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Design and control of a process to produce furfuryl alcohol

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ABSTRACT

The design and control of a process to produce furfuryl alcohol is reported. Furfural is hydrogenated to furfuryl alcohol in a gas phase packed bed reactor with high selectivity and conversion. The product alcohol is separated from unreacted furfural and byproducts water and 2-methyl furan in a single low-pressure distillation column. Catalyst dilution is employed to increase the area available for heat transfer in the reactor. Control studies indicate that single-point temperature control of the distillation column is adequate to maintain product purity and avoid excessive loss of valuable material from the top of the column. A reactor effluent composition controller cascaded onto a reactor temperature controller can compensate for catalyst deactivation by raising the reactor temperature.

1. Introduction

Furfuryl alcohol (FOL) is an industrial chemical used primarily in binders for foundry sands in the production of cores and molds in metalworking [1]. Furfuryl alcohol can be produced by hydrogenation of furfural (FAL) in the gas phase over a copper chromite catalyst. Furfural itself can be produced sustainably from agricultural wastes such as corn cobs, bagasse, *etc*. Thus furfuryl alcohol and other furfural derivatives can be considered to be environmentally friendly, sustainable chemicals.

Conceptual flowsheets for the furfural alcohol process with vapor phase reaction have been published [1,2], however no detailed modeling studies of this process are available in the literature to our knowledge. That is the purpose of this contribution. Section 2 of this article describes the assumptions employed in the modeling. Section 3 reports the results of the steady-state design and optimization. Section 4 reports the results of the dynamic modeling and control. Finally, conclusions are drawn in Section 5.

2. Process model

2.1. Reactions and kinetics

The desired reaction is the hydrogenation of furfural:

$$\text{Furfural} + H_2 \rightarrow \text{Furfuryl alchohol}$$

Further hydrogenation of furfuryl alcohol produces the undesired byproduct 2-methyl furan:

$$\text{Furfuryl alcohol} + H_2 \rightarrow \text{2-methyl furan} + H_2O$$

Although the desired reaction is theoretically reversible, the equilibrium constant permits conversion greater than 99% at standard operating conditions and therefore many of the kinetic models published in the literature approximate the reaction as irreversible. Several authors have studied the hydrogenation of furfural and reported kinetic data and/or kinetic models for the reaction [3–19]. A variety of different types of catalysts have been investigated for the reaction, including copper chromite, copper/sodium silicate and platinum catalysts. Copper chromite is the most widely used catalyst in the industry [2] and offers good yield and high selectivity to furfural alcohol with 2-methyl furan and water being the only significant byproduct. Therefore, in this work, the kinetics reported by Borts et al. [3] using a copper chromite catalyst are employed:

$$r_{FOL} = 3.14 \times 10^{16} \exp\left(-\frac{10{,}740}{T}\right) C_{FAL} C_{H_2}^2$$

where the concentration of reactants C_{FAL} and C_{H_2} are in mol/L and the temperature T is in Kelvin. Borts et al. do not provide data or a kinetic model for the rate of the undesired reaction. However, information about the production of 2-methylfuran at 99% conversion of furfural and at different temperatures is provided by Zeitch [2]. These data were used to regress parameters of a kinetic rate expression for the second reaction. The result is:

$$r_{2\text{-MF}} = 1.41 \times 10^{20} \exp\left(-\frac{19{,}000}{T}\right) C_{FOL} C_{H_2}$$

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Table 1
Sources of binary interaction parameters.

	Furfural	Furfuryl alcohol	2-Methylfuran
Furfuryl alcohol	Aspen Databank		
2-Methylfuran	Regressed[a]	Regressed[b]	
Water	Aspen Databank	Aspen Databank	Regressed[c]

[a] Regressed from data reported by Holdren and Hixon [20].
[b] Regressed from data reported by Tai [21].
[c] Regressed from data reported by Smith and Labonte [22].

Table 2
Thermodynamic stationary points at 0.2 bar in the furfuryl alcohol process.

Temperature (°C)	Classification	FAL	FOL	MF	H_2O
124.21	Stable node	0	1	0	0
110.35	Saddle	1	0	0	0
60.06	Saddle	0	0	0	1
57.47	Saddle	0.1322	0	0	0.8678
22.2	Saddle	0	0	1	0
19.16	Unstable node	0	0	0.8331	0.1669

where temperature and concentration have the same units as for the desired reaction.

As with any industrial process, small quantities of other chemicals in addition to furfural alcohol, methylfuran and water may be formed in the reactor. Possible additional byproducts include tetrahydrofurfural alcohol, 1,2- and 1,5-pentanediol and *n*-amyl alcohol. However, if a copper chromite catalyst is used these byproducts are expected to be produced in sufficiently small amounts that they do not significantly affect the process.

2.2. Thermodynamics

The NRTL model with the Hayden–O'Connell correlation was used to model the vapor–liquid equilibrium in the simulation. The source of binary interaction parameters is given in Table 1. The predicted temperature and composition of stationary points at 0.2 bar is given in Table 2. Values are provided at a reduced pressure because the distillation column discussed later is designed at a lower pressure. Furfural alcohol and water form an azeotrope at atmospheric pressure but the azeotrope is not present at reduced pressure [23]. The binary *T*–*xy* diagrams for all pairs of species except those with hydrogen are given in Fig. 1. The numerical values of the NRTL binary interaction parameters are given in Table 3.

3. Process design and optimization

The process flowsheet is shown in Fig. 2. Because high conversion and high yield of the desired product can be achieved in the reactor, the design of the reactor and separation system do not affect each other significantly and therefore they can be designed separately. Therefore they are discussed separately in this section.

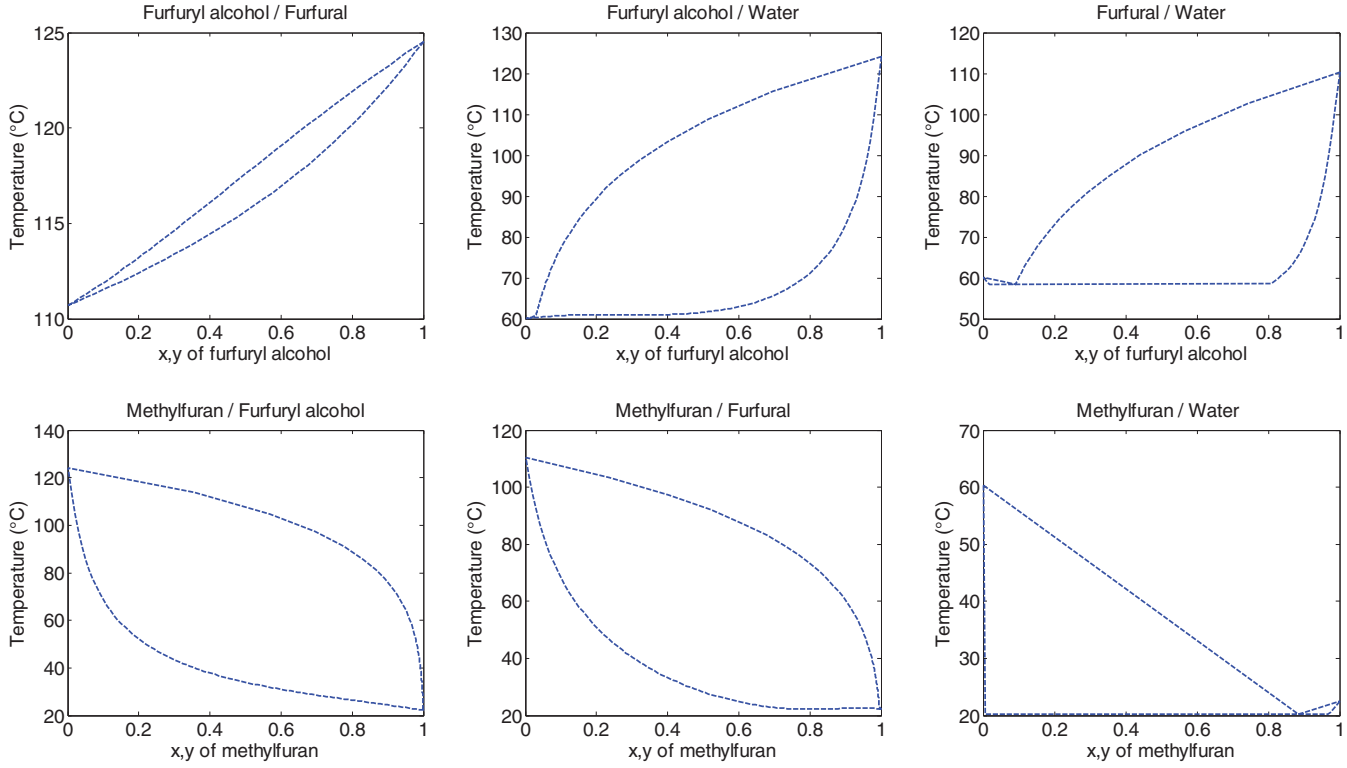

Fig. 1. *T*–*xy* diagrams of all species at 0.2 bar.

Table 3
NRTL binary parameters.

Component *i* / Component *j*	FAL / FOL	FAL / H_2O	FOL / H_2O	MF / FOL	MF / FAL	MF / H_2O
a_{ij}	0	−4.7563	0	1.6859	0.007942	0
a_{ji}	0	4.2362	0	0.1097	−0.001577	0
b_{ij} (K)	69.0160	1911.4222	60.3941	−154.3	1319.0490	852.5402
b_{ji} (K)	24.0213	−262.2408	845.5429	−126.8	−279.9706	1915.0555
α_{ij}	0.3	0.3	0.3	0.3	0.3	0.3