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Furfural production from xylose in a bi-phasic set-up

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Abstract

The production of furfural (FUR) from xylose was carried out using a biphasic batch reaction system. Isophorone and 2-methyltetrahydrofuran (MTHF) have been used to extract FUR and enhance overall furfural yield by limiting its degradation to humins. The effect of time, temperature, and organic to aqueous ratio on xylose conversion and FUR yield were investigated. Experiments conducted at two temperatures (170 and 190 °C) were investigated in a stirred microwave-assisted batch reactor, which established the optimal conditions to obtain the highest FUR yield. The maximum FUR yields obtained from xylose were 82 mol% when using MTHF in 180 min (at 190 °C) and 43 mol% when using isophorone in 180 min (at 190 °C) with an aqueous to organic phase ratio of 5:1.

Keywords: xylose, furfural, hemicellulose, prehydrolyzate liquor, biorefinery, MTHF, CPME, isophorone

Introduction

In recent years we have witnessed much activity to upgrade sugars contained in side-streams from the pulp and paper industry into ethanol and other value-added chemicals. An interesting catalytic route, namely the dehydration of sugars to furans, is considered one of the most promising routes for the production of platform chemicals and fuels. Furans such as FUR are highlighted in the "Top 10 + 4" by the United States Department of Energy list as the most rewarding bio-based platform molecules¹. The current FUR production uses mineral acids at approx. 200 °C, providing around 50 mol% yield. These mineral acids possess several drawbacks, e.g., high toxicity, corrosiveness, difficult recovery and large salt waste after work-up.

Several studies have suggested ways to inhibit the formation of humins and subsequently increase the FUR yield. One approach is to selectively extract the FUR from the aqueous solution into an organic phase. Trimble and Dunlop² were the pioneers to implement this idea using ethyl acetate as the extracting media. Subsequent research included studies on various organic solvents such as methyl isobutyl ketone (MIBK)^{3,4}, toluene⁴, 2-methyltetrahydrofuran (MTHF)⁵ and γ -valerolactone⁶.

The purpose of this study is to evaluate the production of FUR from xylose using a biphasic system in which FUR is extracted into a water immiscible solvent removing it from the acidic environment that would catalyze yield reducing condensation and resinification reactions. Besides, this bi-phasic system performs better than aqueous systems as this study demonstrates.

The results of this work could be used to produce platform chemicals, especially FUR, from sugar-based side-streams in the forest industry, in particular from the pre-hydrolyzate liquor generated during dissolving pulp production. These obtained value-added products have applications in a wide range of industrial branches (biofuel, pharmaceutical, agrochemical, petrochemical and chemical industry, among others).

Experimental

The effect of xylose concentration on FUR production was studied in biphasic systems made with Isophorone and 2-MTHF serving as the organic phase and an aqueous xylose solution in a 1:5 vol/vol ratio.

Samples for analysis were drawn from both the organic phase (top) and aqueous phase (bottom) after microwave heating. Xylose and FUR from aqueous phase were analyzed separately by High Performance Liquid Chromatography (HPLC) using a Dionex UltiMate 3000 HPLC (Dionex, Sunnyvale, CA, USA) device equipped with refractive index (RI) and ultraviolet (UV) diode array detectors. Product separation was achieved on a HyperRez XP Carbohydrate Ca²⁺ column (Thermo Scientific, Waltham, MA, USA). Aqueous sulfuric acid (0.0025 mol l⁻¹) was used as eluent with a flow rate of 0.8 ml min⁻¹.

FUR from the organic phase was analyzed by gas chromatography with a flame ionization detector (GC-FID) relative to iso-butanol as internal standard (IS). The columns used was a DB-WAXetr (30 m, 0.32 mm i.d., 1 μ m film thickness) from Agilent Technologies Inc. The injected samples (1 μ L) were subjected to a 10:1 split ratio in the inlet maintained at 200 °C. Helium was used as the carrier gas

The following equations have been used for the mathematical evaluation of the obtained results:

The FUR yields, xylose conversion and selectivity to FUR are calculated using equations 1, 2 and 3,

$$Y_{fur} = \frac{c_{fur,org}^f + c_{fur,aq}^f}{c_{xyl}^{in}} \times 100 \quad [\%] \quad (1),$$

$$X_{xyl} = \frac{c_{xyl}^{in} - c_{xyl}^f}{c_{xyl}^{in}} \times 100 \quad [\%] \quad (2),$$

$$S_{xyl}^{fur} = \frac{Y_{fur}}{X_{xyl}} \times 100 \quad [\%] \quad (3),$$

where Y, X, S are the– furfural yield, conversion of xylose and selectivity to FUR, respectively; c is the– concentration in mmol l⁻¹ (the subscripts to be read as follows: *xyl*, *fur*, *org*, *aq*, *in*, *f* are the– xylose, FUR, organic phase, aqueous phase, initial, final).

Results and Discussion

Effect of aqueous to organic phase ratio

The effect of aqueous to organic phase ratio on furfural production was studied in biphasic systems made with isophorone and MTHF serving as the organic phase and an aqueous solution of 186 mmol l⁻¹ at 190 °C in 30 min. The FUR yield, xylose conversion and selectivity to FUR are shown in Figure 1 and are calculated using equations 1, 2 and 3.

It can be seen in Figure 1a that the FUR yield when using isophorone increases as the aqueous to organic ratio increases. The highest FUR yield (9%) is reached (at 190 °C in 30 min) when employing an aqueous to organic phase ratio of 5:1. When using MTHF, there are two ideal aqueous to organic phase ratios in which high FUR yield can be reached: 1:1 (13%) and 5:1 (12%) at 190 °C in 30 min.

The xylose conversion tends to decrease as the aqueous to organic phase ratio increases (Figure 1b). For samples working with isophorone as the organic solvent, the average xylose conversion is 36% (standard deviation 5%). When MTHF is employed, the average xylose conversion is 43% (standard deviation 5%). This difference could be due to a higher solubility of xylose in MTHF than in isophorone.

The maximum selectivity to FUR formation during biphasic reactions with isophorone was 30% in an aqueous to organic phase ratio of 5:1 (Figure 1c). In the case of biphasic reactions when MTHF was in use, two values of selectivity to furfural were identified: 30% and 32% for an aqueous to organic phase ratios of 1:1 and 5:1, respectively.

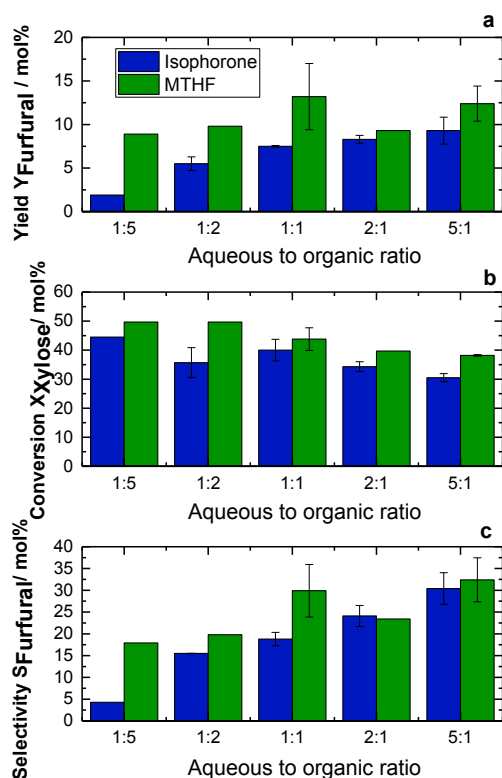


Figure 1. Effect of aqueous to organic ratio on FUR yield (a), xylose conversion (b) and selectivity to FUR (c) when employing isophorone and MTHF. The effect was determined for a solution of xylose (186 mmol l^{-1}) heated at $190 \text{ }^{\circ}\text{C}$ in 30 min at five different ratios of aqueous to organic solvent: 1:5, 1:2, 1:1, 2:1, 5:1 (v/v). The error bars shown are one standard deviation from duplicate analyses.

Effect of reaction temperature

The effect of reaction temperature on the production of FUR was studied by conducting reactions between 100 and $200 \text{ }^{\circ}\text{C}$ in 30 min employing a 186 mmol l^{-1} xylose solution. The FUR yield varied between 0 and 23 mol%. The effect of reaction temperature on FUR yield, xylose conversion and selectivity to FUR when working with an aqueous to organic ratio of 5:1 was further investigated. A low FUR yield was obtained from 100 to $150 \text{ }^{\circ}\text{C}$ (approximately 0%). The reason for lower FUR yield at the low reaction temperature was due to incomplete xylose conversion (below 15%). The highest FUR yield when employing MTHF is 23% (at a xylose conversion of 47%), and when using isophorone is 18% (at a xylose conversion of 50%) at $200 \text{ }^{\circ}\text{C}$ (in 30 min).

Effect of reaction time

The effect of reaction time on the production of FUR was studied by conducting reactions between 30 to 180 min at 170 and $190 \text{ }^{\circ}\text{C}$ with MTHF and isophorone with a 186 mmol l^{-1} xylose solution. Figure 2 shows the effect of reaction time on FUR yield, xylose conversion and selectivity to FUR.

In agreement with previous studies ⁷, FUR yield and xylose conversion were observed to be strongly influenced by the reaction temperature (Figure 2a-b, 2d-e). As seen in Figure 2a, after the first 60 min of the treatment the FUR yield was increased up to five times by increasing the temperature from 170 to $190 \text{ }^{\circ}\text{C}$ when employing isophorone. The highest FUR yield (42%) when using isophorone as organic solvent was reached at $190 \text{ }^{\circ}\text{C}$ in 3 h. The maximum selectivity (Figure 2c) to FUR formation was 44% and 48% at temperatures of 170 and $190 \text{ }^{\circ}\text{C}$, respectively.

When employing MTHF (Figure 2d), after the first 60 min of the hydrothermal treatment, the FUR yield was increased up to five times by increasing the temperature from 170 to $190 \text{ }^{\circ}\text{C}$, similar to the effect observed when using isophorone. The highest FUR yield (82%) was reached at $190 \text{ }^{\circ}\text{C}$ in 3 h. With MTHF, the maximum selectivities (Figure 2f) to FUR formation was 65% and 98% at temperatures of 170 and $190 \text{ }^{\circ}\text{C}$, respectively.

For both isophorone and MTHF as organic solvent, the amount of converted xylose at the temperatures studied in the present research (Figure 2b and 2e) was similar. When using isophorone, the maximum xylose conversions were 37% and 89% at 170 and $190 \text{ }^{\circ}\text{C}$ (in 3 h), respectively. When using MTHF, the maximum xylose conversions were 41% and 84% at 170 and $190 \text{ }^{\circ}\text{C}$ (in 3 h), respectively.

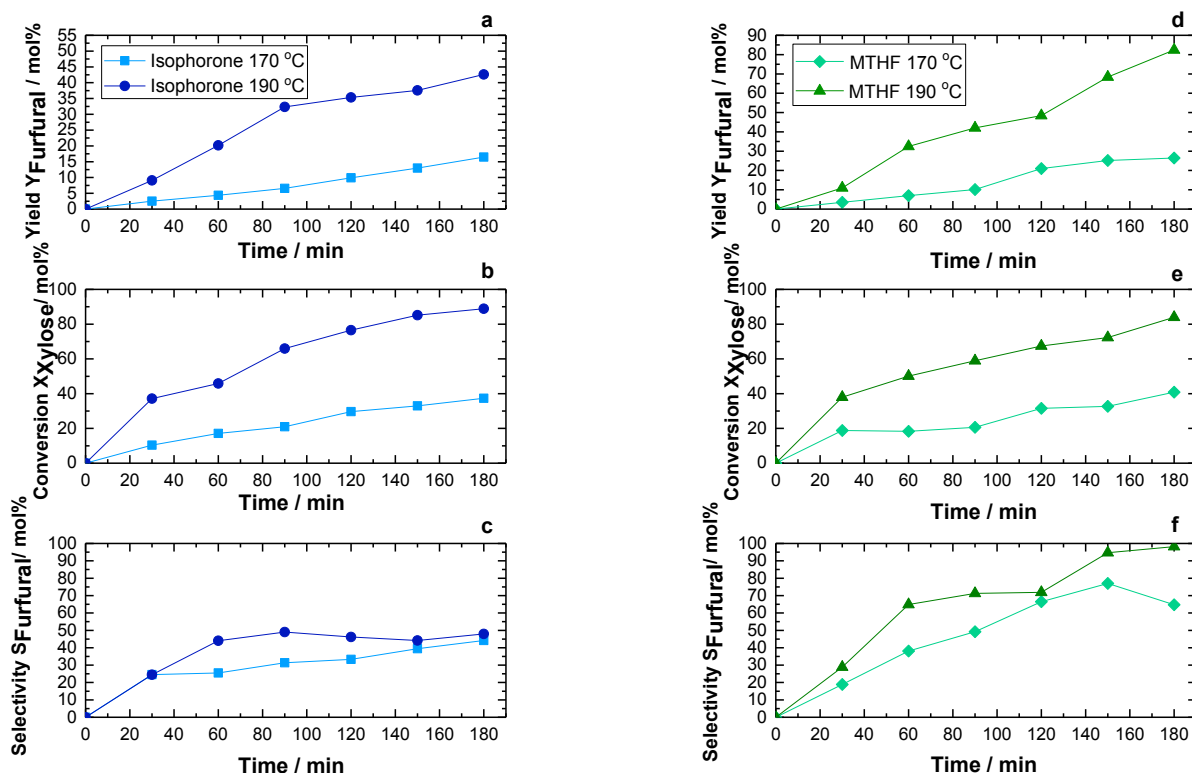


Figure 1 Effect of reaction time on (a) FUR yield, (b) xylose conversion, (c) selectivity to FUR in the dehydration of 28 g l⁻¹ xylose when using isophorone and MTHF as organic solvents. Dark blue circles – isophorone at 190 °C, light blue squares – isophorone at 170 °C, dark green triangles – MTHF at 190 °C, light green diamonds – MTHF at 170 °C, lines are to guide the eye. Aqueous ratio to organic solvent was 5:1.

Conclusions

From this study, it can be concluded that:

- The ideal aqueous to organic phase ratio is 5:1 when employing MTHF and isophorone as organic solvents to extract FUR in the dehydration of xylose.
- The selectivity to FUR is higher when working with MTHF than with isophorone.
- The highest FUR yield (82%) was reached at 190 °C in 3 h employing MTHF as the organic solvent and an aqueous to organic phase ratio of 5:1.
- Studies involving the separation after reaction and further reusability of MTHF could give an interesting approach for a *greener* process.

References

1. Bozell JJ, Petersen GR. Technology development for the production of biobased products from biorefinery carbohydrates-the US department of energy's "top 10" revisited. *Green Chem.* 2010;12(4):539-554.
2. Trimble F, Dunlop AP. Recovery of furfural from aqueous solutions. *Ind Eng Chem Anal Ed.* 1940;12(12):721-722.
3. Weingarten R, Cho J, Conner J, Wm. Curtis, Huber GW. Kinetics of furfural production by dehydration of xylose in a biphasic reactor with microwave heating. *Green Chem.* 2010;12(8):1423-1429.
4. Mittal A, Black SK, Vinzant TB, O'Brien M, Tucker MP, Johnson DK. Production of furfural from process-relevant biomass-derived pentoses in a biphasic reaction system. *ACS Sustainable Chem Eng.* 2017.
5. vom Stein T, Grande PM, Leitner W, Domínguez de María P. Iron-catalyzed furfural production in biobased biphasic systems: From pure sugars to direct use of crude xylose effluents as feedstock. *ChemSusChem.* 2011;4(11):1592-1594.
6. vom Stein T, Grande PM, Kayser H, Sibilla F, Leitner W, Dominguez dM. From biomass to feedstock: One-step fractionation of lignocellulose components by the selective organic acid-catalyzed depolymerization of hemicellulose in a biphasic system. *Green Chem.* 2011;13(7):1772-1777.
7. Danon B, Hongsiri W, van der Aa L, de Jong W. Kinetic study on homogeneously catalyzed xylose dehydration to furfural in the presence of arabinose and glucose. *Biomass Bioenergy.* 2014;66(0):364-370.

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