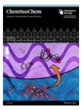

Reactive Extraction Enhanced by Synergic Microwave Heating: Furfural Yield Boost in Biphasic Systems

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Reactive extraction is an emerging operation in the industry, particularly in biorefining. Here, reactive extraction was demonstrated, enhanced by microwave irradiation to selectively heat the reactive phase (for efficient reaction) without unduly heating the extractive phase (for efficient extraction). These conditions aimed at maximizing the asymmetries in dielectric constants and volumes of the reaction and extraction phases, which resulted in an asymmetric thermal response of the two phases. The efficiency improvement was demonstrated by dehydrating xylose (5 wt% in water) to furfural with an optimal yield of approximately 80 mol% compared with 60–65 mol% under conventional biphasic conditions, which corresponds to approximately 50% reduction of byproducts.

Reactive extraction has emerged recently as a promising technology for the conversion of biobased feedstock.[1–3] This technique is a cost-effective way to circumvent problems in biorefinery, such as recovering and recycling catalysts, separating products, and suppressing side reactions.[1–3] Reactive extraction shows a wide scope of applications and can be also used in the conversion of sugars into furans (e.g., furfural).[3]

Furfural is recognized as a top value-added chemical. It has a rich source of derivatives and can be used as an additive for fuels with promising performance.[4,5] Furfural can be obtained from the acid-catalyzed dehydration of D-xylose, a monomeric subunit of hemicellulose, which is a component of lignocellulosic feedstock.[4–7] The industrial approach for furfural production, which employs aqueous medium and mineral acid catalysis (H_2SO_4), does not deliver furfural yields beyond approximately 45 mol% on xylose base.[4,5,7–9] This shortcoming is mainly caused by the formation of insoluble byproducts called humins, resulting from furfural–xylose condensation and direct resinification of furfural at high conversion.[4,5,8]

Several examples of high-yield (>80 mol%) furfural production have been reported using polar aprotic organic solvents.[10,11] However, such approaches suffer from the need to extract the xylose from the aqueous phase to resolubilize it in the polar organic solvent. An alternative approach, based on reactive extraction in biphasic operation, reached furfural yields of approximately 65 mol%.[11–13] This selectivity enhancement is generally assigned to continuous extraction of furfural into the organic phase, with the consequent inhibition of furfural degradation.[8,12,14–17]

Microwave heating has been widely applied to organic synthesis in general and has been abundantly used for the dehydration of sugars to furans, for example, of xylose to furfural.[15,18–20] When applied to monophasic aqueous xylose solution, microwave heating does not result in improvement of the selectivity but only in a rate enhancement.[9] This has been explained through purely thermal effects such as inhomogeneous heating.[9,21–23]

Incidentally, biphasic operation has been combined with microwave heating, but no specific effects have been recognized.[24,25] We nevertheless reasoned that the combination of microwave heating and biphasic operation could have a synergic effect on the selectivity of the furfural production (Figure 1). Microwave heating could heat up the aqueous phase to accelerate the dehydration of xylose while leaving the organic phase colder to favor the extraction of furfural. We show here that the combination of microwave heating and biphasic operation can indeed create a synergic effect that permits operation at higher xylose conversions than normally applied and pushes the yield into a section of the reaction parameter space that cannot be attained by one of the conditions alone (Figure 2a). Application to the combined microwave–biphasic operation may thus yield a further enhancement owing to the synergic effect, moving the optimal operation point to high xylose conversion, with an effect that is related with the microwave responsiveness of the two phases (Figure 2b). By unravelling the basis of this effect, we believe that we open the door to improving a wide range of reactive extraction processes.

In biphasic systems, the microwave responsiveness of each phase is strongly dependent on its dielectric properties: a higher polarity corresponds to a higher dielectric loss at microwave conditions, which results in a more efficient heating.[26,27]

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Supporting Information and the ORCID identification number(s) for the author(s) of this article can be found under: https://doi.org/10.1002/cssc.202000966.

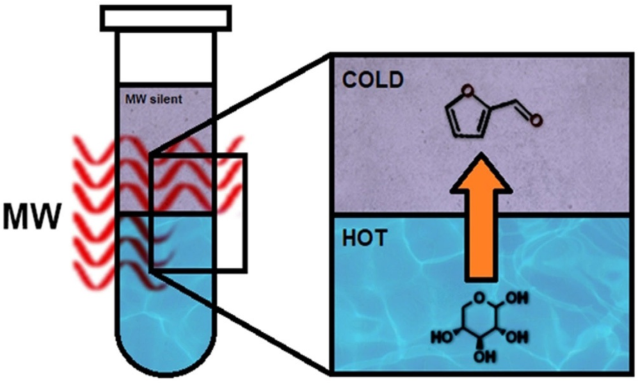

Figure 1. Visualization of the effect of having an asymmetric response in the biphasic system on reactive extraction of furfural. Furfural is formed in the microwave-active "hot" aqueous phase and extracted and stored in the MW-silent "cold" toluene phase.

The combination of a non-polar organic solvent (e.g., toluene or methylcyclohexane) and a highly polar aqueous phase (e.g., water with a high ionic strength) might lead to an inhomogeneous temperature distribution between the two phases because the aqueous phase gets selectively heated by the microwave irradiation.[12,16]

It is crucially important to monitor the reaction temperature under microwave conditions accurately.[9,21–23] Fiber-optic sensors are commonly used to internally monitor the temperature, but if the homogeneity of the mixing cannot be ensured such sensors show surprisingly large temperature gradients throughout the reaction medium.[21] Owing to the high operation temperatures applied in this study and the necessity to seal the pressurized reaction vessels, we monitored the temperature by using an IR temperature control system. The accuracy of this control system was ensured following a calibration procedure prior to use, showing a standard deviation of ±1 °C.[9] Under microwave heating, more information about the global temperature of the medium is obtained by comparing the operating pressure (≈18–20 bar) to the equivalent saturated pressure (Figure S1 in the Supporting Information). The operating pressure measured in the presence of the biphasic water/toluene mixture of 1:1 volume ratio suggests a bulk liquid temperature that deviates less than ±10 °C from that measured by the IR sensor.[28] Nevertheless, we fully realize that these calibration data do not give any quantitative information on local temperature differences between the two liquid phases.[9]

For this study a biphasic system of an aqueous solution of xylose (350 mM, pH 1 from H_2SO_4) and an organic solvent of choice was heated to 200 °C both at traditional batch and microwave heating conditions. To tune the microwave responsiveness of the biphasic system, the volume ratio of the two phases and their chemical composition were varied. Toluene, commonly used as organic phase under biphasic conditions, was chosen as a benchmark hydrophobic solvent for its low dielectric constant ($\varepsilon_r = 2.4$), which results in negligible microwave activity, and for its aromaticity, which ensures high affinity for the extraction of furfural. The toluene phase is heated slightly upon contact with the aqueous phase, but this effect is minimized by operating at high toluene/water ratio. Our experimental setup did not allow us to gather information on the temperature of the two different phases. However, in the biphasic system the two phases remained immiscible even at high temperature (Figure S2 in the Supporting Information).

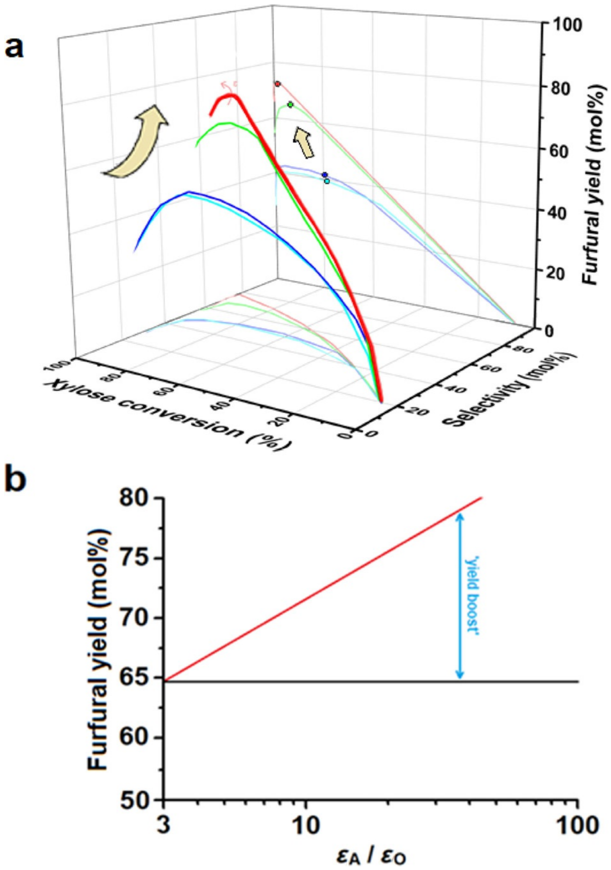

Figure 2. (a) Visualization of the selectivity and yield enhancement in relation with the reaction conditions. The blue and cyan curves correspond to the monophasic system at traditional and microwave heating conditions, respectively. Moving from monophasic to biphasic conditions results in an overall improvement at traditional heating conditions (green curve). The maximum furfural yield is reported to increase from approximately 45 to 65 mol %. Upon implementing microwave heating at biphasic conditions (red curve, current work) at the optimal operation point, represented by high xylose conversion (>90 %), there is a further improvement in selectivity and yield, which is also related to the dielectric constants of the two phases. (b) Visualization of the "yield boost" at biphasic conditions in relation with the difference in polarity between the two phases of the system, in which ε_A is the dielectric constant of the aqueous phase and ε_O is that of the organic phase. The "yield boost" at microwave conditions will arise at a higher ratio (red line), as the microwave responsiveness changes accordingly, whereas at traditional heating conditions the difference in dielectric properties does not have any influence on the heating profile, resulting in an unvaried final yield (black line).

Because the dehydration of xylose is acid catalyzed, the composition of the aqueous phase (pH 1 from H_2SO_4) ensures both optimal catalytic conditions for furfural formation and high ionic strength for microwave responsiveness.[29,30] The concentrations of furfural and unreacted xylose in the crude reaction mixture were evaluated through ^1H NMR spectroscopy (Figure S3 in the Supporting Information) to determine the rate and the selectivity of the xylose dehydration into furfural at biphasic conditions, which can also be compared with the monophasic system (Figures S4 and S5 in the Supporting Information).

At a 1:1 water/toluene ratio, both traditional heating and microwave heating could achieve full xylose conversion. Under traditional heating full xylose conversion was obtained after 360 min, at microwave conditions in 15 min (Figure S4 in the Supporting Information), illustrating the rate enhancement obtained under microwave conditions. The two heating methods can also be compared in terms of furfural selectivity and yield as well as their optimal points of operation. At xylose conversions from 0 to 85–90 %, selectivity and yield run parallel for both heating methods (Figures 3 a and Figure S4 in the Supporting Information). In contrast, for xylose conversions >90 % a higher furfural yield is recorded with microwave heating (Figure 3 b), reaching a yield of approximately 75 mol % (at a conversion >95 %), whereas traditional heating provides a maximum yield of approximately 65 mol %, reached at approximately 85 % conversion, as has also been observed in literature.[4,5,7–9] Correspondingly, at traditional heating conditions the selectivity maximum is obtained at approximately 85 % xylose conversion (after 240 min of reaction; Figure S4 in the Supporting Information), whereas under microwave heating the maximum is reached at >95 % xylose conversion (after $\approx$13 min of reaction; Figure S4 in the Supporting Information).

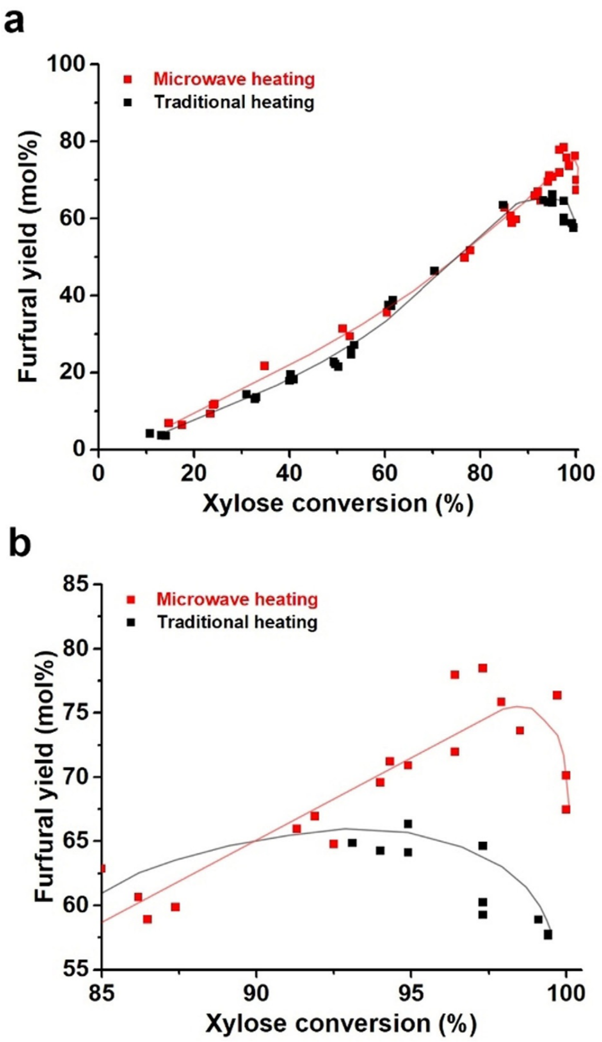

Figure 3. (a) Furfural yield [mol %] versus xylose conversion [%], at pH 1, 1:1 water/-toluene ratio, under traditional and microwave heating at 200 °C. (b) Zoom-in of the graph of (a) at xylose conversions >85 % for the visualization of the "yield boost" ($\approx$10 mol %) and the maximum selectivity shift to higher xylose conversion [%]. Lines are guides to the eye.

This observed rate enhancement cannot simply be assigned to a higher bulk temperature of the medium under microwave heating.[9] Such differences in the reaction rate would correspond to effective bulk temperatures up to 50 °C higher than the measured ones. Not only do these values exceed the deviations shown by the calibration, they would result in an excessive saturated pressure that was not observed experimentally.

The observed "yield boost" is thus a result of a shift of the optimal operating point (maximum furfural yield) to higher xylose conversions. This can be rationalized by inhibition of furfural degradation pathways in the late stage of the reaction, provided by an improved furfural extraction from the highly reactive aqueous phase. The selectivity enhancement upon microwave-assisted biphasic operation appeared to depend on the toluene volume fraction (Figure S6 in the Supporting Information). Varying the solvent volume ratio affected the overall dielectric properties of the system as well as the extraction capacity. As a result, the maximum yield at high xylose conversions slightly increased with the toluene volume fraction when operated under microwave irradiation, and these higher yields were again achieved at higher xylose conversions (Figure 4 a). Thus, a maximum "yield boost" of approximately 30 mol % was achieved upon changing operation from monophasic to biphasic at 90 vol % toluene (Figure 4 b). Control experiments showed that the toluene fraction did not affect the final furfural yield under traditional heating (Figure S6 b in the Supporting Information).

The observed "yield boost" can be explained by the suppression of the acid-catalyzed degradation and condensation reactions of furfural, that is, by a "medium effect". The furfural is extracted and stored safely in the organic phase (Figure S7 in the Supporting Information), which at microwave conditions has a lower temperature than the aqueous phase. This difference in temperature arises only at microwave conditions because the selective heating of the aqueous phase cannot be observed under traditional heating conditions, resulting in no selectivity enhancement under traditional heating. No significant yield enhancement could be obtained by raising the toluene percentage over 80 % (Figure 4 b). This upper limit for the yield can be rationalized by the fact that furfural partitions between the organic phase and the aqueous phase, in the latter of which acid-catalyzed degradation can occur.

As mentioned above, the relative polarity of the two phases is important (Figure 2 b), and it can be influenced by independently varying the dielectric constants of the organic phase and of the aqueous phase. Various organic solvents with different polarities were employed to show the effect of varying the dielectric constant of the organic phase on this "selectivity boost" (Figure 5 a). As expected, based on the previous experiments,

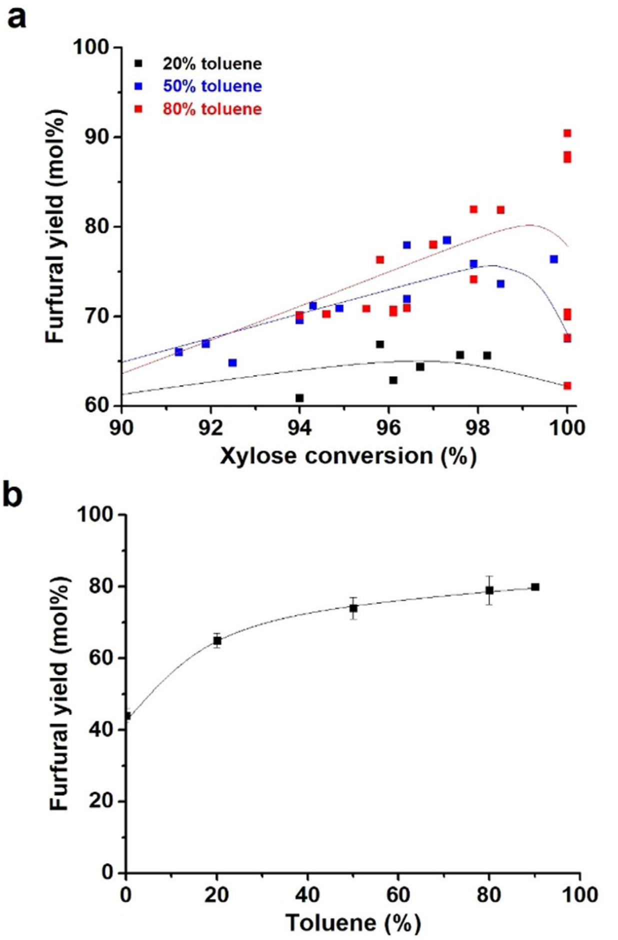

Figure 4. (a) Furfural yield [mol %] versus xylose conversion [%], at pH 1, at various water/toluene ratios, under microwave heating at 200 °C (section at conversions $>90\%$ shown). The multiple points at 100 % xylose conversion represent the progressive degradation of furfural with increasing reaction time. (b) Visualization of the "yield boost" obtained at the optimal operation points (at high xylose conversion) varying the toluene percentage. The data point at 90 % toluene is the result of a single experiment and is therefore reported without an error bar.

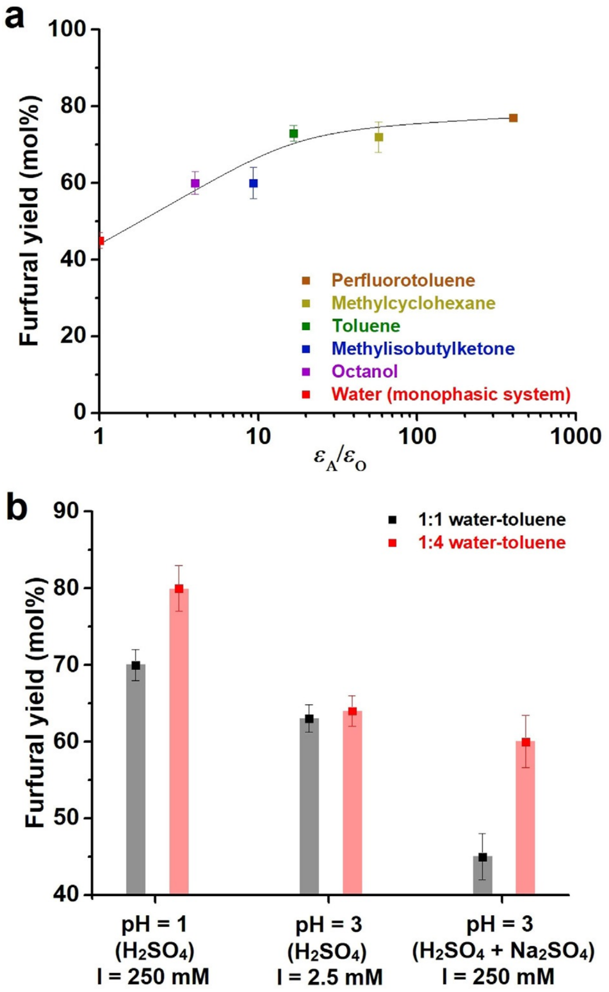

Figure 5. (a) Maximum furfural yield [mol %] at xylose conversions $>90\%$ as a function of the ratio of the dielectric constants of the aqueous and organic phases (15–20 min, 200 °C, 1:1 solvent ratio, pH 1). The line is a guide to the eye. (b) Visualization of the xylose-to-furfural "yield boost" in the reaction of xylose dehydration observed when varying the water/toluene ratio from 1:1 to 1:4 (200 °C, microwave heating), in relation with the ionic strength of the aqueous phase (dependent on acid and salt concentrations); data obtained at the optimal operation point (i.e., at maximum yield).

at microwave conditions the polarity of the solvent appeared to strongly affect the conversion of xylose to furfural (Figure 5 a and Figure S8 in the Supporting Information). At 1:1 biphasic conditions, a maximum furfural yield of approximately 75 mol % was obtained for low-polarity solvents such as toluene ($\varepsilon_r = 2.4$), methylcyclohexane (MCH, $\varepsilon_r = 0.7$), or perfluorotoluene ($\varepsilon_r \approx 0$). Upon moving to solvents with a higher polarity and significantly higher microwave absorption, the furfural yield decreased significantly, for example, to approximately 60 mol % with methylisobutylketone (MIBK, $\varepsilon_r = 4.3$) and octanol ($\varepsilon_r = 10$). In comparison, 45 mol % was achieved for the monophasic water system under microwave heating. Upon using toluene/water at traditional heating, only 65 mol % yield was achieved.

The microwave responsiveness of the aqueous phase can also be tuned by varying the pH and/or salt concentration of the aqueous solution (Figure S9 in the Supporting Information).[29] Two new sets of experiments were performed, one at pH 3 from H_2SO_4 (at a significantly lower ionic strength) and one additional control in which a passive, non-reactive ion source (Na_2SO_4) was added to achieve the high ionic strength of the solution at pH 1 used above while keeping the pH 3. Both sets were performed at 1:1 and 1:4 water/toluene ratios (Figures S10 and S11 in the Supporting Information).

As described above, at pH 1 under microwave heating, the toluene percentage clearly influenced the process (Figure 4 b). In contrast, at pH 3 no yield enhancement was observed (Figure 5 b and Figure S10 in the Supporting Information) upon varying the solvent ratio. However, upon adding an inert salt to the solution at pH 3 to reach the same ionic strength of the experiment performed at pH 1 (Figure S11 in the Supporting Information), a similar "yield boost" was observed when varying the solvent ratio (Figure 5 b). This enhancement was, however, always limited (as in the previous cases) at high xylose conversions, and the optimal operation point was reached in approximately 15–20 min of reaction (Figures S10 and S11 in the Supporting Information). This shows that the microwave responsiveness of the aqueous phase, which is directly related to the ionic strength, is crucial to achieve the conditions that lead to a selectivity enhancement.[29,30] However, the best results in terms of furfural yield (mol%) were obtained in the system at pH 1, indicating that a fast reaction is mandatory to prevent degradation and humins formation. This is arguably owing to the reaction rate outcompeting the rate of heating the toluene phase upon contacting the aqueous phase.

In conclusion, we report a consistent yield improvement of approximately 10–15 mol% in the dehydration of xylose by synergistically combining two different factors: microwave heating and reactive extraction using two phases with asymmetric polarity and volumes. Generally, the improvement of the yield of a chemical process is obtained by the development and optimization of a catalyst, possibly assisted by plasmonics or ultrasound, or by varying the solvent system and using membranes or other components for the in situ separation of the various products.[31–37] In this study, we show how a more optimal section of the reaction parameter space can be reached by the combination of microwave heating and specific biphasic conditions and by varying the dielectric properties of both phases. Such forms of synergism can become an important tool for organic synthesis and chemical processes. By unravelling the critical parameters of this process optimization, we believe this approach can be applied to improve other reactive extraction processes.

Acknowledgements

Financial support from Royal Dutch Shell plc is gratefully acknowledged. L.R. is grateful for the fruitful discussions with Richard J. M. Egberink and for part of the experimental work by Matthijs van Berkel.

Conflict of interest

The authors declare no conflict of interest.

Keywords: biomass · biphasic · furfural · microwave chemistry · synergy

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Manuscript received: April 14, 2020
Revised manuscript received: May 14, 2020
Accepted manuscript online: May 24, 2020
Version of record online: June 25, 2020