Comment on "Acid-catalyzed conversion of xylose, xylan and straw into furfural by microwave-assisted reaction [Yemis and Mazza, 2011, Bioresour. Technol. 102, 7371-7378]"

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In their article, Yemis and Mazza [1] study the effects of different Bronsted acids, temperatures, times, substrate concentrations, and pH on the acid-catalyzed conversion of xylose, xylan and straw into furfural by microwave-assisted reaction. In Section "3.4. Influence of initial pH on furfural yield," the authors report a large sensitivity in the furfural yield that is dependent on pH (using HCl as the acid), with a yield variation of about one order of magnitude within the narrow pH ranges of 1.12→2.05 and 1.12→0.13 (see Figure 1(d) in ref. [1], with maximum conversion occurring at a pH of 1.12). Thus, a pH variation of less than one unit can mean a furfural yield variation of almost 10-fold.

Subsequently, in Section "3.5. Influence of type of acid-catalyst on furfural yield," Yemis and Mazza [1] go on to claim that "[w]e studied the effect of three strong mineral acids (hydrochloric acid, sulfuric acid, and nitric acid) and three weak organic acids (phosphoric acid, acetic acid, and formic acid). The furfural yields obtained from xylose and xylan in the presence of hydrochloric, sulfuric, nitric, phosphoric, acetic, and formic acid are presented in Fig. 2. The process conditions were a temperature of 180°C, a solid:liquid ratio of 1:100, a residence time of 20 min, and a pH of 1.12." Phosphoric acid is not an organic acid as Yemis and Mazza [1] claim; it is a mineral acid.

More importantly, how do the authors achieve process conditions that include a pH of 1.12 in the two "weak" organic acids? At pK_a/maximum concentration values of 4.75/17.4 M and 3.75/23.6 M for acetic and formic acid, respectively, it appears the lowest pH values that can be reached with concentrated reagents are 1.76 (acetic acid at 99.8% wt/wt strength) and 1.19 (formic acid at 90.0% wt/wt strength). As noted above, since even small pH variability can result in large yield variations, readers need further experimental details from Yemis and Mazza (2011) on how they achieved the pH values stated using the "homogeneous acids" they claim to have used. If the pH of all acid solutions was not 1.12 as stated, this could explain much of the reported yield differences between samples.

References

[1] O. Yemis, G. Mazza, Acid-catalyzed conversion of xylose, xylan and straw into furfural by microwave-assisted reaction, Bioresource Technology 102 (2011) 7371–7378.

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