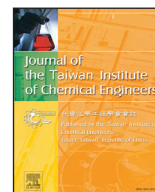Contents lists available at ScienceDirect

Journal of the Taiwan Institute of Chemical Engineers

journal homepage: www.elsevier.com/locate/jtice

Design and control of a process to produce furan from furfural

Hao-Yeh Lee [a], Tzu-Yu Huang [b], Po-Hsien Lee [b], Jeffrey D. Ward [b,*]

[a] Department of Chemical Engineering, National Taiwan University of Science and Technology, Taipei 106, Taiwan
[b] Department of Chemical Engineering, National Taiwan University, Taipei 106, Taiwan

A R T I C L E   I N F O

A B S T R A C T

The design and control of a process for the production of furan by the catalytic decarbonylation of furfural is studied. Starting with a conceptual flowsheet presented in the literature [8] modifications to the flowsheet are proposed and optimal values of design variables minimizing the total annual cost of the process are determined.

After an optimal process design is determined the control of the process is also studied. Two control structures are considered: one in which production rate changes are accommodated by changing the catalyst concentration, and one in which production rate changes are accommodated by changing the reactor temperature. Both control structures work well for both production rate changes of ±20% and changes in the concentration of water impurity in the feed.

© 2016 Taiwan Institute of Chemical Engineers. Published by Elsevier B.V. All rights reserved.

1. Introduction

Furfural is an important platform for second-generation biomass utilization processes [1]. It can be formed from the acid digestion of hemi-cellulose rich agricultural waste such as corn cobs and rice and oat hulls. Furfural can be further converted into a variety of useful chemical products, including furan, which is itself an intermediate in the production of several specialty chemicals.

Furan can be produced from furfural by direct decarbonylation over a palladium catalyst: Furfural → CO + Furan. This reaction has been studied in both the vapor [2–3] and liquid [4–7] phases. Zeitsch [8] presents a conceptual flowsheet of a process to produce furan from furfural. However, we are not aware of any detailed conceptual designs including stream and column properties, nor control studies, in the open literature.

Therefore, the objective of this paper is to study the design and control of a process to produce furan from furfural. Aspen Plus V8.4 and Aspen Plus Dynamics are used to simulate the process. Basic information about design of unit operations is taken from Seider et al. [9].

2. Reaction kinetics and thermodynamics

In the process designed in this work the reaction takes place at a pressure slightly greater than 1 atm in the liquid phase at approximately 158 °C, a few degrees less than the boiling point of furfural at 1 atm, 161.7 °C. The boiling point of furan at that pressure

is only 31.1 °C, and therefore both reaction products (furan and carbon monoxide) readily vaporize. Therefore the reactor liquid composition is almost entirely furfural, and the reaction rate can be considered to depend only on the reaction temperature and the catalyst concentration.

The kinetic model for the reaction rate used in this work is taken from Jung et al. [4] and is based on these assumptions. Jung et al. performed experiments over a range of temperatures from 157 °C to 161 °C. In the column design discussed later, the nominal value of the temperature of the reactive column reboiler is set to be 158 °C, slightly below the boiling point of furfural, so that most of the furfural remains in liquid phase. No reaction takes place on the trays (no catalyst is placed on the trays) so the kinetic model is not applied to determine the reaction rate at any temperature other than that of the reboiler, which always remains near to 158 °C.

The rate of reaction is expressed as follows:

$$R_{\text{furan}} = k = k_0 e^{\frac{-E_a}{RT}} \tag{1}$$

where $k_0 = 3.809734 \times 10^{36}$ g/h g_{cat} and $E_a = 310$ kJ/mol. The pre-exponential factor k_0 was determined from the Arrhenius plot given by Jung et al. [4].

The Non-Random Two-Liquid (NRTL) activity coefficient model is used to describe the phase equilibrium in this work and parameters not available in the Aspen database were estimated using UNIFAC. There are four species in this system, so six pairs of binary parameters are needed. However, only the furfural–water pair was available in the Aspen database. All other interaction parameters are estimated by UNIFAC as shown in Table 1. Values of the NRTL interaction coefficients are shown in Table 2. The boiling points of

* Corresponding author. Fax: +886 2 2369 1314.
  E-mail addresses: jeffward@ntu.edu.tw, jeffward97@gmail.com (J.D. Ward).

Table 1
Sources of binary interaction parameters.

Binary interaction parameters (NRTL)			
	Furfural	Furan	CO	Water
Furfural				
Furan	UNIFAC			
CO	UNIFAC	UNIFAC		
Water	Aspen build-in	UNIFAC	UNIFAC	

Table 2
Binary parameters for the NRTL model. The temperature unit is °C.

Component i	Furfural	Furfural	Furfural	Furan	Furan	CO
Component j	Furan	CO	Water	CO	Water	Water
Source	UNIFAC	UNIFAC	ASPEN-VLE	UNIFAC	UNIFAC	UNIFAC
Aij	0	0	−5.87	0	0	0
Aji	0	0	7.11	0	0	0
Bij	78.73	1022.49	2335.05	−61.82	668.92	191.33
Bji	739.23	−618.27	−1265.84	12.98	1408.21	−118.65
Cij	0.3	0.3	0.3	0.3	0.3	0.3

Table 3
Temperature of stationary points and pure component melting points at 1 atm.

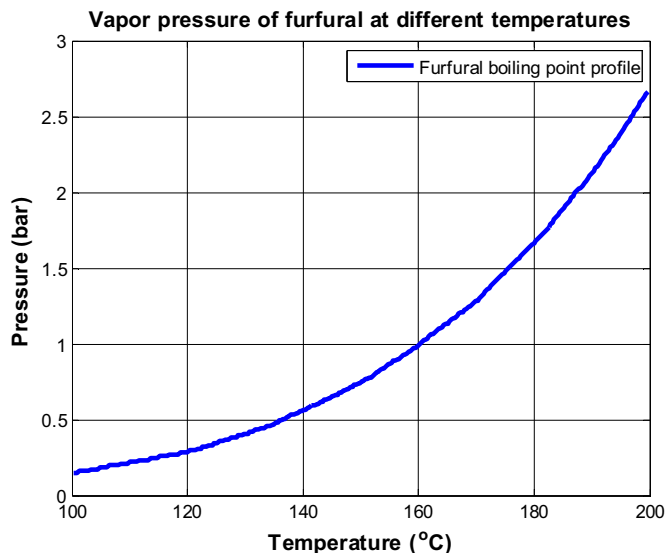| Component	Temp. (°C)	Composition (mole basis)	Melting point (°C)
Furfural	161.7	1	−37
Water	100	1	0
Furfural/Water	96.92	0.1217/0.8783	
Furan	31.1	1	−85.6
CO	−192.5	1	−205.02

Fig. 1. Vapor pressure of furfural at different temperatures.

stationary points including the furfural/water azeotrope predicted by the model and the melting points of all pure components are shown in Table 3.

Since furfural is the reactant in this process and reaction occurs in the liquid-phase, it is important to know the boiling point of furfural at different pressures. The vapor pressure of furfural as a function of temperature based on pure component data in Aspen Plus is shown in Fig. 1. The T–xy diagrams for furfural/water and furfural/furan predicted by the NRTL model are shown in Fig. 2. The NRTL model predicts one azeotrope between furfural and water at a composition of 87.73 mol% water at 1.013 bar.

3. Steady state process design

An initial conceptual design was developed based on the design presented by Zeitsch [8] as shown in Fig. 3. Commercially available furfural contains a small amount of water [1]; therefore the process feed is taken to be furfural with 0.2% weight water. The feed enters a CSTR where the reaction takes place in the liquid phase at 158 °C. The gaseous phase emanating from the reactor contains carbon monoxide, furan vapor, furfural vapor, and some water vapor. This gaseous phase enters a rectifying column (C-1). The column is operated so that furfural condenses and returns to the reactor. Furan, CO and some water travel up the column. The condenser of C-1 is cooled to −30 °C in order to condense as much of the furan as possible. Therefore water must be removed first, otherwise ice will form in the condenser. A side stream is withdrawn from C-1 to remove water. The composition of the side stream is near to the composition of the furfural/water azeotrope.

Because of the low temperature of the liquid distillate from C-1, a significant amount of CO is dissolved in this stream. Therefore, the liquid distillate stream from C-1 is fed to a stripping column (C-2) in order to remove CO and increase the purity of the furan. As the temperature of the liquid increases, the solubility of CO decreases, so furan that is nearly free of carbon monoxide can be collected in the sump.

The vapor streams from C-1 and C-2 contain mostly CO, but they also have some furan. Therefore, they are combined and enter absorption tower (A-1) where furan is removed from the vapor stream by stripping with furfural. As indicated in the diagram, a fraction of the feed stream is diverted to a mixing point, where it mixes with liquid effluent from the absorption tower. A fraction of this mixed stream then serves as the liquid feed for the absorption tower while the remainder is fed to the reactor.

3.1. Potential process improvements

Several potential opportunities for process improvement were identified as shown in Fig. 4. The first opportunity for improvement considered in this work is related to the mixing point and the absorption tower. In the process presented by Zeitsch, a fraction of the feed is mixed with the liquid outlet stream from the absorber. This seems unnecessary and therefore the mixing point and the performance of the absorber are studied in greater detail.

The second opportunity for improvement is related to the composition of the C-1 side stream. The furfural /water azeotrope occurs at a concentration of 87.83 mol% water at 1 atm. If the column operation could be modified to increase the composition of water in the side-draw, then less furfural would be removed from the process.

The third possible improvement considered relates to the way that water is removed from the process. Trace amounts of water present in the feed must be removed to prevent the formation of ice in the condenser of column C-1. In the original process water is removed by a side-draw from column C-1, but another possibility would be to remove water first with a separate distillation column.

The final possible process improvement is related to the temperature of the C-1 condenser. The purpose of the condenser is to condense furan while CO remains in the gas phase. The boiling point of furan is 30 °C, but the condenser is cooled to −30 °C. Lower temperature lowers the partial pressure of furan in the CO stream. However, lower condenser temperature increases costs. Therefore the temperature of the condenser is an important design variable.

3.2. Analysis of the mixing point and the absorption tower

In this section the absorption tower A-1 which is shown in Fig. 5 is studied as a separate unit. The purpose of the absorption