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The effect of solvent polarity on autocatalytic furfural production confirmed by multivariate statistical analysis

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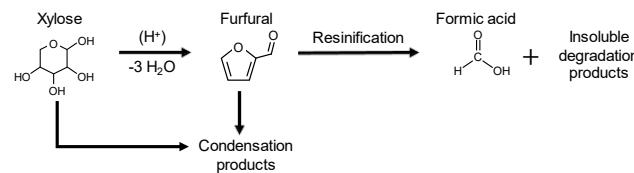
Abstract: Autocatalytic dehydration of xylose to furfural was studied in pure aqueous and monophasic organic/water mixtures to determine the effect reaction media and conditions have on conversion and yield. This study identified that reaction severity (R_o) and polarity, as determined by the Hansen Solubility Parameter, δ_p , strongly correlate with xylose conversion and furfural yield. Increasing the R_o and δ_p increased both conversion and yield in pure aqueous and organic/water mixtures of sulfolane, γ -butyrolactone, γ -valerolactone, γ -hexalactone, and tetrahydrofuran. Additionally, it was found that at a specified R_o and δ_p , similar conversions and yields were achieved using different combinations of time, temperature, and solvent mixture. Using principal component analysis and projection to latent structures, a semi-empirical model was developed that provided estimates of xylose conversion and furfural yield over a range of experimental R_o and δ_p values.

Furfural has been recognized as an important building block for fuels, solvents, and other value-added chemicals,^[1] and numerous recent publications have focused on optimizing furfural production from model sugars and lignocellulosic biomass. The use of organic solvents for xylose dehydration reactions has recently gained interest due to faster reaction rates^[2] and the higher furfural yields obtained, which have been reported as high as 80% in biphasic systems.^[3] Solvent selection has been identified as an important reaction variable with mentions of solvent polarity^[4] and the number of oxygen containing groups^[5] being potential explanations as to why solvents improve furan yields, but currently no systematic method for solvent selection exists. Researchers have previously used Kamlet-Taft theory^[6] or Hansen Solubility Parameters (HSPs)^[7] to explain differences in selectivities, conversions, and yields; however, these solvent parameters (dispersion (δ_D), polarity (δ_p), and hydrogen bonding (δ_H) for HSP) are functions of both solvent mixture and temperature,^[8] which often times are not considered.

This work aims to bridge the gap between xylose conversion, furfural yield, and solvent properties to guide solvent selection in monophasic, autocatalytic systems. Previous research has explored acid-catalyzed reactions in organic solvent mixtures for both monophasic and biphasic systems.^[3, 9] In biphasic systems using aluminium sulfate as the catalyst, Yang et al. hypothesized that as the polarity of a solvent increases, furfural yields increase

in γ -valerolactone (GVL), methyl isobutyl ketone, tetrahydrofuran (THF), and 2-methyltetrahydrofuran;^[10] however, no direct measure of solvent polarity was provided.

Although acid catalysts increase the rate of reaction, furans can be produced through an autocatalytic process (Scheme 1), with the mechanism initiated by the formation of hydronium ions in high temperature water.^[11] Additionally, formic acid, a degradation product, has been shown to contribute to the reaction activity.^[12] Previous publications on autocatalytic furfural production have focused on pure aqueous systems,^[12a, 13] and although organic solvent mixtures have been explored for autocatalytic HMF production,^[14] to our knowledge, the present work is the first that studied monophasic, organic solvent mixtures for autocatalytic furfural production.



Scheme 1. Reaction scheme of the dehydration of xylose to furfural and potential pathways for degradation reactions.

The dehydration of xylose to furfural is a function of both time and temperature, which can be combined into a single variable, severity (R_o), which is defined as:

$$R_o = \log_{10} [t_{rxn} \exp((T_{rxn} - 100)/14.75)] \quad 1$$

where T_{rxn} is the reaction temperature [$^{\circ}$ C] and t_{rxn} is the reaction time [min].^[15] Herein, the effect R_o and δ_p have on xylose conversion and furfural yield is reported for pure aqueous and organic/water solvent mixtures of either sulfolane, γ -butyrolactone (GBL), GVL, γ -hexalactone (GHL), or THF in autocatalytic reactions. Using principal components analysis (PCA) and projection to latent structures (PLS), the strength of the correlations between R_o and δ_p to xylose conversion and furfural yields were determined and a semi-empirical model was developed that estimates conversion and yield within a range of R_o and δ_p .

At a temperature of 463 K, increasing the reaction time, which increases R_o , increased both xylose conversion (Figure 1A) and furfural yield (Figure 1B) for most solvent mixtures. The maximum furfural yields of the 50/50 w/w solvent mixtures ranged from 51% for THF (12 h; $R_o=5.5$) to 61% for sulfolane (5.5 h; $R_o=5.2$) at 96% and 93% xylose conversion, respectively. These results were comparable to the pure aqueous system (59% furfural yield at 95% xylose conversion; Figure S1), which was a higher yield than

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previously reported.^[9a, 16] Unsurprisingly, in the pure aqueous system at severities near 100% xylose conversion ($R_o > 5.45$; Figure S1), furfural yields decreased due to the rate of furfural degradation exceeding the rate of furfural formation, which was also seen for sulfolane at 12 h ($R_o = 5.5$; Figure 1B).

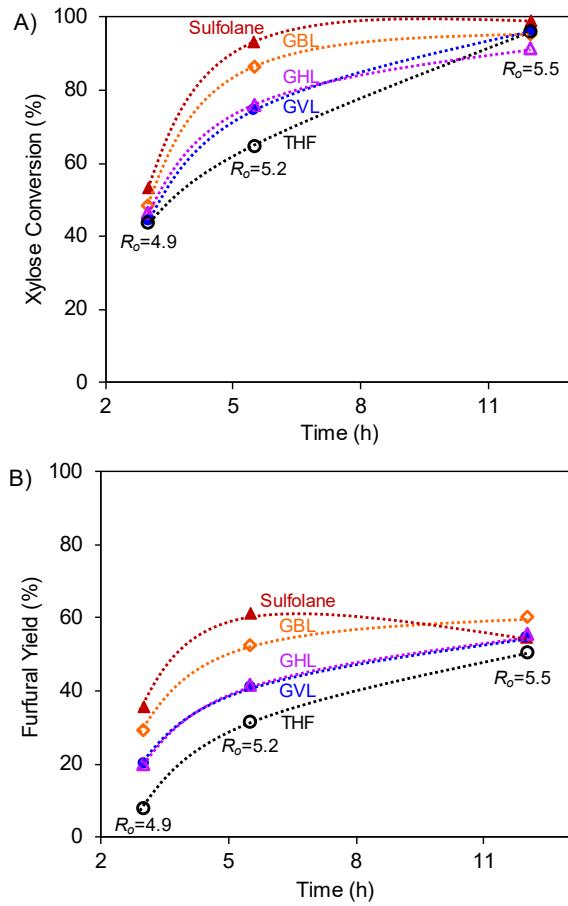


Figure 1. Effect of increased reaction time on A) conversion and B) yield in 50/50 w/w solvent systems (463 K; 2 wt% xylose) with sulfolane (▲), GBL (◊), GHL (●), GVL (△), and THF (○).

Since R_o is a function of time and temperature, as time increases, R_o increases at a given temperature, as shown in Figure 1. Xylose conversion and furfural yield typically increased as R_o increased, with sulfolane and THF achieving the highest and lowest values, respectively. Correlation plots of kinetic parameters (temperature, time, and R_o) and solvent properties (δ_P , δ_H , and δ_D) showed that both xylose conversion and furfural yield positively correlated with R_o at the 5% significance level (Figure S2). This result affirms the validity of R_o to represent the reaction conditions (time and temperature). Additional confirmation was found at an R_o of 5.2, where similar conversions and yields were achieved for each solvent system at different combinations of time (21 h and 5.5 h) and temperature (443 K and 463 K; Figure 2, blue and orange points). Likewise, the pure aqueous system showed similar results at an R_o of 5.0 (Table S1). The relationship between δ_P and xylose conversion or furfural yield can be seen in Figure 1,

where there is indeed a clear trend that as the δ_P increased (Table S2), the conversion and yield generally increased at a given R_o (THF < GHL \approx GVL < GBL < sulfolane). Regardless of solvent type, as δ_P increased, xylose conversion and furfural yield trended upward for all severities (Figure 2); however, at an R_o of 5.5, the dependence on δ_P decreased, likely due to the nearly complete conversion of xylose (Figure 2A). The correlation between δ_P and furfural yield may be explained by the proposed mechanism for xylose to furfural in which a carbocation is formed and could be stabilized by a polar solvent through H-bond formation.^[17]

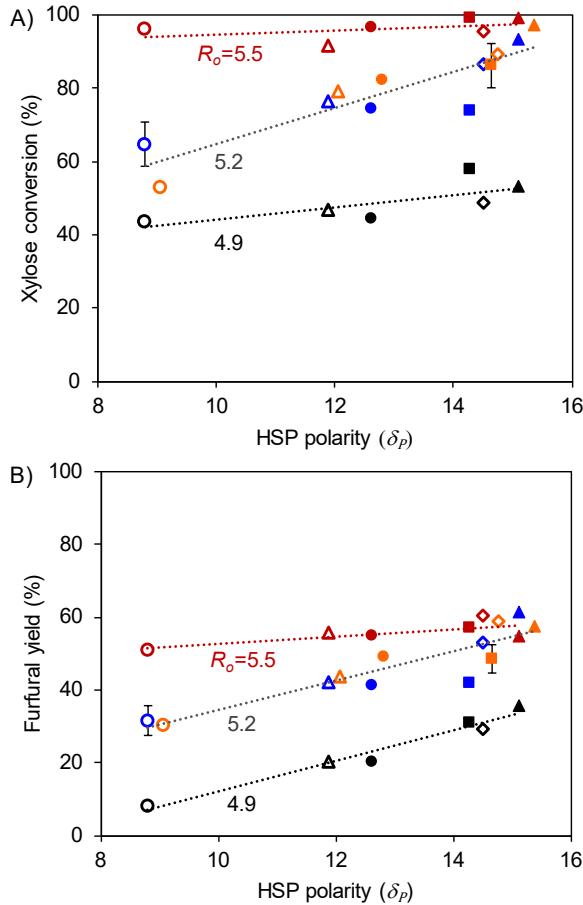


Figure 2. Effect of R_o and δ_P on A) conversion and B) yield at 443 K (orange) and 463 K (all others) in water (■) and 50/50 w/w solvent systems of sulfolane (▲), GBL (◊), GVL (●), GHL (△), and THF (○). Best fit lines are shown for severities of 5.5 (red), 5.2 (gray), and 4.9 (black).

The presence of formic acid as a degradation product (Scheme 1) was observed in the pure aqueous and most monophasic organic/water systems at xylose conversions above 30%. However, the formic acid yields tended to be less than 10% and there was no significant correlation between formic acid and xylose conversion or furfural yield at the 5% significance level. This indicates the autocatalytic reaction mechanism has little contribution from the formic acid.

Since the δ_P for mixtures is a function of volume percent, it can be tuned within the range of the δ_P of water and the δ_P of the pure

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solvent (Table S2). Observing all of the solvents collectively (Figure S3), increasing the δ_P of the organic/water mixture by changing the solvent ratio resulted in a nonlinear trend in both xylose conversion and furfural yield. For mixtures with a pure solvent δ_P greater than that of water, such as GBL and sulfolane, increasing the weight percent of organic solvent increased the δ_P of the system, which led to increased conversions and yields. In the sulfolane/water system, increasing δ_P with a 70/30 w/w mixture led to a maximum furfural yield of 67% at 97% xylose conversion and an R_o of 4.9 (Table S3). Further increases in R_o led to decreased furfural yields since the rate of furfural degradation exceeded production near 100% xylose conversion. Interestingly, GBL has a pure solvent δ_P near that of water, limiting the possible δ_P range to 14.37–14.63 at 463 K. As expected, xylose conversions and furfural yields were limited (48–66% and 29–34%, respectively, R_o = 4.9) for mixtures ranging from 20/80 to 70/30 w/w GBL/water.

In contrast, for organic solvents that have a pure solvent δ_P less than the δ_P of water, as the percent organic solvent in the mixture increased, δ_P decreased, resulting in lower conversions and yields. For example in THF/water mixtures, increasing the solvent from 20/80 to 70/30 w/w decreased xylose conversion from 52 to 42% and furfural yield from 30 to 4%, respectively. Similar trends were seen for furfural yields in GVL/water mixtures (Table S3), but this decrease in yield with increasing solvent percent differs from what has been reported previously for monophasic systems using an acid catalyst.^[18] This opposing trend may be explained by the large effect pH can have on severity,^[15] which could minimize the effect of δ_P , or the effect the acid has on δ_P , which is not easily accounted for.

To determine the contribution that R_o and δ_P each have on xylose conversion and furfural yield, multivariate statistical modeling (MSM) methods, including PCA and PLS,^[19] were used to account for collinearity and correlation among the variables. To maximize the usefulness of the MSM methods, the data were limited to $11.89 \leq \delta_P \leq 15.11$ and $4.9 \leq R_o \leq 5.33$ to avoid the highly nonlinear region of the data (Figure S3). Additionally, to generate a more robust model, the experimental dataset included random variability from normal distributions defined by the known experimental errors (Supplemental 1.2). It is important to note that the coefficients of the model used to estimate the dependent variables were identified simultaneously, which demonstrates the power of the PLS method to fit the correlated and collinear data.

Although multiple combinations of variables were considered (Table S5), the PLS analysis using R_o and δ_P as the regressor variables demonstrated the greatest correlation to the dependent variables (xylose conversion and furfural yield), as evidenced by the higher amount of variance accounted for (85.47%; Table S6). Almost all of the estimations of the experimental data (Equation S8) fell within the 95% prediction interval (Figure 3, black points); however, some of the estimated points were outside the experimental error ($\pm 6\%$ for xylose conversion and $\pm 4\%$ for furfural yield). Near the boundaries of the model range, the estimations of the experimental data were less accurate, likely due to nonlinear correlations unaccounted for by the PLS method (Figure S3). Importantly, the multivariate statistical analyses confirmed that over a range of R_o and δ_P , that xylose conversion

and furfural yield can be estimated within experimental error in most cases.

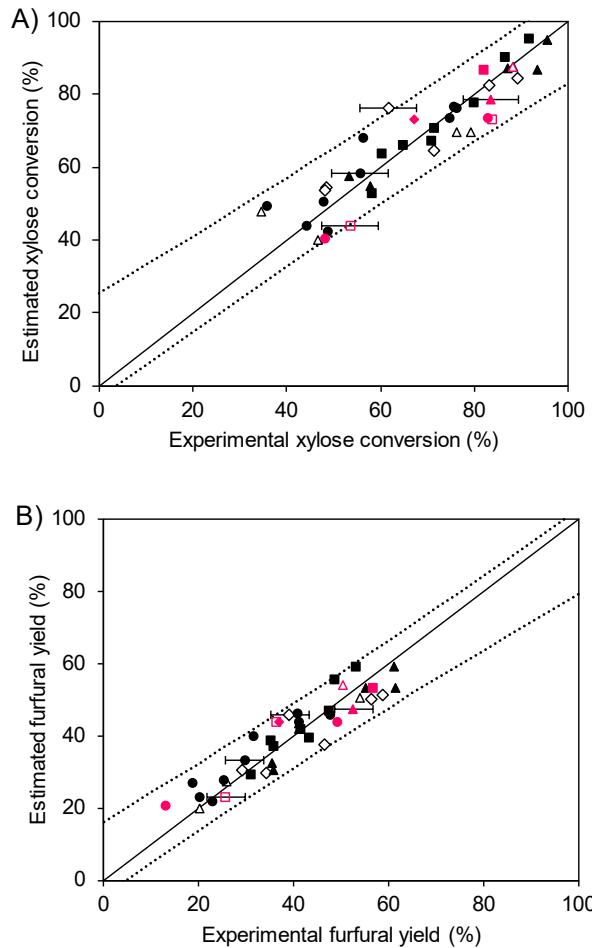


Figure 3. Estimated versus experimental data (black) and validation points (pink) for A) xylose conversion and B) furfural yield for mixtures of sulfolane (▲), GBL (◇), H₂O (■), GVL (●), GHL (△), BuOH (◆), and acetone (□). The 95% prediction interval (dotted lines) is shown.

Given the regressor variables, R_o (Equation 1) and δ_P ,^[8] the model is an implicit function of time, temperature, and solvent type in its estimates of xylose conversion and furfural yield. A key finding supported by the analyses is that given a specified R_o and δ_P , the same xylose conversion and furfural yield can be achieved within experimental error regardless of the organic/solvent mixture (Table 1). This important discovery must be interpreted with caution, however, as the experimental furfural yield in the 20/80 w/w THF/water mixture was approximately 10% higher than all other solvent mixtures at a similar δ_P (Figure S3; $\delta_P = 11.93$; $R_o = 4.9$) and the xylose conversion of GHL (Table 1; $\delta_P = 12.61$; $R_o = 5.2$) was lower than model estimates. Since these experimental data were confirmed with multiple experiments, discrepancies may be the result of an inexact pure solvent δ_P value given by the HSPiP program (see Supplemental 1.1), repeated experimental errors, or an unaccounted for difference in the reaction mechanism.

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Table 1. Experimental and estimated values of conversion and yield for different solvent blends with similar HSP polarity values. Reaction conditions: $R_o = 5.2$, 2 wt% xylose.

Solvent	Organic solvent percent (wt%)	HSP polarity (δ_P)	Xylose conversion (%)		Furfural yield (%)	
			Expt.	Est.	Expt.	Est.
THF	17	12.26	76	72	49	43
GVL	50	12.61	74	73	41	44
GHL	35	12.61	57	73	41	44
BuOH	15	12.65	67	73	37	44

The prediction ability of the regression model (Equation S8) was evaluated with validation points not included in the calibration data (Figure 3, red points; Table S7). All xylose conversions and furfural yields for the validation set were estimated within the 95% prediction interval; however, validation points containing 50 wt% or more organic solvent were underestimated for conversion. This result may be explained in part due to increased rate of reactions as Mellmer et al. reported when using GVL.^[2] Thus, the accuracy of the model estimates for higher weight percent solvent mixtures may be improved if reaction kinetics were taken into account.

Even with the limited number of solvents explored (sulfolane, GBL, water, GVL, GHL, and THF), the regression model (Equation S8) successfully estimated xylose conversion and furfural yield for acetone (Figure 3 and Table S7), which was not included in the calibration data. Remarkably, even when considering another new solvent, 1-butanol (BuOH), the multivariate statistical analyses confirmed experimental findings that given values of R_o and δ_P that are within the range of the model calibration, similar xylose conversions and furfural yields will be achieved (Table 1). The success of the regression model in confirming the significance of R_o and δ_P , should be tempered by the obvious limitation that the range of data used to develop the model exhibited a high degree of linearity. For example, at the lower bounds of δ_P , although the model accurately estimates the conversion and yield of the 50/50 w/w GHL/water mixture, it does not accurately estimate the 70/30 w/w GVL/water mixture (Table S7). Additionally, the model is not accurate above a R_o of 5.3, where most solvents achieve 100% xylose conversion and furfural degradation may occur.

In summary, the effect of R_o and solvent parameters were studied in order to determine the relationship they have on xylose conversion and furfural yield. Increasing R_o and δ_P , regardless of the time and temperature combination or organic solvent, increased xylose conversion and furfural yield. The availability of HSP data allowed for easy solvent selection based on δ_P , and reaction conditions can be tailored for temperature and time restrictions using R_o . Correlations and collinearity among these variables were confirmed by multivariate statistical analyses enabling a more systematic way for choosing experimental conditions to achieve high xylose conversions and furfural yields in xylose to furfural autocatalytic reactions.

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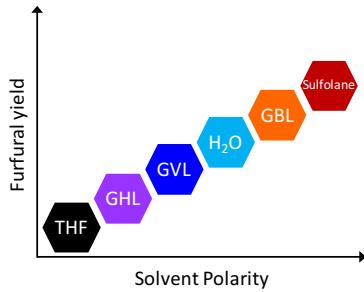
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Monophasic solvent systems with higher polarity significantly improved furfural yields in the autocatalytic dehydration of xylose. A semi-empirical model was developed that confirms reaction severity and solvent polarity lead to higher furan yields. This increase is likely attributed to the stabilization of the carbocation that forms during the reaction.



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