

## Sulfonated Sporopollenin as an Efficient and Recyclable Heterogeneous Catalyst for Dehydration of D-Xylose and Xylan into Furfural

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**ABSTRACT:** The natural acidity of sporopollenin, the biopolymer coating the outer walls of pollen grains, was enhanced by the sulfonation of its surface. Modified sporopollenin displaying sulfonic acid groups has been prepared, characterized by elemental analysis, SEM, EDX, FTIR and XPS and tested as a heterogeneous catalyst in the dehydration of D-xylose and xylan to produce furfural. The optimal reaction conditions involve 10 wt % of sulfonated sporopollenin in the presence of 1.5 mmol of NaCl in a biphasic water-CPME system. When heated at 190 °C, the reaction affords furfural in a yield of 69% after 40 min under microwave irradiation. The time dependence of the dehydration and influence of temperature, pentose loading and positive effect of chloride ions on the reaction rate are reported. It was found that the catalytic system,

recharged with the pentose and solvent, could be recycled ten times without loss of performance. The transformation of xylan into furfural at 190 °C for 50 min gave furfural in a yield of 37%.

**KEYWORDS:** *Furfural, D-xylose, xylan, sporopollenin, biphasic system, microwave-aided dehydration*

## **INTRODUCTION**

With an increasingly severe outlook for the depletion of oil-based resources, wood based biomass and especially plant waste rich in lignocellulosic feedstocks, appear to be the main alternative to producing many kinds of platform molecules such as furan derivatives. One of these high-value materials is furfural, which is produced largely from dehydration of hemicellulose-rich biomass and more specifically from D-xylose, the main monomer sub-unit of hemicellulose and xylan. Furfural is a key compound for the preparation of furfuryl alcohol by reduction of its aldehyde function,<sup>1</sup> which is also the precursor of commercially available levulinic esters.<sup>2</sup> Furfural is currently the feed-stock for the synthesis of organic solvents such as tetrahydrofuran (THF) and methyltetrahydrofuran (MeTHF).<sup>3</sup> It could also become an important starting material for the preparation of new bioactive compounds or materials. Industrial production of furfural is achieved by either batch or continuous acid hydrolysis of xylan<sup>4</sup> into D-xylose followed by dehydration of the xylose precursor to give furfural. The reaction is usually carried out at temperatures that can range from 170 °C to 185 °C under conventional heating. These processes require strong aqueous mineral acids such as HCl,<sup>5,6</sup> H<sub>2</sub>SO<sub>4</sub><sup>7</sup> or H<sub>3</sub>PO<sub>4</sub>,<sup>8</sup> which are also the main cause of corrosion, safety and handling problems. Recovery of furfural involves high-energy processes of distillation and additional treatments such as neutralization, which generate large waste streams. Unfortunately, in a monophasic system, furfural yield and selectivity are often limited by the formation of by-products derived from the cross polymerization between furfural and D-xylose in excess, or from the resinification of furfural itself.

To date the use of easy-to-handle, solid sulfonated organic polymers, recognized for their strong Brønsted acidity, such as protonated Amberlyst<sup>9-12</sup> or Nafion,<sup>13,14</sup> have shown promising results in the field of green chemistry. Both materials are sulfonyl group-decorated polymers and are alternatives to other types of heterogeneous catalysts such as zeolites<sup>15, 16</sup> or heteropolyacids.<sup>17</sup> However, during the process of xylose dehydration, these polymers have the disadvantage that a layer of humin, a black insoluble carbonaceous by-product generated by the degradation of the furfural, forms upon their surfaces which results in their deactivation. These layers almost cover the entire active surface of the solid catalyst and reduce the number of catalytic cycles possible. In addition, these materials are thermally sensitive and are usually subjected to degradation when employed at temperatures above 150 °C. In one of our recent studies, we demonstrated the efficiency of Nafion NR50 resin, in the presence of NaCl in a biphasic system, to produce furfural under microwave irradiation. In this system, one of the most promising approaches to inhibit formation of side products, like humin derivatives, is to add an organic co-solvent such as cyclopentylmethyl ether (CPME), a low water-miscible and eco-friendly solvent.

Sporopollenin is a potential alternative to synthetic organic polymers for a variety of supported catalyst applications. It is the main component of the outer walls of plant spores and pollens, and this biopolymer is extremely resistant to biological and chemical degradation as well as high temperatures.<sup>18</sup> Its stability is due to its being a highly cross linked structure involving tertiary carbons and ethers. It possesses aliphatic chains bound to aromatic moieties, conjugated phenols, aliphatic alcohols, lactones and carboxylic acids. Morphologically it is relatively similar to the spores and pollens from which it is extracted; hence, it is isolated in the form of an empty microcapsule (exine). Due to the presence of a large hydrophobic cavity in the exine, sporopollenin exines have been shown to sequester edible oils from emulsions efficiently, encapsulate various polar and non-polar materials and act as a drug delivery system with excellent enhanced bioavailability.<sup>19-23</sup> Sporopollenin has also acted as an efficient green support for covalent immobilization of a lipase.<sup>24</sup> As a naturally occurring alternative polymer to the synthetic sulfonated polymers, Amberlyst<sup>9-12</sup> or Nafion,<sup>13,14</sup> sporopollenin exines were converted into a heterogeneous acidic catalyst by attaching sulfonyl groups to their surfaces *via*

sulfonation of the aromatic components of sporopollenin. Whilst a form of sulfonated sporopollenin was previously reported as part of a preliminary study to examine the potential of sporopollenin to act as an ion-exchange support,<sup>25</sup> the product of sulfonation was not fully characterized or explored as a potential strong acid catalyst. In accordance with our recent work on the dehydration of D-xylose using homogeneous catalysis,<sup>31</sup> this present work focuses on the employment of sulfonated sporopollenin (SSP) as heterogeneous catalyst in the presence or absence of NaCl in an aqueous biphasic system under microwave irradiation.

## EXPERIMENTAL SECTION

**Materials.** Substrates were purchased from Acros Organic (D-xylose  $\geq 99\%$ , xylan from Beechwood  $\geq 90\%$ ). Solvents were purchased from Acros (cyclopentyl methyl ether, ethanol, and acetone) and Fisher Scientific (acetonitrile). Furfural (99%) for use as a reference was obtained from Acros. All materials were used without further purification. The water used in all experiments was a Millipore Milli-Q grade.

**Catalyst preparation.** Raw spores of *L. clavatum* (100 g) were added to acetone (450 mL) and stirred for 4 h at 60 °C. The mixture was filtered and the solid dried under a vacuum overnight. The solid was stirred and heated at 80 °C in aqueous 6 % KOH for 6 h. The KOH solution was refreshed and the mixture was heated for a further 6 h. The mixture was recovered by filtration and washed with deionized water (6  $\times$  200 mL). After drying under vacuum overnight, the solid was heated at 80 °C in 700 mL of orthophosphoric acid (700 mL) for 8 days. The mixture was filtered and washed successively with hot water (2 L), 2.5 M NaOH (2  $\times$  125 mL), hot water (6  $\times$  250 mL), phosphate buffered saline (2  $\times$  125 mL), hot water (2  $\times$  250 mL), ethanol (2  $\times$  125 mL). The resulting exines were refluxed in 450 mL ethanol for 4 h, filtered and washed with ethanol (2  $\times$  125 mL) and then acetone (2  $\times$  125 mL). The solid was suspended in acetone (600 mL) and sonicated for 30 min, filtered and dried under vacuum overnight to afford the desired extracted sporopollenin microcapsules. A sample of this isolated material (2.0 g) was added to dry dichloromethane (150 mL). The solution was cooled in an ice bath

and chlorosulfonic acid (4 mL) was added slowly. The mixture was stirred 4 h at room temperature. Then, the mixture was filtered, washed with dichloromethane (50 mL) and water ( $6 \times 50$  mL) and dried under reduced pressure. The sulfonated sporopollenin was treated with 2 M sodium hydroxide (50 mL) for 24 h at room temperature. The mixture was filtered and washed with water ( $2 \times 50$  mL). The solid was added to 2 M hydrochloric acid (50 mL) and stirred for 4 h. The mixture was then filtered, washed with water ( $2 \times 50$  mL) and kept under reduced pressure. The enhanced acidity of the material was measured as follow. A sample (0.1 g) was added to a conical flask with a solution of sodium bicarbonate (0.1 M, 20 mL) and stirred for 16 hours. After filtration through Celite®, the filtrate was collected then titrated against a solution of hydrochloric acid (0.1 M) using methyl orange as the indicator.

**Catalyst characterization.** Elemental analysis was performed using an EA-1108 CHNS Elemental Analyzer (Fisons)

SEM (Scanning Electron Microscopy)-EDX (Energy Dispersive X-ray Diffraction) analysis of native and recovered sulfonated sporopollenin at different stage of the experiments was performed on a Quanta FEG 250 (FEI) equipped with a microanalysis detector for EDX (Brucker). SEM micrographs acquired in secondary electron mode were obtained at low vacuum, 15 kV of accelerating voltage with a 10 mm working distance. EDX spectra were collected at  $30^\circ$  angle, 15 kV accelerating voltage and 10 mm working distance.

FTIR spectra were recorded on a Perkin-Elmer SPECTRUM 2000 FTIR instrument in the range of  $400\text{-}3700\text{ cm}^{-1}$ .

XPS measurements were performed in an ultra-high vacuum (UHV) multipurpose surface analysis system (Specs™ model, Germany) operating at pressures of  $<10^{-10}$  mbar using a conventional X-ray source (XR-50, Specs, Mg K, 1253.6 eV) in a « stop-and-go » mode to reduce potential damage due to sample irradiation. The survey and detailed Fe and Cu high- resolution spectra (pass energy 25 and 10 eV, step size 1 and 0.1 eV, respectively) were recorded at room temperature with a Phoibos 150-MCD energy analyser. Powdered samples were deposited on a sample holder using

double-sided adhesive tape and subsequently evacuated under vacuum ( $<10^{-6}$  Torr) overnight. Eventually, the sample holder containing the degassed sample was transferred to the analysis chamber for XPS studies. A survey spectra were firstly recorded after which detailed element XPS (typically C, O and S) were recorded. Data were processed using the program Casa XPS.

XRD experiments were recorded on a PanAnalytic/Philips X'pert MRD diffractometer (40 kV, 30 mA) using Cu K $\alpha$  ( $\lambda = 0.15418$  nm) radiation. Scans were performed over a  $2\theta$  range from 10 to 80, at step size of  $0.018^\circ$  with a counting time per step of 5 s.

Nitrogen adsorption measurements were carried out at 77 K using an ASAP 2000 volumetric adsorption analyzer from Micromeritics. The samples were outgassed for 24 h at  $100^\circ\text{C}$  under vacuum ( $p_0 \cdot 10^{-2}$  Pa) and subsequently analysed. The linear part of the BET equation (relative pressure between 0.05 and 0.30) was used for the determination of the specific surface area. Mean pore size diameter (DBJH) and pore volumes (VBJH) were obtained from porosimetry data.

**General procedure for the synthesis of furfural in water-CPME as biphasic media from D-xylose or xylan.** In a typical experiment, a 10 mL glass vessel was charged with water (1 mL), CPME (3 mL), D-xylose or xylan (150.0 mg, 1.0 mmol), sulfonated sporopollenin (SSP) (10 wt%) and 0-2.50 mmol of NaCl. The vessel was sealed with a septum, placed in the microwave apparatus (Anton Paar Monowave 300) and heated to the desired temperature under magnetic stirring (600 rpm) for the desired time. Temperature in the vessel was measured by means of an IR sensor. At the end of the reaction, the vessel was cooled down to  $40^\circ\text{C}$  using compressed air. Then, the two phases were separated. The aqueous phase was diluted in 200 mL of distilled water and filtered prior to analysis through a filter paper (10-20  $\mu\text{m}$ , VWR). The organic phase was diluted

in 100 mL of acetonitrile and filtered prior to analysis through a syringe filter (PTFE, 0.45  $\mu\text{m}$ , VWR). All experiments were repeated at least three times, and the deviation was lower than 5%.

An identical procedure was followed using 0.15 g of xylan in place of the xylose.

**Product analysis.** Each sample of the reaction mixture was analyzed separately by means of a Shimadzu Prominence HPLC. Xylose was detected with a low temperature evaporative light scattering detector (ELSD-LTII) and the products were detected with a UV-Vis detector (SPD-M20A) at a wavelength of 275 nm. The column used was a Grace Prevail C18 column (250 x 4,6 mm 5 $\mu\text{m}$ ). The mobile phase was MeOH-H<sub>2</sub>O (9:1) solution flowing at rate of 0.5 mL.min<sup>-1</sup>. The column oven was set at 40 °C. D-xylose conversion ( $X$ ), furfural yield ( $Y_i$ ) and furfural selectivity ( $S_i$ ) were calculated by the following eq 1-3:

$$X = \frac{(\text{Initial xylose amount (mol)} - \text{Final xylose amount (mol)})}{\text{Initial xylose amount (mol)}} \times 100 \quad (1)$$

$$Y_i = \frac{\text{Final furfural amount (mol)}}{\text{Initial xylose amount (mol)}} \times 100 \quad (2)$$

$$S_i = \frac{\text{Furfural yield}}{\text{Conversion of xylose}} \times 100 \quad (3)$$

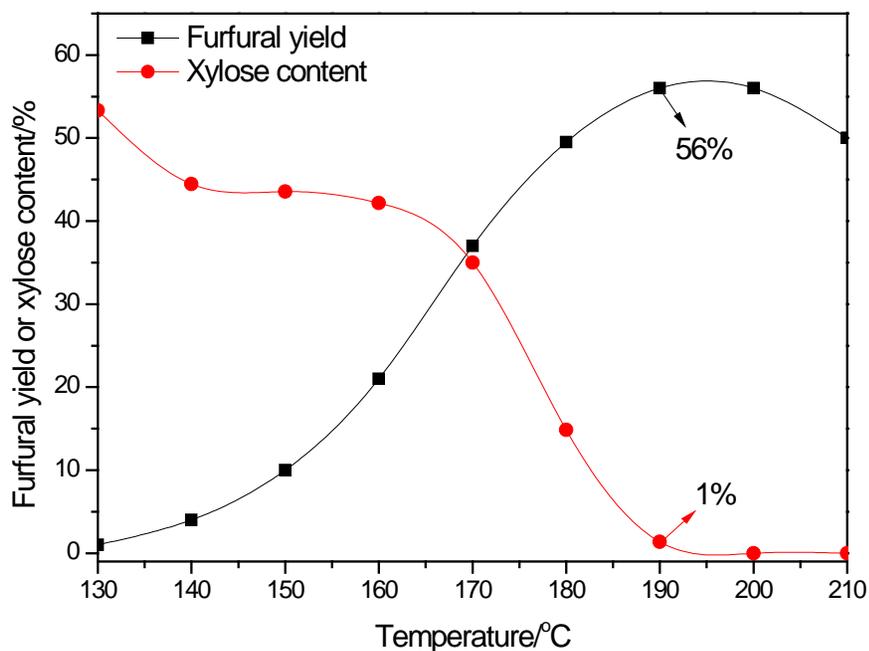
The calibration curve was checked regularly, in order to avoid eventual experimental errors associated with all measurements reported below.

## RESULTS AND DISCUSSION

**Modification of the surface of sporopollenin.** Sulfonated sporopollenin (SSP) was extracted by successive treatments starting from raw spores of *Lycopodium clavatum*. After conventional treatment,<sup>20</sup> the desired material was obtained and then treated with chlorosulfonic acid to afford sulfur-containing sporopollenin derivatives. Successive treatments in basic and in acidic conditions gave the target sulfonated sporopollenin. For subsequent experiments, sulfonated sporopollenin (SSP) with an average acidity of 1 mmol.g<sup>-1</sup> was chosen as the catalyst. A 10 wt % SSP aqueous suspension in 10 mL deionized water gave a pH of 2.3 before starting the experiments. Elemental analysis of SSP showed the presence of sulfur (51.3% C, 5.8% H, 0% N and 6.6% S), with no sulfur detection observed for natural unfunctionalised sporopollenin (62.7% C, 7.3% H, 0% N and 0% S). The initial morphology of the material was determined by SEM observations. SEM images confirmed no significant changes could be observed on sporopollenin morphology as a consequence of sulfonic acid loading (Supporting Information). The presence of the sulfur containing groups as assayed by elemental analysis were confirmed by EDX spectra (Supporting Information). Additionally, FTIR and XPS experiments were conducted to ascertain the nature of the sulfur species in the materials. FTIR spectra showed absorption bands at 1166 cm<sup>-1</sup> and 1038 cm<sup>-1</sup>, assigned to O=S=O stretching vibration of SO<sub>3</sub>H groups ((Supporting Information).<sup>26,27</sup> The presence of hydroxyl groups in both native sporopollenin and in SSP could also be observed, with a reduction of the intensity and broad OH band in sulfonated sporopollenin (Supporting Information). XPS spectra (Supporting Information) further confirmed the presence of S species on the external surface of SSP. S2p spectra featured essentially one main band that has been conventionally assigned to sulfur as SO<sub>3</sub>H species,<sup>28-30</sup> in good agreement with assignments in the FTIR spectra presented in (Supporting Information). The results obtained by XRD method showed that SP and SSP have got amorphous structure (Supporting Information). The BET analysis showed that SP and SSP materials are non

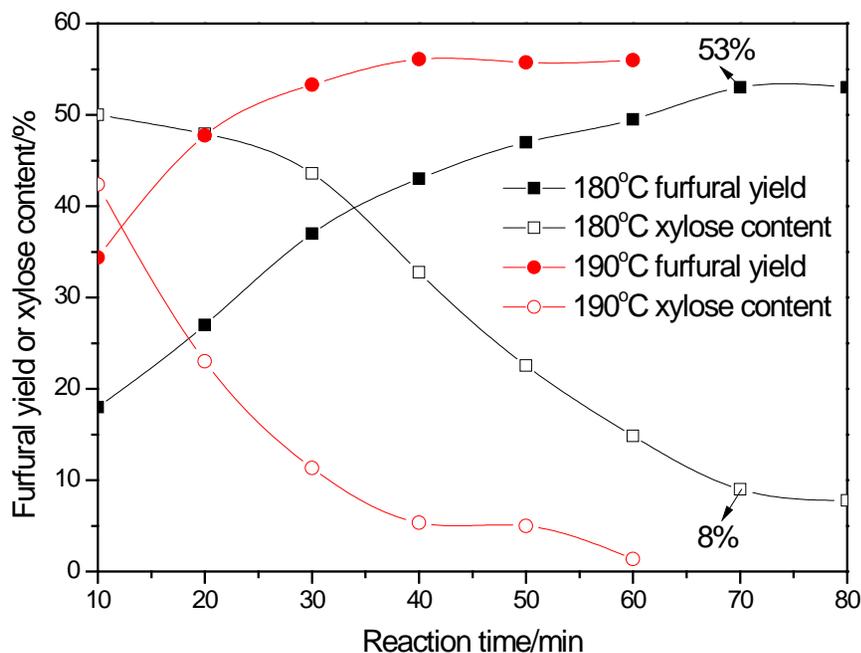
porous as expected with a negligible surface areas (below  $10 \text{ m}^2 \text{ g}^{-1}$ ).

**Effect of reaction temperature.** Reaction temperature is significant factor in influencing the dehydration reaction rate. In our case, variation of temperature from  $130 \text{ }^\circ\text{C}$  to  $210 \text{ }^\circ\text{C}$  for 60 min under microwave irradiation in a batch process was investigated in order to determine the most favourable reaction temperature using sulfonated sporopollenin (SSP) as catalyst. CPME, considered as a promising green co-solvent, can greatly enhance the dehydration of D-xylose to furfural by isolating the formed aromatic aldehyde derivative just after its formation in the aqueous layer. According to previous studies, the optimized water-CPME biphasic ratio was set as (1:3, v/v)<sup>31</sup> for the whole study, and catalyst loading was initially set at 10 wt % of D-xylose. At temperatures below  $180 \text{ }^\circ\text{C}$ , conversion of D-xylose and the yield of furfural were poor (Figure 1). However, it was noted that conversion of D-xylose catalyzed by SSP reached 45 % even at the lowest temperature of  $130 \text{ }^\circ\text{C}$ , whereas hardly any furfural was produced. Obviously, the catalyst can lead to partial dehydration of D-xylose, even at relatively lower temperatures, but was not found to be able to accomplish the complete production of furfural from the intermediates produced. Interestingly, the yield of furfural reached a maximum value of 56%, with almost complete conversion of D-xylose at  $190 \text{ }^\circ\text{C}$ . It was noticeable that at temperatures higher than  $170 \text{ }^\circ\text{C}$  humin formation was also observed even in our bi-phasic system. Interestingly, on the corresponding SEM micrograph of the recovered SSP after the reaction (Supporting Information), only a small amount of humin was adsorbed in the cavities of the catalyst surface, but the presence of carbonaceous material masking the sulfonic groups was evident by the partial suppression of sulfur signal on EDX spectrum. The experiments showed that the optimized reaction temperature was obtained at  $190 \text{ }^\circ\text{C}$ , displaying furfural selectivity of 56 %. Furthermore, a blank test was undertaken in which the reaction was carried out at  $190 \text{ }^\circ\text{C}$ , under the same conditions, with 10 wt % of the non-sulfonated sporopollenin. In this case, only 19 % of furfural was eventually formed, which convinced us to pursue these experiments with SSP.



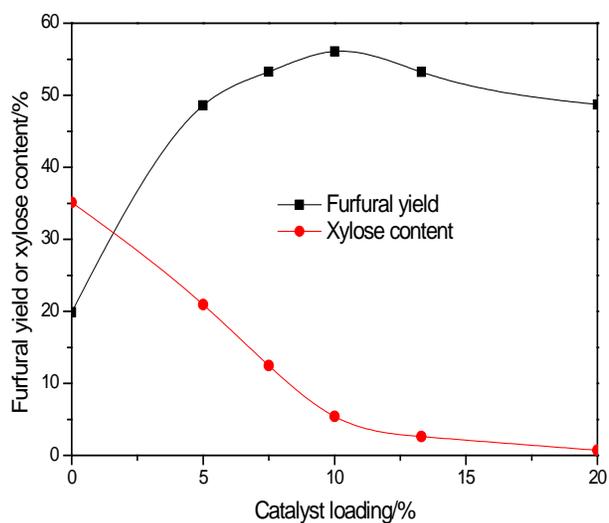
**Figure 1.** Effect of temperature on the yield of furfural and D-xylose content. Reaction conditions: SSP (10 wt%), D-xylose (1.0 mmol), water (1 mL), CPME (3 mL), MW, 60 min.

**Effect of reaction time.** The residence time effect on furfural yield and D-xylose conversion was investigated at 180 °C and 190 °C (Figure 2). At 190 °C, conversion of D-xylose increased with the reaction time, and the yield of furfural reached its maximum value of 56 % after 40 minutes. Here the maximum selectivity was 59 % for the optimum reaction time. This phenomenon was in accordance with the results currently found in literature<sup>11-17</sup> for other types of heterogeneous catalyst. It was noticeable that addition of CPME to the reaction mixture was favorable towards inhibiting formation of humins when the reaction temperature was lower than 180 °C. Unfortunately, despite the possible non-diffusion of the acid species into the organic layer, the optimum temperatures in our case were above 170 °C, which promoted side reactions and reduced the selectivity of the reaction. Nevertheless, by decreasing the temperature, the yield obtained at 180 °C (53% yield after 70 minutes) was inferior to the result obtained at 190 °C (56% after 40 minutes). This demonstrated that high reaction temperatures are necessary to diminish the reaction time for the dehydration of D-xylose catalyzed by SSP under microwave-assisted irradiation in a batch reactor.

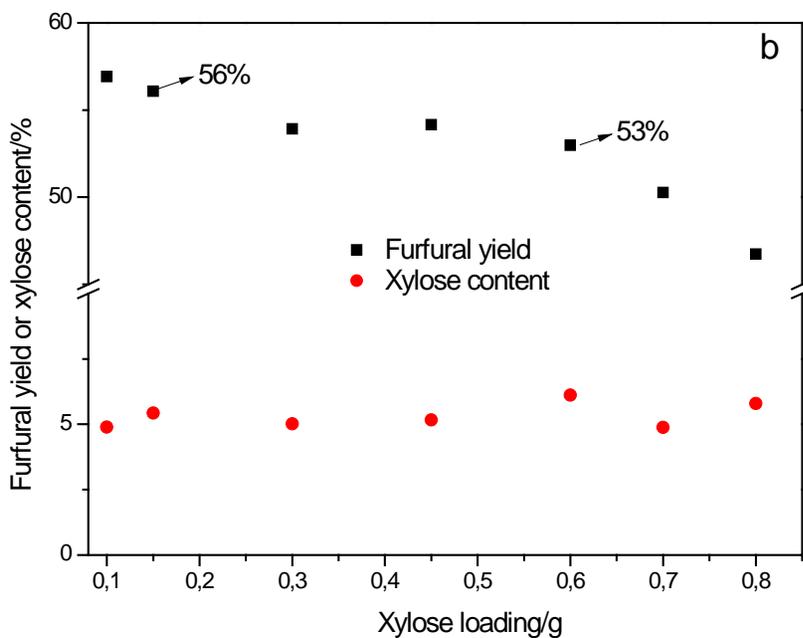


**Figure 2.** Effect of reaction time on the yield of furfural and D-xylose contents. Reaction conditions: SSP (10 wt%), D-xylose (1.0 mmol), water (1 mL), CPME (3 mL), MW, 190 °C.

**Effect of catalyst and substrate loading.** The effects of different initial SSP catalyst (amounts varying from 5 to 20 wt %) and D-xylose loadings in a mixture of water-CPME (1:3, v/v) were studied when heated at 190 °C for 40 min (Figure 3 and 4). Firstly, a catalyst loading greater than 10 % significantly affected the D-xylose selectivity and furfural yield (Figure 3). Higher catalyst concentration gave a lower yield of furfural, due to further degradation of adsorbed furfural or possibly due to its sequestration inside the hydrophobic cavity of the catalyst. On the other hand, all of the D-xylose cannot be sufficiently transformed when catalyst concentration is lower than 10 %. In any case, it was observed that there was no significant gain in the conversion of D-xylose to furfural with the increase of substrate loading (Figure 4). Thus, when D-xylose loading was greater than 0.3 g (2.0 mmol), furfural accumulating on the surface of SSP could promote the cross-polymerization with the unreacted surrounding sugar. Therefore, these results confirmed that the initial loading of 10 wt % and 150 mg of D-xylose in water remained the optimum ratio at 190 °C after 40 minutes under microwave-assisted irradiation.

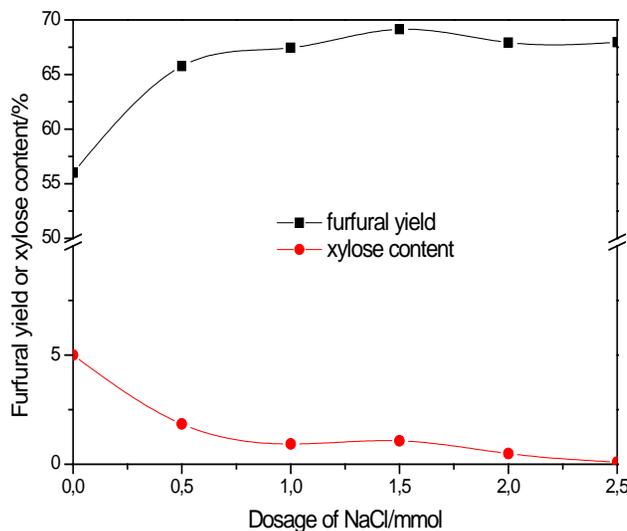


**Figure 3.** SSP catalyst loading on the yield of furfural and xylose contents. Reaction conditions: D-xylose (1.0 mmol), water (1 mL), CPME (3 mL), MW, 190 °C, 40 min.



**Figure 4.** D-Xylose loading on the yield of furfural and xylose contents. Reaction conditions: SSP (10 wt%), water (1 mL), CPME (3 mL), MW, 190 °C, 40 min.

**Effect of NaCl addition.** Usually, sodium chloride shows significant effects on the rate of furfural formation by complexing with carbocation intermediates during the D-xylose dehydration. Furthermore, addition of NaCl also promotes the transfer of furfural formed in water phase into organic phase by a “salting-out” effect. The impact of NaCl concentration, varying from 0 to 2.5 mol.L<sup>-1</sup> during the process, was investigated while keeping the previously optimized conditions constant [D-xylose (1.0 mmol), SSP (10 wt%), water (1 mL), CPME (3 mL), MW, 190 °C, 40 min.]. With the addition of NaCl, the yield of furfural increased by 10 % on average, and conversion of D-xylose was also slightly enhanced (Figure 5). A maximum of yield of 69% was obtained with 1.5 mmol of NaCl. Increased amounts of NaCl did not change the yield of furfural and contributed to side-reactions. In our optimized reaction conditions [D-xylose (1.0 mmol), SSP (10 wt %) and NaCl (1.5 mmol)], the initial pH of 2.3 dropped to pH 1.16. In our hands, furfural was obtained with a maximum yield of 69%. These results are in accordance with literature data showing that a strongly acidic medium is necessary to dehydrate xylose with a pH close to 1.12.<sup>8</sup>



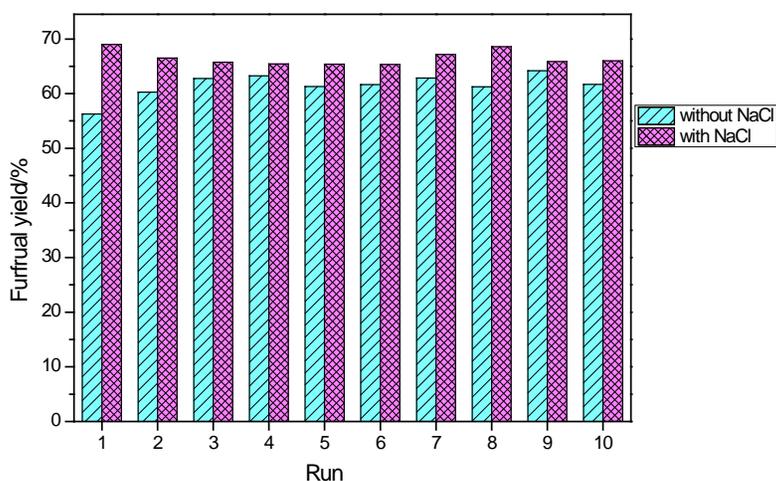
**Figure 5.** Effect of NaCl addition on the furfural yield and xylose contents. Reaction conditions: D-xylose (1.0 mmol), SSP (10 wt%), water (1 mL), CPME (3 mL), MW, 190 °C, 40 min.

It is notable that furfural production is possible with NaCl only.<sup>32</sup> Using our conditions but without sulfonated sporopollenin, furfural is obtained in only 40% yield, showing the

necessity of the sulfonated sporopollenin for a higher yield.

For comparison, the optimized method (D-xylose (1.0 mmol), SSP (10 wt%), water (1 mL), CPME (3 mL), MW, 190 °C, 40 min) was also performed using conventional heating. As expected, D-xylose conversion and furfural selectivity were a little lower for the conventional heating compared to microwave irradiation (95% *vs* 98% for the conversion and 57% *vs* 69% for the yields respectively). This result confirmed the effectiveness of our optimized microwave-assisted method.

**Effect of catalyst recovery.** Recycling performance is an important condition to evaluate the performance of a catalyst. In order to estimate the properties of recovered catalysts, at least ten cycles of experiments must be carried out under optimized conditions. In this work, after each catalytic run the reaction medium was separated from the organic CPME phase containing the furfural. Then, D-xylose (150 mg) and fresh CPME (3 mL) were added to the recycled aqueous phase containing the original sample of SSP, without being subjected to further treatment before starting the next cycle. In our hands, the activity of SSP was maintained during 10 consecutive tests (65–69%) (Figure 6). By way of comparison, a similar procedure without the NaCl was undertaken and this showed an average 10 % reduction in yield.

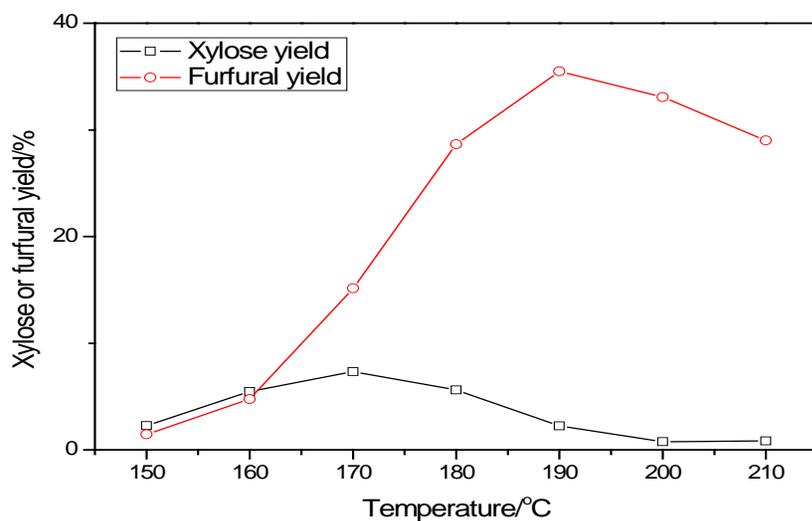


**Figure 6.** Reusability of the catalyst. Reaction conditions: D-xylose (1.0 mmol), SSP (10 wt%), NaCl (1.5 mmol), water (1 mL), CPME (3 mL), MW, 190 °C, 40 min.

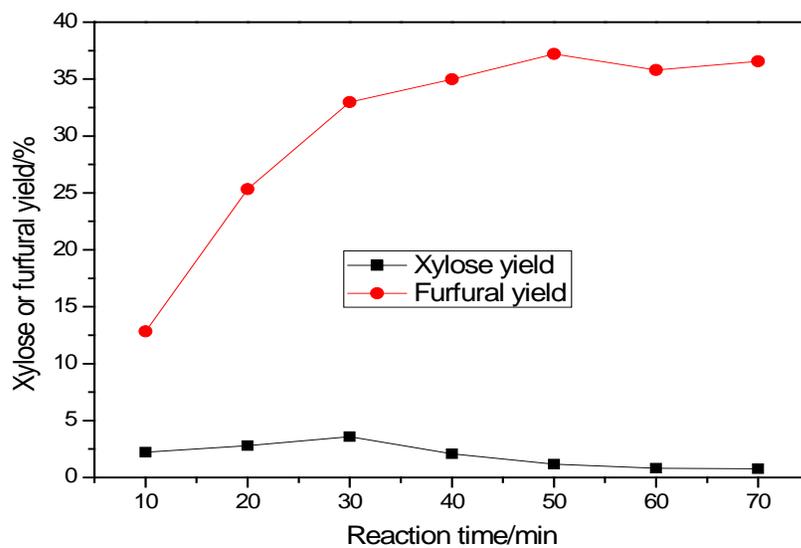
Compared to our previously described Nafion NR 50/NaCl catalytic system,<sup>33</sup> when restarting an experiment with SSP there is no need to regenerate the catalyst using concentrated HCl aqueous solution. This is because of the unfavourable exchange between protons of the sulfonate groups in SSP and NaCl.

**Furfural production from xylan.** Prior to extending this study to furfural production from lignocellulosic biomass, our optimized method was transferred to xylan as a suitable model (Figure 7). Under the optimized conditions [xylan (1.0 mmol based on D-xylose units), SSP (10 wt %), NaCl (1.5 mmol), water (1 mL), CPME (3 mL), MW, 190 °C, 40 min], the furfural yield reached 35%. As expected, the furfural yield was lower than from D-xylose because direct production of furfural from xylan involves a two-step process: a pseudo-first order irreversible depolymerization followed by dehydration of release pentose sub-unit.<sup>34</sup> For this reason, variation of both the temperature (from 150 to 210 °C) for 40 minutes (Figure 7), and the reaction time (from 10 to 70 minutes) at 190 °C (Figure 8), were studied to optimize furfural production from xylan.

At 170 °C, the temperature was insufficient for the formation of furfural but enough to hydrolyze xylan into monomers and oligomer sub-units (Figure 7). At 190 °C, as usual furfural formed quickly even if D-xylose was barely detectable. For temperatures higher than 190 °C, side-reactions occurred and caused a decrease in the yield of furfural. When heated at 190 °C, the furfural yield first increased gradually between 10 to 50 minutes, then remained almost constant after 50 min (Figure 8). Based on these results, an optimized formation of furfural from xylan was found using 190 °C for 50 min under microwave irradiation in the presence of 10 wt % of sulfonated sporopollenin and sodium chloride (1.5 mmol) in water-CPME (1:3, v/v).



**Figure 7.** Furfural yield and D-xylose contents from xylan against temperature. Reaction conditions: xylan (1 mmol based on D-xylose units), SSP (10 wt%), NaCl (1.5 mmol), water (1 mL), CPME (3 mL), MW, 40 min.



**Figure 8.** Furfural yield and xylose contents from xylan against reaction time. Reaction conditions: xylan (1 mmol based on xylose units), SSP (10 wt%), NaCl (1,5 mmol), water (1 mL), CPME (3 mL), MW, 190 °C.

## **CONCLUSIONS**

In summary, this work reports a new efficient process using sulfonated sporopollenin in presence of NaCl for the production of furfural from D-xylose in 69% yield. This new composite biomaterial is an active and recyclable solid acid catalyst in a water-CPME biphasic system under microwave irradiation. It is proposed that these promising results, employing the new bio-based SSP, shows the potential of SSP to replace synthetic materials as acid catalyst with the advantage of being less toxic and environmentally friendly.

## **ASSOCIATED CONTENT**

### **Supported Information**

Morphology of native and sulfonated sporopollenin, SEM; elemental composition of sulfonated sporopollenin, EDX; functional groups of native and sulfonated sporopollenin, FT-IR; sulfonated sporopollenin, XPS; amorphous structure of native and sulfonated sporopollenin, XRD.

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### **Notes**

The authors declare no competing financial interest.

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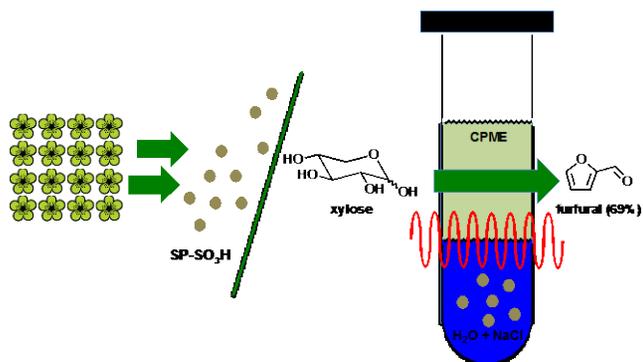
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## Sulfonated Sporopollenin as an Efficient and Recyclable Heterogeneous Catalyst for Dehydration of D-Xylose and Xylan into Furfural

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### Synopsis

An efficient catalytic system using sustainable sulfonated sporopollenin was developed for the production of furfural starting from D-xylose and xylan.