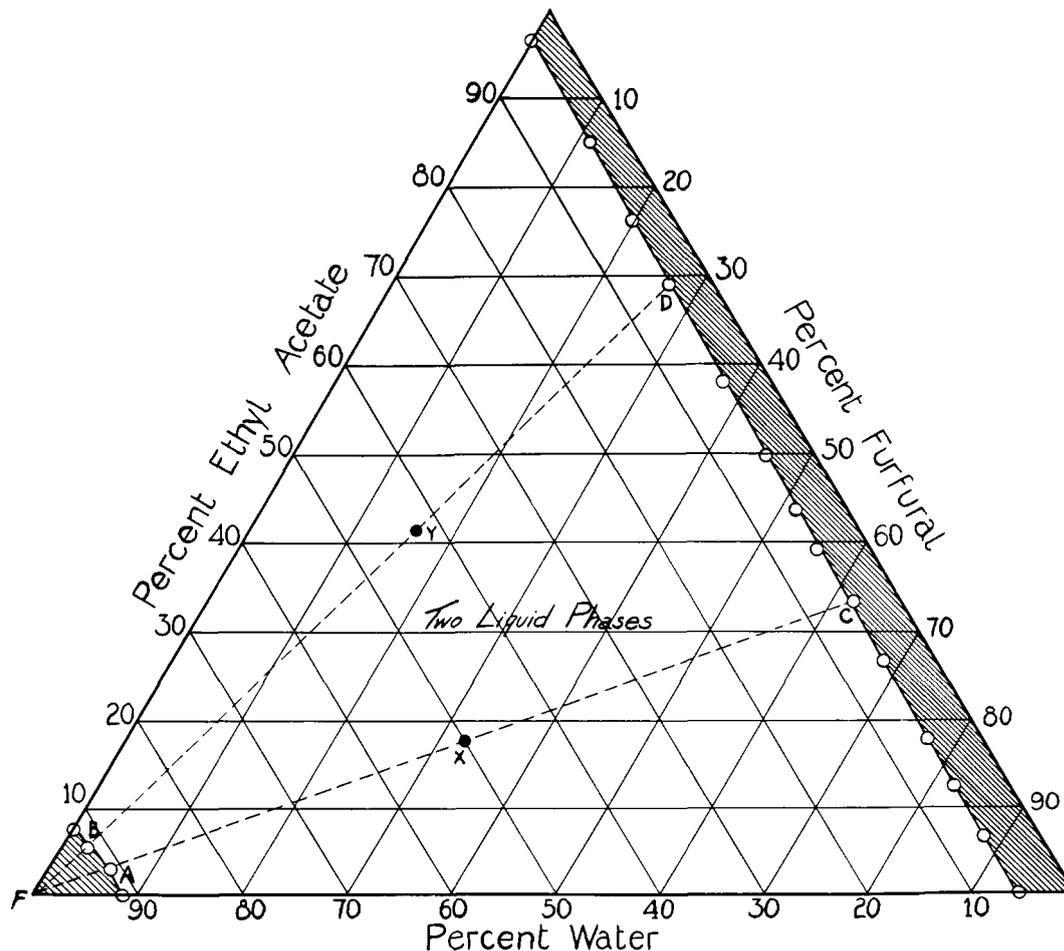


FIGURE 1. MISCIBILITY RELATIONSHIPS OF FURFURAL, ETHYL ACETATE, AND WATER AT 25° C.

To illustrate the method of reading Figure 1, refer to point *X*. This point represents a mixture comprising 50.0 per cent water (scale at base of triangle), 17.5 per cent ethyl acetate (scale at left side of triangle), and 32.5 per cent furfural (scale at right side of triangle).

The focal point, *F*, was located in the following manner after Figure 1 had been plotted: Two known mixtures of furfural, ethyl acetate, and water (represented by points *X* and *Y* in Figure 1) were prepared and allowed to stand at 25° C. until equilibrium conditions were attained. Each mixture formed two layers which were separated and analyzed for furfural by the Hughes-Acree method (2). From the results obtained, points were located on the water layer and solvent layer boundary lines. Composition *X* separated to form two layers, the compositions of which are represented by points *A* and *C*. Similarly composition *Y* formed two phases of compositions *B* and *D*. Lines were then drawn through points *DYB* and *CXA*, focus *F* being established at the point of intersection.

Any mixture of composition lying within the two-phase area (blank region in Figure 1) on a line extended through *F* will separate into two layers represented by the compositions where this line intersects the boundary curves. Because of the difference in the densities of the two layers, however, one cannot read directly from the graph the per cent of furfural that is extracted from a given aqueous solution of the latter. This can be determined experimentally or by the mathematical method described by Evans (1). Application of the Evans method shows that one extraction of a 7 per cent aqueous solution of furfural with an equal weight of pure ethyl acetate removes 93.5 per cent of the furfural from the water layer. A second extraction of the water layer would remove over 90 per cent of the remaining furfural.

In the laboratory, using a 240-cm. (8-foot) extraction column packed with 6-mm. porcelain Raschig rings, a 7 per cent aqueous solution of furfural was extracted countercurrently with an equal weight of ethyl acetate. Analysis of the solvent layer indicated that 99.9 per cent of the furfural had been extracted. On distillation at atmospheric pressure the solvent layer yielded the following fractions:

- | | |
|-------------------------------------------------|---------|
| 1. Ethyl acetate-water constant-boiling mixture | 70° C. |
| 2. Ethyl acetate | 77° C. |
| 3. Furfural | 160° C. |

Under the above conditions the final furfural is obtained in an anhydrous condition.

Equipment and Steam Requirements

FOR EXTRACTION METHOD. The equipment necessary for the application of the ethyl acetate extraction method for the recovery of furfural is illustrated in Figure 2.

In operation an aqueous solution of furfural is led into the top of the extraction tower, *A*. Simultaneously ethyl acetate is fed into the bottom of this tower and flows upward against the descending stream of aqueous furfural. During this countercurrent separation the ethyl acetate extracts the furfural from the water and passes out the top of tower *A* as the feed to fractionating column *B*. As can be determined from the foregoing data, this feed is composed of a high concentration of ethyl acetate with lesser amounts of water and furfural. The first two components are removed in column *B* as overhead distillate which is collected in reservoir *D* and returned to tower *A* as the selective solvent. The bottoms stream from column *B* is the desired product, an anhydrous grade of furfural.

The extracted water layer issuing from the bottom of tower *A* is saturated with ethyl acetate which must be recovered in an economical process. This is accomplished by fractional distillation in column *C*, the overhead distillate being the constant-boiling mixture ethyl acetate-water.

For the purpose of comparing the steam requirements of the extraction and distillation methods for the recovery of furfural the following conditions were fixed: (1) starting material, 7 per cent aqueous furfural solution; (2) recovery of furfural, 99.9 per cent; (3) heat losses due to radiation, etc., 10 per cent; (4) savings by heat exchangers omitted.

We shall assume that equal weights of feed and of ethyl acetate are used in tower *A* (Figure 2). The heat requirements in column *B* were calculated to be 3.4 kg. of steam per kg. of anhydrous furfural. It is necessary, however, to add to this the heat necessary to recover the ethyl acetate in column *C*, which raises the total steam expenditure to approximately 5 kg. per kg. of anhydrous furfural.

FOR STEAM DISTILLATION METHOD. The equipment necessary for this process has been described by Mains (4). However, the steam requirement in the authors' case differs from that of Mains, because of the use of a higher feed concentration and a different reflux ratio.

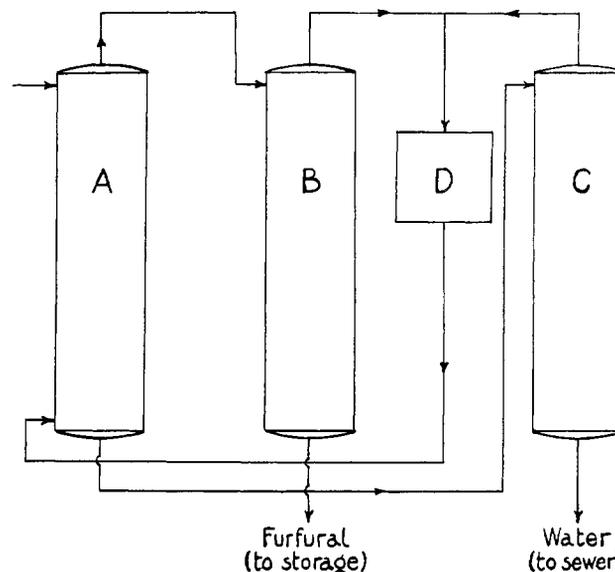


FIGURE 2. FLOWSHEET OF EXTRACTION PLANT

In the present process it is necessary to raise the temperature of the feed to approximately 100° C. (212° F.) and, in addition, to supply enough heat to evaporate the constant-boiling mixture, furfural-water. Experience has shown that this distillation can be carried out efficiently using a reflux ratio of 2 to 1. Calculations based on this information show that 6.25 kg. of steam are required per kg. of furfural in this step.

In order to obtain the furfural in an anhydrous condition a dehydrating column is required. This involves an additional 0.2 kg. steam per kg. of furfural. The total requirement therefore is approximately 6.5 kg. of steam per kg. of anhydrous furfural.

Discussion

The recovery of furfural from a water solution using ethyl acetate as the extractant compares favorably with the well-known steam-distillation method. Other solvents include various ethers and aromatic hydrocarbons which can be employed in this extraction process with results similar to those obtained with ethyl acetate. Perhaps the most important factors influencing the choice of solvent are selectivity, stability and recoverability, cost and availability, toxicity, corrosive action, and cost of operation.

Literature Cited

- (1) Evans, T. W., *IND. ENG. CHEM.*, **26**, 860 (1934).
- (2) Hughes, E. E., and Acree, S. F., *Ibid.*, *Anal. Ed.*, **6**, 123 (1934).
- (3) International Critical Tables, 1st ed., Vol. 3, p. 388, New York, McGraw-Hill Book Co., 1928.
- (4) Mains, G. H., *Chem. Met. Eng.*, **31**, 307 (1924).