KINETIC STUDY OF FURFURAL FORMATION ACCOMPANYING SUPERCRITICAL CARBON DIOXIDE EXTRACTION

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Furfural formation from xylose is a typical successive reaction in which the furfural produced in a reactor disappears by side reactions such as polymerization and decomposition. In this work we investigated the effect of the extraction of furfural by supercritical CO₂ on the selectivity and yield of the furfural. Furthermore, based on kinetic data we proposed a reaction model for furfural formation with or without supercritical CO₂ extraction.

Judging from the experimental results, the recovery of furfural from the reaction mixture by supercritical CO₂ extraction greatly improved the selectivity and yield of the furfural owing to the suppression of its side reactions. A simple reaction model could represent satisfactorily the change in furfural selectivity and yield with the xylose conversion for the reaction without supercritical CO₂ extraction, while the model could explain fairly well the reaction accompanying supercritical CO₂ extraction.

Introduction

Much research is underway to find applications of supercritical fluids in various fields such as separations, chemical reactions and material processing operations.^{4,5)} Use of supercritical fluid in chemical reactions has the potential advantage of increasing the selectivity of the reaction while maintaining high conversion. A typical application is that for a successive reaction in which a highly reactive product is lost by side reactions. In this case, a supercritical fluid can be used to extract the product from the reaction mixture quickly and to improve the selectivity and yield of the reaction. Furthermore, the extract can be deposited easily and selectively from

the supercritical fluid by small changes in pressure or temperature.

From the viewpoint of sources of renewable and environment-friendly chemical feedstocks or fuels, intense interest has been given to biomass residues available from agricultural and forest processing.⁸⁾ Furfural, used in the chemical and petroleum refining industries,¹⁾ is produced from hemicellulose, which is one of the three main components of biomass such as bagasse, with acid catalyst as follows: hemicellulose → xylose → furfural.

The most serious problem in the furfural production process is that the furfural produced must be removed from the reactor as soon as possible owing to its high reactivity. Steam distillation is often used to recover it from the reaction mixture²⁾, but is undesirable because of the high energy consumption.

In the previous work,⁷⁾ we measured high-pressure

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vapor-liquid equilibria among supercritical CO₂ (SC-CO₂), furfural and water, and showed that SC-CO₂ had the potential to extract the furfural selectively from the reaction mixture and to concentrate it using a supercritical fractionation technique. Additionally, we showed that the new furfural production process accompanying SC-CO₂ extraction offered high xylose conversion and low energy consumption.

In this work we experimentally investigated the possibility of recovery of furfural from the reaction mixture by using SC-CO₂ and made an analysis of the reaction with or without SC-CO₂ extraction.

1. Experimental Apparatus and Procedure

The effect of SC-CO₂ extraction on furfural formation from xylose was investigated by using an apparatus shown in Fig. 1. The apparatus was a semiflow type and consisted of four main sections: a device to supply a continuous SC-CO₂ flow, a reactor with an inlet for SC-CO₂, a cooling trap for extract and devices to measure temperature, pressure and flow rate of CO₂.

The SC-CO₂ supply device provided SC-CO₂ at constant temperature and pressure. The CO₂, which was liquified by a cooler (3) and compressed by a high pressure pump (5), was heated in a preheater (8) and reached supercritical condition. The SC-CO₂ pressure was controlled by a back-pressure regulator (6) and its flow rate was maintained by a metering valve (22) installed downstream of the reactor.

The reactor (15), 68 mm in I.D., 140 mm in O.D. and 1000 cm³ in volume, was designed for maximum working temperature and pressure of 500 K and 50 MPa respectively. It had a self-inducing stirrer (16), baffles (17) and a CO₂ dispersion disk (18) to promote contact between the SC-CO₂ and the liquid phase. The reactor temperature was controlled by an electric furnace (14). Three series of cooling-trap bottles (23) were used to recover the furfural and water completely from the CO₂ gas. The freezing mixture of the first and third trap bottles was NaCl + ice and that of the second was methanol + ice.

The reaction temperature was measured with a calibrated platinum resistance thermometer (19) inserted in the reaction mixture. Its accuracy was within ± 0.3 K. As the temperature of the outer wall of the reactor was 30–50 K higher than that of the reaction mixture, there is a possibility that the temperature of the inner wall was a little higher than that of the reaction mixture. The reaction pressure was measured using a calibrated Bourdon tube pressure gauge (7) and the accuracy was within ± 0.05 MPa.

The experimental procedure without SC-CO₂ extraction was as follows. After the aqueous xylose

Fig. 1. Schematic diagram of experimental apparatus

solution was fed into the reactor, controlled at a given temperature and agitated at 1100 rpm, a small amount of liquid phase was sampled and analyzed to determine the initial xylose concentration. Then, as soon as the sulfuric acid solution was charged into the reactor the furfural formation began. At intervals a part of the reaction mixture was sampled by using a liquid-phase sampler (13) and the composition was determined using a liquid chromatograph.

The experimental procedure with SC-CO₂ extraction was as follows. The charging of xylose and sulfuric acid and the determination of initial xylose concentration were the same as those in the experimental procedure without SC-CO₂ extraction except for keeping the reactor in the saturation state of SC-CO₂. After the sulfuric acid was charged into the reactor, the SC-CO₂ was introduced from the bottom of the reactor and began to extract the aqueous furfural solution successively. Then the flow was expanded to atmospheric pressure by the metering valve, and the aqueous furfural solution dissolved in the SC-CO₂ was condensed in the cooling trap. At the end of the run, the furfural produced and the unreacted xylose were analyzed as soon as possible to avoid side reactions of the furfural. The total amount of furfural produced was the sum of the amount of furfural in the reaction mixture, that dissolving in the SC-CO₂ in the reactor and that in the cooling-trap bottles. On the other hand, xylose existed only in the reaction mixture. A gas chromatograph was used for analyzing the furfural in the SC-CO₂ and cooling-trap bottles, and a liquid chromatograph was used for analyzing

the furfural and xylose in the reaction mixture.

The column arrangement of the gas and liquid chromatographs is summarized in **Table 1**. The analytical accuracy was $\pm 1.0\%$ for both chromatographs.

The CO_2 gas used was supplied by Showa Tansan Co., and its purity was $>99.9\%$. The xylose was provided by Nacalai Tesque, Inc. and its purity was 98%. The CO_2 gas and xylose were used without further purification. Deionized and distilled water was used in the experiment.

2. Furfural Formation from Xylose

2.1 Furfural formation without SC-CO_2 extraction

Furfural formation from xylose without SC-CO_2 extraction was carried out at a reaction temperature of 423 K, initial xylose concentrations of $6.06 \times 10^{-5} \text{ mol/cm}^3$ (0.91 wt%) and $1.33 \times 10^{-4} \text{ mol/cm}^3$ (2.0 wt%), and sulfuric acid concentration of $5.0 \times 10^{-5} \text{ mol/cm}^3$ (0.1 N). The experimental results are given in **Table 2**, where the conversion of the xylose, the selectivity and the yield of furfural were defined by

$$\text{Conversion (\%)} = \frac{n_{X0} - n_X}{n_{X0}} \times 100$$

$$\text{Selectivity (\%)} = \frac{n_F}{n_{X0} - n_X} \times 100$$

$$\text{Yield (\%)} = \frac{n_F}{n_{X0}} \times 100$$

Figures 2 and 3 show the change in furfural selectivity with xylose conversion at 423 K. Furfural selectivity decreased rapidly as xylose conversion increased, since the furfural was not removed from the reactor. Consequently, as shown in **Figs. 4 and 5**, the furfural yield reached maximum value at 70–80% xylose conversion. This showed that the furfural in the reactor disappeared by side reactions such as polymerization and decomposition. This phenomenon was confirmed by the fact that the color of the reaction mixture after the run turned dark brown in the presence of water-insoluble by-products. Since the furfural concentration was very low near the beginning of the reaction, accurate experimental data could not be obtained in this region. Therefore, the initial furfural selectivity was determined by extrapolating boldly to the initial reaction time. The value was about 85%. From this result, we proposed a parallel reaction model for the xylose conversion under these conditions.

2.2 Furfural formation with SC-CO_2 extraction

The effect of SC-CO_2 extraction of the furfural on its selectivity and yield was investigated. The experimental conditions of reaction temperature, initial xylose concentration and sulfuric acid concentration were the same as those without SC-CO_2

Table 1. Column arrangement of gas chromatograph and liquid chromatograph

(1) Gas chromatograph
Column: PEG-6000 (3 mm ϕ $\times$ 1 m) at 373 K
Detector: FID
Carrier gas: He
(2) Liquid chromatograph
Column: ULTRON PS-80H (8 mm ϕ $\times$ 10 cm) at 333K
Detector:
1) RI for xylose
2) UV ($\nu=228 \text{ nm}$) for furfural
Mobile phase: Distilled water

Table 2. Experimental results of furfural formation without SC-CO_2 extraction

Time [min]	Conversion of xylose [%]	Selectivity of furfural [%]	Yield of furfural [%]	Conc. of furfural in reactor [mol/cm ³]
(a) $6.06 \times 10^{-5} \text{ mol/cm}^3$ initial xylose concentration				
60	24.8	77.6	19.2	1.2×10^{-5}
90	41.1	68.9	28.3	1.7×10^{-5}
150	56.0	61.2	34.3	2.1×10^{-5}
240	78.3	47.9	37.5	2.3×10^{-5}
(b) $1.33 \times 10^{-4} \text{ mol/cm}^3$ initial xylose concentration				
120	46.6	69.2	32.2	4.3×10^{-5}
180	58.7	57.0	33.5	4.4×10^{-5}
240	77.4	52.0	40.2	5.3×10^{-5}
290	83.2	43.1	35.9	4.7×10^{-5}

Fig. 2. Change in furfural selectivity with xylose conversion at 423 K and $6.66 \times 10^{-5} \text{ mol/cm}^3$ (1 wt%) initial xylose concentration

extraction. However, in this run the SC-CO_2 at 20 MPa and $5000 \text{ cm}^3/\text{min}$ (at 273.2 K, 101.3 kPa) flowed through the reactor to extract the produced furfural successively.

The experimental results are presented in **Table 3** for $6.66 \times 10^{-5} \text{ mol/cm}^3$ (1.0 wt%) and $1.33 \times 10^{-4} \text{ mol/cm}^3$ (2.0 wt%) initial xylose concentration. The change in furfural selectivity with xylose conversion at 423 K is shown in **Figs. 2 and 3**, and the relation

between furfural yield and xylose conversion is given in Figs. 4 and 5. In contrast to the run without SC-CO₂ extraction, constant and high furfural selectivity (more than 80%) was obtained even when the xylose conversion was above 50%. As a result of the high selectivity, the furfural yield increased greatly in comparison with the run without SC-CO₂ extraction. This improvement was caused by the

Fig. 3. Change in furfural selectivity with xylose conversion at 423 K and 1.33×10^{-4} mol/cm³ (2 wt%) initial xylose concentration

Fig. 4. Change in furfural yield with xylose conversion at 423 K and $6.66 \times 10^{-5} \text{ mol/cm}^3$ (1 wt%) initial xylose concentration

rapid extraction of produced furfural by SC-CO₂ prior to disappearance by the side reactions. As given in Table 3, the amount of furfural in the reactor was maintained at a low level. The effect of SC-CO₂ extraction was also verified by the color change of the reaction mixture after the run. That is, the color of the mixture was thin and the amount of by-products in this run was much smaller than that in the run without SC-CO₂ extraction.

3. Reaction Analysis

The following reaction model was proposed for furfural formation from xylose.

This model was derived from the following assumptions. (1) The xylose had two kinds of reaction paths: conversion to furfural and condensation to carbonaceous compounds. (2) The reactive furfural

Fig. 5. Change in furfural yield with xylose conversion at 423 K and 1.33×10^{-4} mol/cm³ (2 wt%) initial xylose concentration

Table 3. Experimental results of furfural formation with SC-CO₂ extraction

	Conversion of xylose [%]	Selectivity of furfural [%]	Yield of furfural [%]	Amount of furfural in reactor [mol]	Amount of water extracted [mol]	Ratio of extracted to produced furfural [%]
(a)	6.66×10^{-5} mol/cm ³ initial xylose concentration					
	32.9	79.8	26.3	0.0025	0.75	71.1
	51.4	78.8	40.5	0.0032	1.47	76.5
	70.4	81.8	57.6	0.0030	2.55	84.2
	73.2	81.3	59.5	0.0019	3.91	90.3
	81.4	82.1	66.8	0.0026	3.84	88.5
(b)	1.33×10^{-4} mol/cm ³ initial xylose concentration					
	40.7	82.8	33.7	0.0068	1.12	69.8
	68.2	81.4	55.5	0.0058	2.11	84.2
	83.2	84.0	69.9	0.0067	2.69	85.6

disappeared by side reactions such as polymerization and decomposition. (3) The rate constants k_1 , k_2 and k_3 were first-order constants. The first assumption was supported by the experimental result that the selectivity of the furfural was about 85% at the initial reaction time, and the second was proposed in the literature.³⁾ For the third assumption, k_1 and k_2 were reported to be first-order rate constants,^{6,9)} though no information on k_3 was available. Here the third assumption was adopted because of the simplicity of the reaction analysis.

The rate equations on mole basis for furfural formation without SC-CO₂ extraction were as follows:

$$\frac{dn_X}{dt} = -k_1 n_X - k_3 n_X = -k_4 n_X \quad (1)$$

$$\frac{dn_F}{dt} = k_1 n_X - k_2 n_F \quad (2)$$

$$\frac{dn_P}{dt} = k_2 n_F \quad (3)$$

$$\frac{dn_C}{dt} = k_3 n_X \quad (4)$$

where $k_4 = k_1 + k_3$. Equations (1) to (4) could be solved analytically and the number of moles of the components were represented respectively by

$$n_X = n_{X0} \exp(-k_4 t) \quad (5)$$

$$n_F = \frac{k_1 n_{X0}}{k_2 - k_4} [\exp(-k_4 t) - \exp(-k_2 t)] \quad (6)$$

$$n_P = n_{X0} \left[1 + \frac{k_1}{k_2 - k_4} \exp(-k_2 t) - \left(1 - \frac{k_3}{k_4} + \frac{k_1}{k_2 - k_4} \right) \exp(-k_4 t) \right] \quad (7)$$

$$n_C = \frac{k_3 n_{X0}}{k_4} [1 - \exp(-k_4 t)] \quad (8)$$

In this experiment, the concentrations of the xylose and furfural could be determined, while those of the by-products could not. We could use only Eqs. (5) and (6) for determining the three kinetic parameters k_1 , k_2 and k_3 . Therefore, k_1 reported in the literature¹⁰⁾ was adopted and k_2 and k_3 were determined by fitting the kinetic data for the run without SC-CO₂ extraction, which are given in Table 2. The reason for employing the reported k_1 value was that the value of k_1 was considered to be the most reliable among the three rate constants. The estimated k_2 and k_3 values are presented in Table 4. The calculated change in furfural selectivity with xylose conversion is shown in Figs. 2 and 3 and that in furfural yield with xylose conversion is shown

Table 4. Estimated rate constants at 423 K and 5.0×10^{-5} mol/cm³ sulfuric acid

$k_1 = 4.26 \times 10^{-3} \text{ min}^{-1} *$
$k_2 = 3.50 \times 10^{-3} \text{ min}^{-1}$
$k_3 = 0.811 \times 10^{-3} \text{ min}^{-1}$
* reported in the literature ¹⁰⁾

in Figs. 4 and 5. The calculated results represented the experimental data well for both 6.06×10^{-5} mol/cm³ and 1.33×10^{-4} mol/cm³ initial xylose concentrations.

The rate equations for the furfural formation with SC-CO₂ extraction were the same as those without SC-CO₂ extraction except for Eqs. (2) and (3). Assuming that the number of moles of furfural in the reaction mixture was kept at a constant and low value (n_{Fr}) by SC-CO₂ extraction, the rate equations of the furfural, and the polymerization by-product or decomposition by-product were

$$\frac{dn_F}{dt} = k_1 n_X - k_2 n_{Fr} \quad (2')$$

$$\frac{dn_P}{dt} = k_2 n_{Fr} \quad (3')$$

As a result, n_X and n_C were given in Eqs. (5) and (8), while n_F and n_P were represented by

$$n_F = \frac{k_1 n_{X0}}{k_4} [1 - \exp(-k_4 t)] - k_2 n_{Fr} t \quad (6')$$

$$n_P = k_2 n_{Fr} t \quad (7')$$

Under this condition the furfural and water were in the reaction mixture, in the SC-CO₂ and in the extract, while the xylose and by-products were in the reaction mixture only. Therefore, n_F in Eq. (6') was the sum of the amounts of furfural in the three places.

The change in number of moles of each component was predicted by Eqs. (5), (6'), (7'), (8) and the rate constants determined from the experiment without SC-CO₂ extraction and given in Table 4. Judging from the experimental results presented in Table 3, n_{Fr} was set to be 0.0026 mole for 6.66×10^{-5} mol/cm³ initial xylose concentration and 0.0064 mole for 1.33×10^{-4} mol/cm³, regardless of reaction time. The broken lines in Figs. 2 and 3 show the calculated furfural selectivity and those in Figs. 4 and 5 show the calculated furfural yield. Although we employed a simple model, the calculated results represented the experimental data fairly well. The disagreement would be due to several reasons such as the increase in acid concentration by the extraction of water from the reaction mixture and by the dissolution of SC-CO₂ into the reaction mixture, the effect of pressure on the reaction rate, the improve-

ment of stirring efficiency by bubbling the CO_2 , or insufficiency of the reaction model. Among them, the influence on furfural selectivity of extracting water was estimated on the assumption that the rate constants k_1 and k_2 were proportional to acid concentration,¹⁰⁾ while k_3 was independent of acid concentration. At $6.66 \times 10^{-5} \text{ mol/cm}^3$ initial xylose concentration, the estimated furfural selectivity rose by 2% at 75% xylose conversion. However, this increase was still not enough to fit the experimental results.

Conclusion

The effect of SC-CO_2 extraction on the selectivity and yield of furfural in the conversion of xylose to furfural was investigated at 423 K using a semiflow type apparatus. It was confirmed that removing the furfural from the reaction mixture by SC-CO_2 extraction could suppress the side reactions of the highly reactive furfural and improve the selectivity and yield of the furfural greatly. A simple model was used for analysis of the reactions both with and without SC-CO_2 extraction. The model represented satisfactorily the change in selectivity and yield of the furfural for the reaction without SC-CO_2 extraction, and it worked fairly well for the reaction with SC-CO_2 extraction.

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Nomenclature

k_i	= rate constant of i -th reaction	[min^{-1}]
n_i	= number of moles of component i	[mol]
n_{Fr}	= number of moles of furfural in reactor in extraction by SC-CO_2	[mol]
t	= reaction time	[min]
ν	= wave length	[nm]

<Subscripts>

C	= condensation by-product
F	= furfural
P	= polymerization or decomposition by-product
X	= xylose
0	= at initial reaction time

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