IMPROVEMENT OF A FURFURAL DISTILLATION PLANT

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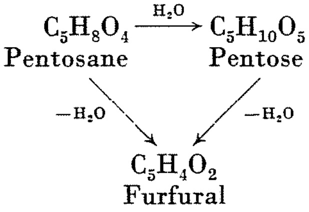
1. Introduction

Furfural is an important chemical, due to its unsaturated bonds and aldehyde group. It is extensively used in plastics and paint manufacture and in precision casting.

Furfural is produced from pentosane-containing agricultural wastes (corncobs, coconut seed hulls etc.) and from hard woods (mainly birch) by acid hydrolysis and subsequent dehydration according to the following equations:



$$\begin{tikzcd}
\underset{\text{Pentosane}}{C_5H_8O_4} \arrow[rr, "H_2O"] \arrow[dr, "-H_2O"'] & & \underset{\text{Pentose}}{C_5H_{10}O_5} \arrow[dl, "-H_2O"] \\
& \underset{\text{Furfural}}{C_5H_4O_2} &
\end{tikzcd}$$

It is also formed as a by-product in wood pulp manufacture where it can be recovered from the effluent by steam stripping.

Steam hydrolysis of pentosane-containing materials yields a reaction product containing 4—6% by weight of furfural, 2—5% of acetic acid, some tenth of a per cent of methyl alcohol and various, mostly unidentified compounds in trace amounts.

2. Recovery of furfural by distillation

2.1. *Conventional flow scheme*

The hydrolysis product is processed by multistep distillation. A conventional sequence of distillation steps is shown in Fig. 1.

The hydrolyzate is fed to a continuous distillation tower *1* provided with side-draw facilities in the rectifying section above the feed inlet plate. The bottom product consists of water and acetic acid; the liquid side-draw product contains 25 to 35% by weight of furfural with small amounts of methyl alcohol and acids, the rest being water; the top product is mainly methyl alcohol.

The side-draw product is cooled to ambient temperature in cooler *2* and led to separator *3* where a furfural-rich (92—95wt-% furfural), and a water-rich (8-10 wt-% furfural) phase are separated by gravity. The water-rich phase is recycled to the hydrolyzate tank.

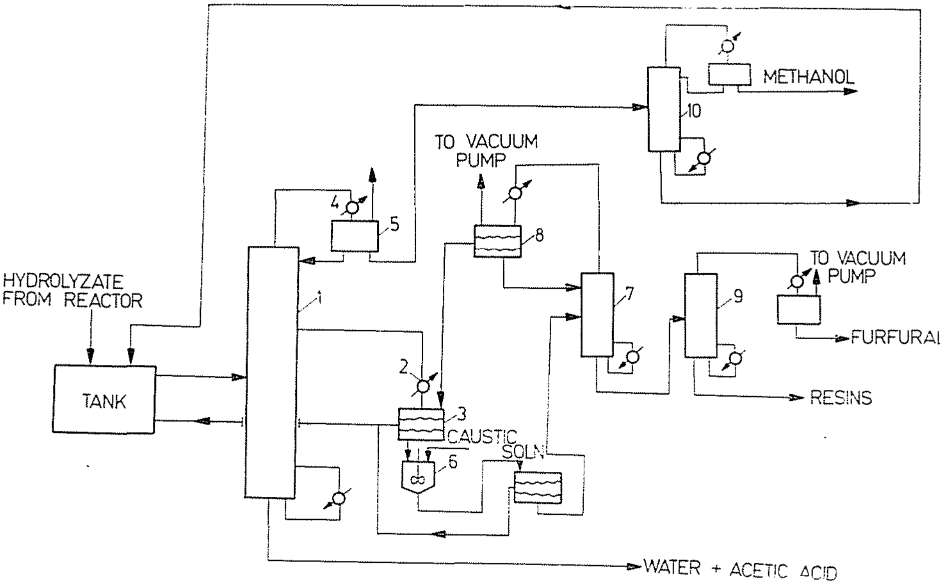


Fig. 1. Conventional furfural recovery scheme

The methyl alcohol-rich top product is condensed in condenser *4* and collected in reflux-accumulator *5*; the liquid reflux needed for heat balance is led back to the top tray, the excess being removed for further fractionation.

The furfural-rich phase separated from the side-draw product is neutralized in neutralizer *6* by mixing it with sodium carbonate solution. The neutralized furfural is dehydrated at reduced pressure by azeotropic distillation in column *7*; the overhead product is the azeotrope of furfural and water, which is separated after condensing and cooling in separator *8*. The furfural-rich phase flows back as reflux to the dehydrating column, the water-rich phase is returned to the hydrolyzate tank.

The bottom product of the dehydration column is dry furfural, discoloured by higher molecular weight resins. In order to obtain water-clear furfural, the bottom product is redistilled in column *9* at reduced pressure.

The top product of column *1* is further processed in column *10*, where a practically furfural-free distillate is obtained consisting mainly of methyl alcohol and other low-boiling compounds. The bottom product of column *10* contains mainly furfural and water and is recycled to the hydrolyzate tank.

As can be seen from Fig. 1 and the above description, for quantitative recovery of furfural from the hydrolyzate by the conventional distillation flow scheme

a) a separate column is needed for the recovery of furfural from the top product of the main atmospheric azeotropic distillation tower

b) all products lean in furfural or contaminated by low-boiling compounds are recycled to the hydrolyzate tank.

These conditions result in an increase of steam consumption by 20 to 50 per cent; additionally, the size of the atmospheric azeotropic distillation column as well as that of the methyl alcohol column had to be chosen 20 to 50% higher in order to handle the larger loads due to recycling.

2.2 *Improved distillation scheme*

Preliminary calculations showed that steam consumption as well as the size of the equipment could be reduced by improving the degree of separation in the atmospheric azeotropic distillation column. The improved distillation flow scheme (Fig. 2) consists of an atmospheric azeotropic distillation column *1* that differs from the atmospheric distillation column in Fig. 1 in the following features,

1. The number of plates above the furfural side-draw plate is increased to such an extent that the overhead product contains practically no furfural, therefore there is no need for the methanol-enriching column *10* in Fig. 1.
2. The water-rich phase formed on cooling the side-draw product is led back to the plate below the side-draw plate (instead of being recycled to the hydrolyzate tank) at plate temperature as liquid in order to increase the quantity of the reflux on the plates between the side-draw plate and feed plate (instead of being returned to the hydrolysis liquor collecting tank). Preheater *10* serves to bring the temperature of this stream to plate temperature.

3. Mathematical model

To be able to calculate the effects of changing feed composition on plate number and heat requirements, a simplified mathematical model of the atmospheric azeotropic column was developed incorporating vapor–liquid equilibria for the main constituents. Components present in trace concentrations were neglected.

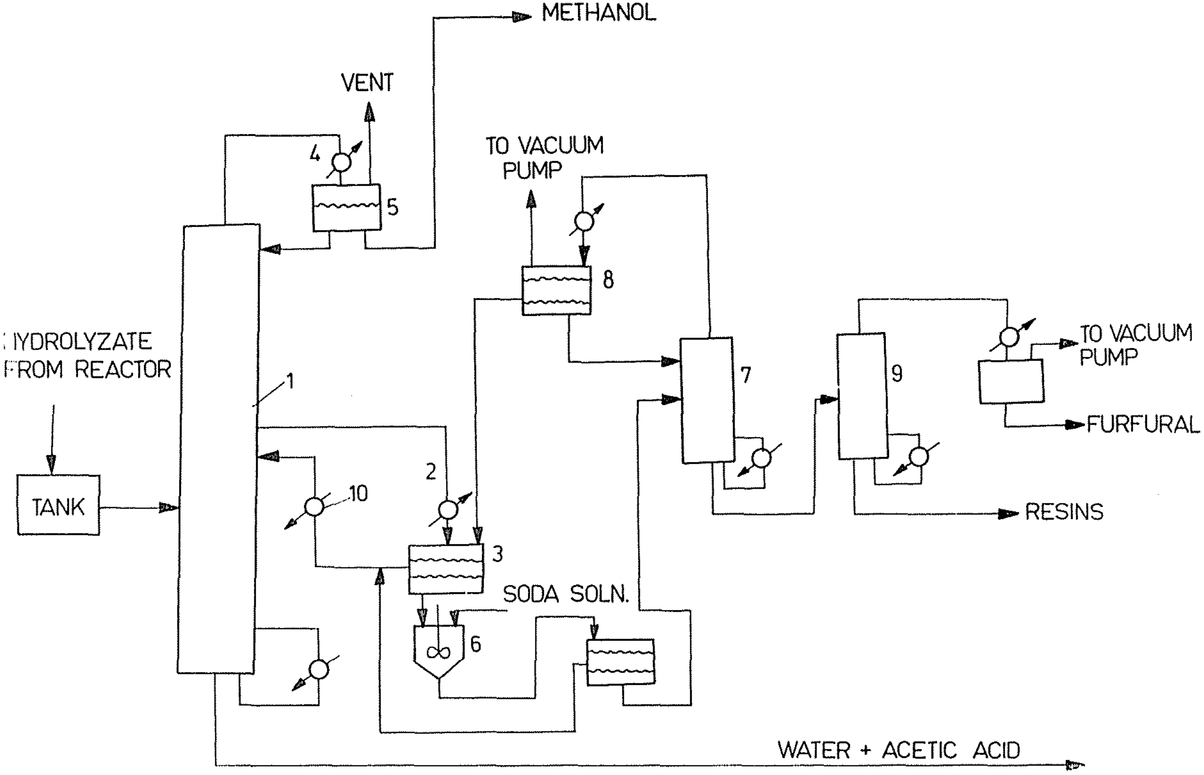


Fig. 2. **Improved flow scheme for furfural recovery**

3.1 *Basic equations*

3.1.1 *Equations for vapor–liquid equilibria*

Binary and ternary vapor–liquid equilibrium data from the literature [1, 2] were used as a basis. Binary and ternary vapor–liquid equilibrium data within the concentration ranges occurring in azeotropic furfural separation were converted to relative volatilities, and plotted at constant third-component concentrations, as well as for the pure binary systems. Curves fitting these data were obtained by regression analysis, and the effect ot the third component was obtained by an interpolation polynomial, assuming a linear effect of third-component concentration on relative volatility.

In this way, the following equations were developed:

1. α_{FV} if $x_E = x_M = 0$

$$\alpha_{FV} = 7{,}93 - 236{,}78x_F + 2324{,}65x_F^2 + 23248{,}32x_F^3 - - 575277{,}65x_F^4 + 2790524{,}82x_F^5$$

2. α_{FV} if $x_M \neq 0$

$$\alpha_{FV} = 0{,}66e^{-7\cdot5x_F}$$

3. α_{FV} if $x_E \neq 0$

$$\alpha_{FV} = 0{,}29\ x_F^{-0\cdot55}$$

4. α_{EV} = if $x_F = 0$

$$\alpha_{EV} = -0{,}16x_E + 0{,}69$$

5. α_{EV} if $x_F \neq 0$

$$\alpha_{EV} = -0{,}75x_E + 0{,}56$$

6. α_{MV} if $x_F = 0$

$$\alpha_{MV} = 7{,}78 - 15{,}59x_M + 27{,}80.x_M^2 - 47{,}19x_M^3 + 49{,}99x_M^4 - - 20{,}52x_M^5$$

7. α_{MV} if $x_F \neq 0$

$$\alpha_{MV} = 1{,}25 \cdot x_M^{-0\cdot62}$$

In cases 3 and 7 the data points could be best approached by using an $y = ax^b$ type of equation, yielding, however, at $x = 0$, an infinite value for y. Therefore for concentrations $x_M < 0{,}05$ and $x_F < 0{,}005$, the highest experimental data for α_{FV} and α_{MV}, respectively, were used.

The equations developed for calculating relative volatilities have been tested by correction calculations; the correlation coefficients thus obtained were in the range of 0.92 and 0.99 showing a good fit. Figure 3 shows such a curve and data points.

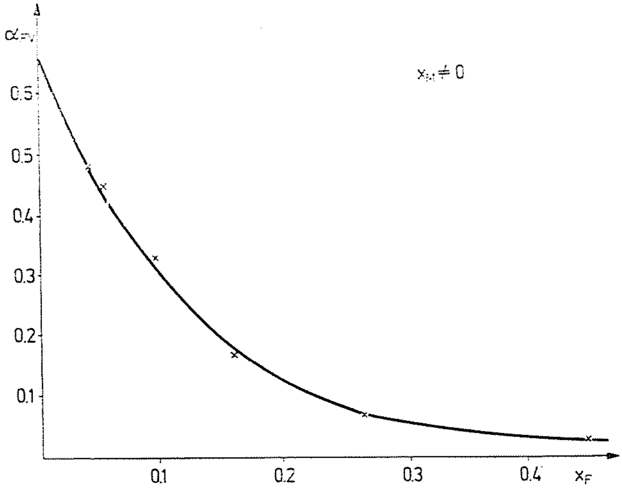


Fig. 3. Relative volatility of furfural to water in the furfural–water–methanol system

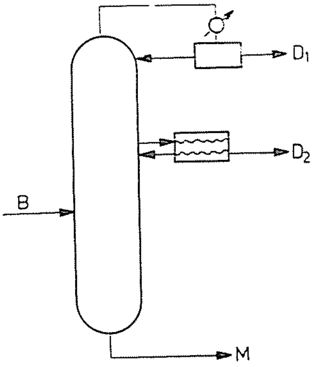


Fig. 4. Furfural distillation overall material balance

3.1.2 *Material balance equations (Fig. 4)*

a) Overall material balance equations

$$B = D_1 + D_2 + M$$

$$Bx_{Bi} = D_1x_{D1i} + D_2x_{D2i} + Mx_{Mi}$$

where

B	feed	kmol/h
D_1	overhead (methanol fraction) product	kmol/h
D_2	side-draw (furfural-rich phase) product	kmol/h
M	bottom product	kmol/h
x_{Bi}	mol fraction of component *i* in feed	
x_{D1i}	mol fraction of component *i* in overhead product	
x_{D2i}	mol fraction of component *i* in side-draw product	
$x_{M,i}$	mol fraction of component *i* in bottom product	

b) Stripping section material balance equations

$$F_m = G_m + M$$

$$F_m x_{m+1,i} = G_m y_{m,i} + M x_{M,i}$$

where:

F_m	liquid rate in stripping section	kmol/h
G_m	vapor rate in stripping section	kmol/h
$x_{m+1,i}$	mol fraction of component *i* in liquid from plate $m + 1$	
$y_{m,i}$	mol fraction of component *i* in vapor from plate *m*	

c) Material balance equations for rectifying section between feed plate and furfural draw-off plate

$$G_n = F_n + D_1 + D_2$$

$$G_n y_{n,i} = F_n x_{n+1,i} + D_i x_{D1,i} + D_2 x_{D2,i}$$

where:

G_n	vapor rate between feed plate and furfural draw-off plate	kmol/h
F_n	liquid rate between feed plate and furfural draw-off plate	kmol/h

d) Material balance equations for upper rectifying section

$$G_n = F_1 + D_1$$

$$G_n y_{1,i} = F_1 x_{1+1,i} + D_1 x_{D1,i}$$

$$F_1 = F_n + D_2$$

$$G_1 = G_n$$

where:

F_1	liquid flow rate in supper rectifying section	kmol/h
G_1	vapor flow rate in upper rectifying section	kmol/h

3.1.3 *Solubility equations*

Solubility data for furfural and water were taken from the cited literature. In the calculations, solvent effects of third components (such as methanol) were neglected, based on the assumption that at the concentrations occurring in the phase-separation equipment their effect would be negligible.

3.1.4 *Heat balance equations*

Constant molal flow rates were assumed in the separate column parts (cf. following chapter).

3.2. *Structure of the model*

The computer program scheme is shown in Fig. 5. The following input data were used in the mathematical model:

- feed rate (kg/h)
- feed composition (methyl alcohol, furfural, acetic acid, water, all in wt-%)
- reboiler heat duty (kcal/h)
- bottom product purity (furfural content, wt-%)
- minimum top product purity (methyl alcohol content, wt-%)
- degree of recovery for furfural (%)

From these data, the followings were computed utilizing the model:

- material balance for the whole column (quantities and composition of bottom product, furfural-rich phase and top product)
- compositions of liquid and vapor in equilibrium with this liquid, resp., for individual plates
- location of feed plate
- location of furfural draw-plate
- location of top tray.

3.3 *Simplifying assumption*

The simplifying assumptions utilized are as follows:

- the molar heat of vaporization on plates below the feed inlet is 10,000 kcal/mol, on plates above the feed inlet 9000 kcal/mol.
- methyl alcohol is absent in plates below the feed plate

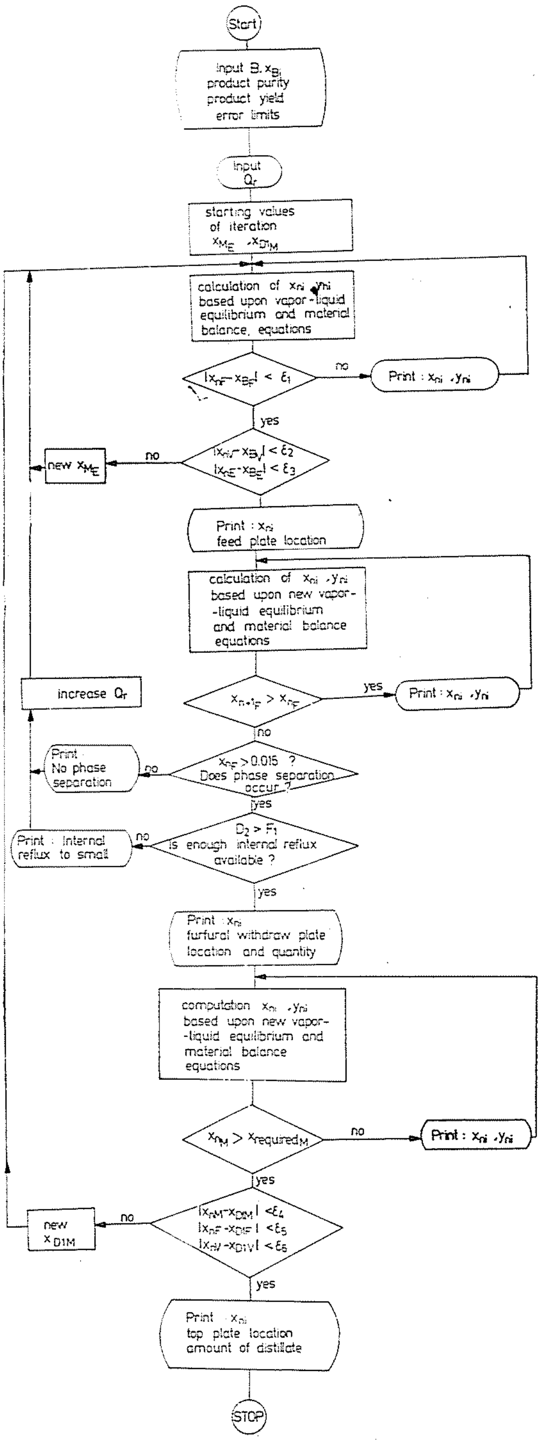


Fig. 5. Computer program scheme

- acetic acid is absent on plates above the feed plate
- the composition of the liquid on the feed plate is equal to that of the feed
- no methyl alcohol leaves *via* side-draw product.

3.4 *Operation*

In addition to the input values listed above, estimated values for bottom product acetic acid and top product methyl alcohol concentrations had to be assumed, because the model computes the material balances by iteration, starting from these values. Iteration continues as long as the calculated values do not reach a predetermined error; arriving at these values, the model computes the acetic acid and methyl alcohol concentrations of the bottom product and of the overhead, respectively.

Subsequently, starting from the bottom product composition, plate-to-plate computations are carried out using the vapor–liquid equilibrium equations and the material balance equation alternatively until the feed composition is approached. After selecting the best feed plate location, the model continues the computation by using vapor–liquid equilibrium equations and the material balance equations. For each plate, the furfural concentration calculated is compared to the previous furfural concentration; draw-off from the plate with the highest furfural concentration is established.

With furfural concentrations less than 8 wt-% no phase separation occurs. Therefore, if the furfural concentration does not exceed 8 wt-% on any plate the computation stops and a display appears: 'NO PHASE SEPARATION, REBOILER DUTY TOO LOW'.

The model also checks if there is enough liquid to satisfy the material balance requirements for furfural draw-off, i.e. whether the plate liquid of the calculated composition can yield after cooling to ambient temperature — the amount of 95% furfural calculated by the overall material balance equation.

If this requirement is not met, a display appears: 'INTERNAL REFLUX TOO SMALL' and the computation stops.

In both cases, the predetermined reboiler duty is too small for the required separation, therefore the computation has to be repeated by using higher reboiler duties.

After having established the correct position of the furfural draw-off plate, the model switches to the material balance equations of the upper rectifying section and continues computation until the required top product composition is reached.

Based on the model described above, a program has been written in BASIC; the program was run on a 8-Kbyte memory Wang 2200 computer.

Input data were fed into the computer by using the keyboard, output was either on CR-display or on an IBM typewriter terminal.

4. Computations and results

The model was used to compute the number of theoretical plates necessary for the recovery of furfural from hydrolyzates with different compositions at different reboiler duties, producing a top product containing at least 90 wt-% of methyl alcohol. The starting data have been varied between the following limits (feed rate was kept constant at 6000 kgs per hour),

Feed composition, wt-%

furfural	4.....6
acetic acid	2.....6
methyl alcohol	0.01.....0.8
Reboiler duty kcal/h	1.10^6.....2.10^6

One output list is shown in Table 1.

The output lists the input data, the compositions of liquids and vapors on individual plates, the locations of feed, side-draw and top plate and the liquid and vapor flow rates in the different sections of the column, as well as the quantities of bottom, side-draw and top products (Fig. 4).

By carrying several computations for varied conditions and comparing results, the following conclusions can be drawn.

(i) At 1.10^6 kcal/h heat duty, neither specified product purities nor required quantities can be reached: the equivalent of minimum reflux ratio lies around $1.2 \cdot 10^6$ kcal/h heat duty.

(ii) The number of plates needed for the specified separation decreases with increasing reboiler heat duty, and furfural concentration on the draw-off plates increase, therefore less liquid must be led to the separator.

(iii) In order to reach the specified limit of furfural concentration in the bottom product, at $2 \cdot 10^6$ and $3 \cdot 10^6$ kcal/h reboiler duty, 6 and 5 theoretical plates, resp., are needed.

(iv) At $2 \cdot 10^6$ and $3 \cdot 10^6$ kcal/h reboiler heat load, 2 to 3 theoretical plates, resp., above the feed plate are necessary to reach maximum furfural concentration in the plate liquid.

(v) At $2 \cdot 10^6$ and $3 \cdot 10^6$ kcal/h reboiler heat load, 3 to 4 theoretical plates, resp., are needed to have a top product with at least 90% methyl alcohol content.

(vi) Considering that plate efficiencies usually range between 40 and 50%, further that changes in the composition of the feed (caused by changes in operating parameters) and lagging of control instruments require additional plates, and atmospheric azeotropic distillation column should contain

Table 1

1 Output list

```
Feed                      = 6000 kg/h
Furfural                  = 6.0 wt-%
Acetic acid               = 4.0 wt-%
Methanol                  = 0.01 wt-%
Water                     = 89.99 wt-%
Reboiler duty             = 1.5 E + 06 kcal/h

Bottoms composition                       XF=0.000060   XE=0.013204   XV=0.986735
Bottoms quantity                          5622.25 kg/h
Liquid  = 452.9 kmol/h
Vapor  = 150.0 kmol/h
                                          YF=0.000390   YE=0.009192   YV=0.990416

      I = 1                               XF=0.000169   XE=0.011875   XV=0.987954
                                          YF=0.001127   YE=0.008260   YV=0.990612

      I = 2                               XF=0.000413   XE=0.011566   XV=0.988019
                                          YF=0.002754   YE=0.008031   YV=0.989213

      I = 3                               XF=0.000952   XE=0.011491   XV=0.987556
                                          YF=0.906319   YE=0.007949   YV=0.985711

      I = 4                               XF=0.002132   XE=0.011463   XV=0.986403
                                          YF=0.013993   YE=0.007866   YV=0.978140

      I = 5                               XF=0.004674   XE=0.011436   XV=0.983889
                                          YF=0.029933   YE=0.007714   YV=0.962351

      I = 6                               XF=0.009953   XE=0.011386   XV=0.978660
                                          YF=0.060753   YE=0.007424   YV=0.931821

      Feed plate = 7                      XF=0.020159   XE=0.011290   XV=0.968549
      Feed                                =6000.00 kg/h
      Liquid = 120.8 kmol/h
      Vapor = 125.6 kmol/h
                                          YF=0.063360   YM=0.000452   YV=0.936178

      I = 8                               XF=0.085003   XM=0.000315   XV=0.964681
                                          YF=0.090928   YM=0.002263   YV=0.906808

      I = 9                               XF=0.063656   XM=0.002197   XV=0.934145
                                          YF=0.103896   YM=0.015534   YV=0.880569

      I = 10                              XF=0.077140   XM=.0015995   XV=0.90863
                                          YF=0.093454   YM=0.103246   YV=0.803299

Furfural withdrawal plate = 10            XF=0.077140   XM=0.015995   XV=0.906863
Liquid withdrawal = 1454.70 kg/h
Water phase feed back = 1077.66 kg/h
      Net drawal = 377.04 kg/h
      Liquid = 125.6 kmol/h
      Vapor = 125.6 kmol/h
                                          YF=0.054275   YM=0.416827   YV=0.528896

      I = 11                              XF=0.054280   XM= 0.416748  XV=0.528970
                                          YF=0.011459   YM=0.732796   YV=0.255744

      I = 12                              XF=0.011456   XM=0.732771   XV=0.255771
Methanol withdrawal plate = 12            YF=0.003028   YM=0.884716   YV=0.112255
      Distillate                          = 0.65 kg/h
      End
```

in the stripping section	about	18
in the furfural enriching section	about	10
in the methyl alcohol rectifying section	about	12
total		40

actual plates

Summary

The authors developed a mathematical model of an improved recovery scheme of furfural from the hydrolysis product of pentosane-containing natural products.

Trial computations were run to establish optimum operating conditions for feeds of different composition. Vapor–liquid equilibria data from the literature were transformed into best fitting mathematical equations and used in the distillation model.

References

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