

Clean and Efficient Synthesis of Furfural From Xylose by Microwave-Assisted Biphasic System using Bio-Based Heterogeneous Acid Catalysts

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Abstract

As an attempt to replacing petroleum-based chemicals with bio-based ones, synthesis of furfural from biomass-derived xylose attracts much attention in recent days. Conventionally, furfural from xylose has been produced via the utilization of highly corrosive, toxic, and environmentally unfriendly mineral acids such as sulfuric acid or hydrochloric acid. In this study, microwave-assisted biphasic reaction process in the presence of novel bio-based heterogeneous acid catalysts was developed for the eco-benign and effective synthesis of furfural from xylose. The microwave was irradiated for reaction acceleration and a biphasic system consisting of H₂O : MIBK (1 : 2) was designed for continuous extraction of furfural into the organic phase in order to reduce the undesired side products formed by decomposition/condensation/oligomerization in the acidic aqueous phase. Moreover, sulfonated amorphous carbonaceous materials were prepared from wood powder, the most abundant lignocellulosic biomass. The prepared catalysts were characterized by FT-IR, XPS, BET, elemental analysis and they were used as bio-based heterogeneous acid catalysts for the dehydration of xylose into furfural more effectively. For further optimization, the effect of temperature, reaction time, water/organic solvent ratio, and substrate/catalyst ratio on the xylose conversion and furfural yield were investigated and 100% conversion of xylose and 74% yield of furfural was achieved within 5 h at 180 °C. The bio-based heterogeneous acid catalysts could be used three times without any significant loss of activity. This greener protocol provides highly selective conversion of xylose to furfural as well as facile isolation of product and bio-based heterogeneous acid catalysts can alternate the environmentally-burdened mineral acids.

Keywords : Xylose, Furfural, Microwave assisted, Biphasic system, Bio-based catalysts

1. Introduction

During the last decade, the awareness of inevitable fossil depletion and climate change has been becoming one of the most important concerns for many nations. Fortunately, abundance in biomass sources is emerging to be a promising alternative to sustainable and green replacement for fuel and energy supply chain on a petroleum-dependent civilization [1]. Among them, the conversion of biomass-derived carbohydrates into valuable intermediates, *so-called* platforms, such as furfural and 5-hydroxymethylfurfural (5-HMF) has gained a great deal of attention from scientific communities as well as manufacturing industry. These intermediates are usually formed by dehydration of corresponding C5 or C6 carbohydrate precursors under the catalytic environment. Furfural is considered to be particularly useful

because of its various applications such as an excellent solvent for organic materials like resins and polymers or feedstock for making gasoline, diesel or jet fuel [2]. It can also be further transformed to many other chemicals of great interest such as furfuryl alcohol, furan, tetrahydrofuran (THF) and 5-HMF [3]. Furfural is obtained from hemicellulose found in the most abundant lignocellulosic biomass via two-step pathways: (i) acidic hydrolysis of hemicellulose into D-xylose then (ii) dehydration of D-xylose into furfural. The dehydration of D-xylose can be achieved with either homogeneous catalysts such as inorganic mineral acids (H₂SO₄, HCl, H₃PO₄) [4] or heterogeneous systems like zeolite or heteropolyacids [2]. However, the task of developing an effective transformation of D-xylose to furfural remains quite challenging. For example, commercial process of making

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furfural from D-xylose using batch or continuous reactors with mineral acids yields only 45 to 50% of furfural together with humins, which are carbonaceous species, as major by-products [5]. In order to prevent the formation of humins, a solution has been suggested by adding an organic solvent to reaction media to selectively extract furfural from the aqueous phase into organic phase during the reaction. This strategy not only helps improve furfural yield by pushing the equilibrium to the right side but also minimize the number of side-products. Several organic solvents such as toluene, nitrotoluene, dichloromethane and MIBK were explored for this purpose [6-9]. Molina *et al.* [10] reported that a hydrated niobium pentoxide (NBO, $\text{Nb}_2\text{O}_5 \cdot \text{H}_2\text{O}$) catalyst in biphasic media (water/cyclopentyl methyl ether) could produce furfural in moderate yields (~50%) at 130 °C within 6 h. Stein *et al.* [11] also showed that $\text{FeCl}_3/\text{NaCl}$ in a biphasic system of $\text{H}_2\text{O}/2$ -methyltetrahydrofuran yielded over 70% of furfural at 140 °C under conventional heating. Stein *et al.* also showed that $\text{FeCl}_3/\text{NaCl}$ in a biphasic system of $\text{H}_2\text{O}/2$ -methyltetrahydrofuran yielded over 70% of furfural at 140 °C under conventional heating [11]. In recent years, the microwave assisted organic synthesis (MAOS) has been demonstrated to be one of the most powerful technologies to support chemical reactions and is listed as one of the 12 principles of green chemistry [12]. Energy efficiency of a microwave system is what makes chemical transformation remarkable. It is proven in many studies that microwave-assisted processes gain much higher yield and selectivity along with shorter reaction time for many types of reactions under much milder conditions [13]. Related to carbohydrate conversion, there are the limited numbers of studies on MAOS, especially for dehydration of D-xylose to furfural. Only a few researches have been done in homogeneous catalytic systems. Yang *et al.* [14] used microwave irradiation with $\text{AlCl}_3/\text{NaCl}$ as catalysts to afford furfural in over 51 - 66% yields. Weingarten *et al.* [5] gave furfural in about 80%

yield with HCl as an acid catalyst at 170 °C in the microwave-assisted biphasic system of $\text{H}_2\text{O}/\text{Methyl isobutyl ketone}$ (MIBK).

In this paper, we report the clean and efficient synthesis of furfural from D-xylose by the microwave-assisted biphasic system in the presence of bio-based heterogeneous acid catalysts, (Figure 3). In this process, furfural was obtained in a relatively good yield over 70% within 5 h reaction time. Furthermore, the catalysts can be readily prepared from lignocellulosic biomass, wood powder and used for alternatives to corrosive and toxic mineral acids.

2. Material and methods

2.1. Materials

Wood powder (from a pine tree, 50-100 μm in diameter) as a raw material for preparation of catalysts was supplied with G-biotech Inc. (Korea). D-Xylose ($\geq 99\%$) as a substrate, methanol ($\geq 99.9\%$) as an external standard (ES), glycerol ($\geq 99.5\%$) as an internal standard (IS), furfural (99%) as an authentic sample, *conc.* sulfuric acid (30% free SO_3 basis, fuming, H_2SO_4), chlorosulfuric acid (99%, HSO_3Cl), methyl isobutyl ketone (98.5%, MIBK), 1,4-dioxane (99.5%), were purchased from Sigma-Aldrich (USA) and directly used without any further purification. Distilled water was used for aqueous phase.

2.2. Typical procedure for the preparation of the catalysts

Bio-based heterogeneous acid catalysts were prepared via incomplete carbonization of wood powder (WP) into amorphous carbonaceous (AC) materials, followed by sulfonation to give sulfonated amorphous carbonaceous (SAC) materials. Wood powders in the ceramic boat ($10 \times 10 \times 5 \text{ cm}^3$) were carbonized by heating at 400 °C under N_2 for 1 (Figure 1(a)). Typically,

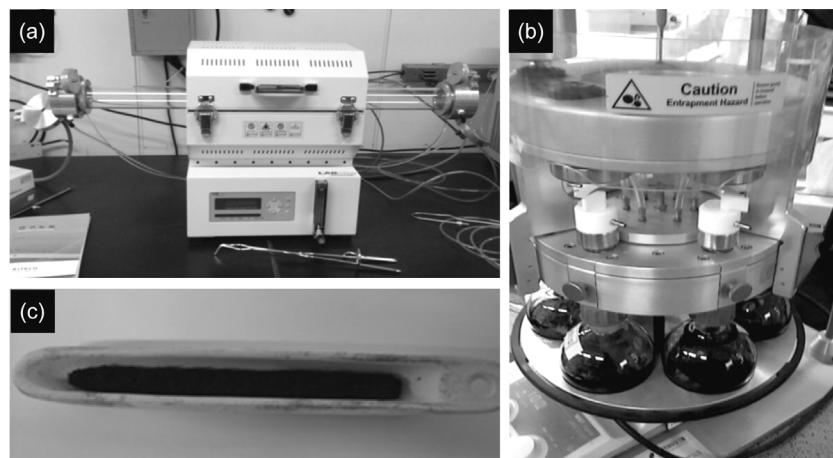


Figure 1. Preparation of sulfonated amorphous carbonaceous (SAC) materials via (a) incomplete carbonization then (b) sulfonation of (c) amorphous carbonaceous (AC) materials.

50 g of wood powder was turned to about 15 g of black carbonaceous materials (carbonization weight yield ~ 29%) (Figure 1(c)). The heating control was set up to increase till 400 °C for 80 min and then was held on temperature for 1 h. Afterward, SO₃H groups were attached to aromatic rings of the prepared AC materials. In 250 mL round bottom flask was placed 10 g of carbonaceous materials and 100 mL of *conc.* H₂SO₄ or ClSO₃H was added as a sulfonating agent. Sulfonation reactions were carried out at 80 °C for 3 h and additionally at room temperature (25 °C) for 3 h (Figure 1(b)). The resulting SAC materials were washed with hot distilled water (70 °C) until the pH paper indicated the neutral color (pH ~ 6.0) and then washed with 1,4-dioxane. Finally, in order to increase the stability by removal of soluble carbon materials, the SAC materials were washed by Soxhlet extraction with 1,4-dioxane for 24 h and dried in vacuum oven overnight. According to sulfonating agents (*conc.* H₂SO₄ or ClSO₃H) treated, the wood powder derived SAC materials were denoted as SAC-wp-H₂SO₄ and SAC-wp-ClSO₃H, respectively.

2.3. Typical procedures for the synthesis of furfural from D-Xylose in biphasic system

In the experiment by microwave irradiation, a 10 mL conical bottom glass vessel was charged with water (0.5 mL), MIBK (1 mL), D-xylose (4.2 mg, 28 μmol) and catalyst (50 wt% of substrate). The vessel was sealed with a septum, placed in the microwave apparatus (Biotage[®] Initiator+) and heated to the desired temperature under magnetic stirring (500 rpm) for the desired time. The temperature in the vessel was measured by means of an IR sensor. At the end of the reaction, the vessel was cooled down to room temperature using compressed air. Then, the aqueous phase was added IS diluted 50 mM in methanol and filtered prior to analysis through a syringe paper (PTFE, 0.45 μm). The organic phase was added IS diluted 50 mM in methanol and filtered prior to analysis through a syringe paper (PTFE, 0.45 μm).

In the experiment by conventional heating, a 100 mL glass tube was charged with water (2.0 mL), MIBK (4.0 mL), D-xylose (17.2 mg, 114 μmol) and catalyst (50 wt% of substrate). The tube was closed tightly with screw Teflon cap, placed in the multiple-reactors (Radley[®] Carousel 12 Plus Reaction Station) and heated to the desired temperature under magnetic stirring (1000 rpm) for the desired time. The temperature of the reaction was measured by a side sensor system. At the end of the reaction, the glass tube was cooled down to room temperature. Then, the aqueous phase was added IS diluted 50 mM in methanol and filtered prior to analysis through a syringe paper (PTFE, 0.45 μm). The organic phase was added IS diluted 50 mM in methanol

and filtered prior to analysis through a syringe paper (PTFE, 0.45 μm).

2.4. Reaction analysis

All products including unreacted D-xylose were analyzed with High Performance Liquid Chromatography (HPLC, Agilent Technologies 1200 series) using 0.001 N H₂SO₄ mobile phase and Bio-Rad Aminex HPX-87H (300 × 7.8 mm) column. A refractive index detector (RID) is a nondestructive enabling downstream analysis combined with using gradient elution of 0.001 N H₂SO₄ mobile phase was employed as eluent with 0.6 mL min⁻¹ flow rate and at 45 °C. The xylose conversion and furfural yield were defined as follows:

$$\text{Xylose conversion} = \frac{\text{(moles of xylose reacted)}}{\text{(moles of initiate xylose)}} \times 100\% \quad (1)$$

$$\text{Furfural yield} = \frac{\text{(moles of furfural produced)}}{\text{(moles of initiate xylose)}} \times 100\% \quad (2)$$

$$\text{Furfural selectivity} = \frac{\text{(moles of furfural produced)}}{\text{(moles of xylose reacted)}} \times 100\% \quad (3)$$

2.5. Catalyst characterization

SAC materials prepared from lignocellulose by incomplete carbonization and sulfonation were characterized with Fourier Transform Infrared Spectroscopy (FT-IR, Nicolet 6700, Thermo Scientific system, USA), and XPS (X-ray photoelectron spectroscopy K-AlphaTM+, Thermo Scientific, USA). The loading amount of sulfur were determined by EA analysis (Automatic Elemental analyzer, FLASH 2000 Series, Thermo Scientific, USA) and surface areas were measured by BET measure (Brunauer-Emmett-Teller, ASAP2010, Micromeritics, USA) respectively.

3. Results and Discussion

3.1. Catalyst characterization

From FT-IR spectrum of a SAC material, the bands at 1,377 and 1,040 cm⁻¹ were found and they were assigned as O = S = O and SO₃⁻ stretching band, respectively (Figure 2(a)) [15]. From XPS, S 2p binding energy of 168 eV corresponding to SO₃H groups was detected (Figure 2(b)).

Unlike activated carbon, the surface area of the amorphous carbonaceous materials obtained by incomplete carbonization were very low. Actually, SAC-wp-H₂SO₄ treated by *conc.* H₂SO₄ showed surface area of less than 100 m² g⁻¹ in BET analysis (~63 m² g⁻¹). On the other hand, the surface area of SAC-wp-ClSO₃H was about 4 times higher than that of SAC-wp-H₂SO₄ (Table 1). It was understood that HSO₃Cl treatment caused further carbonization to some extent and it could increase the crystallinity

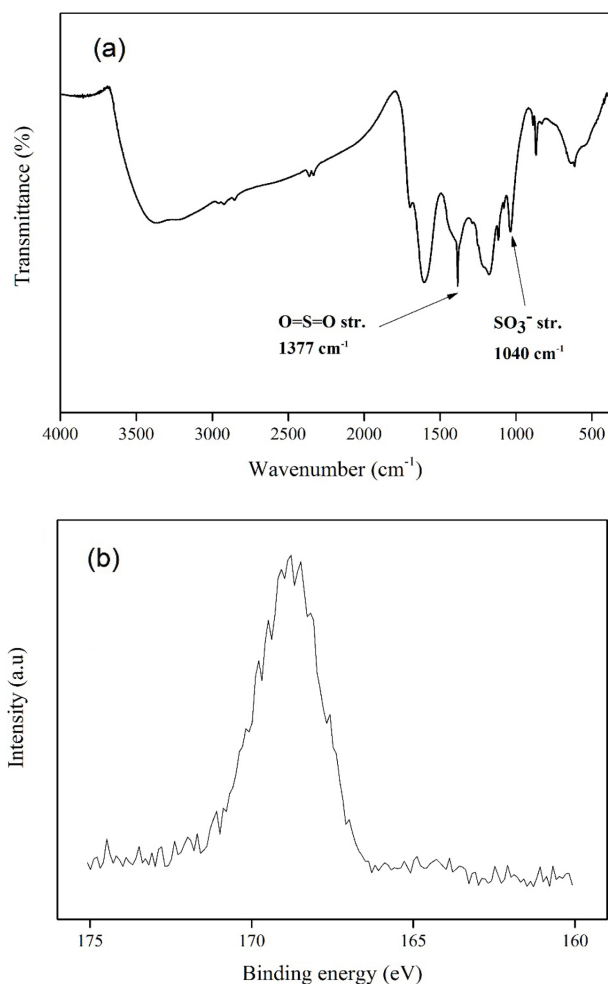


Figure 2. (a) FT-IR and (b) XPS spectrum of SAC material.

of amorphous carbonaceous materials.

The loading levels of sulfur on SAC materials were revealed by elemental analysis. The loading amount of sulfur per gram

Table 1. Surface area and loading level of the sulfur element of SAC materials

| SAC materials | Surface area (m ² g ⁻¹) | Elemental analysis (wt%) | | | | Sulfur loaded (mmol g ⁻¹) |
|---------------------------------------|--|--------------------------|-----|-----|-----|---------------------------------------|
| | | C | H | N | S | |
| SAC-wp-H ₂ SO ₄ | 63 | 68.5 | 3.1 | 1.7 | 2.1 | 0.67 |
| SAC-wp-ClSO ₃ H | 286 | 53.7 | 3.5 | 1.1 | 4.6 | 1.43 |

of SAC-wp-H₂SO₄ and SAC-wp-ClSO₃H was 0.67 mmol g⁻¹ and 1.43 mmol g⁻¹, respectively.

3.2. Process design

Synthesis of furfural from D-xylose using bio-based heterogeneous acid catalysts in the microwave-assisted biphasic system was designed as shown in Figure 3.

In terms of mechanism, the dehydration of D-xylose involves the protonation of hydroxy groups on carbon atoms of pentose ring then three water molecules are eliminated to produce the corresponding furfural product. Therefore, acid catalysts are required to push the reaction and SAC materials were used as bio-based heterogeneous acid catalysts in our system. Microwave irradiation was also utilized for accelerating the reaction and compared with conventional heating.

Furthermore, the biphasic system was adapted to reduce by-products formed by unwanted over-reactions of furfural (Figure 4).

MIBK was chosen as co-solvent for the biphasic system due to its advantageous properties such as low boiling point, low toxicity and high partition coefficient (partition coefficients: 18.57 and 8.39 with and without salt) with furfural [17] which made MIBK an ideal organic solvent for extracting furfural from the aqueous phase.

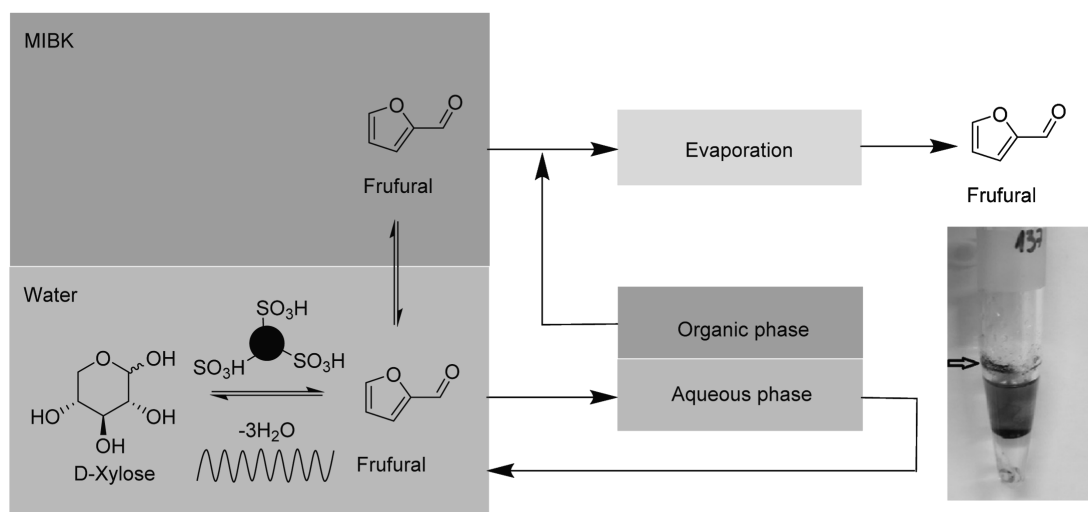


Figure 3. Synthesis of furfural from D-xylose using bio-based heterogeneous acid catalysts in the microwave-assisted biphasic system.

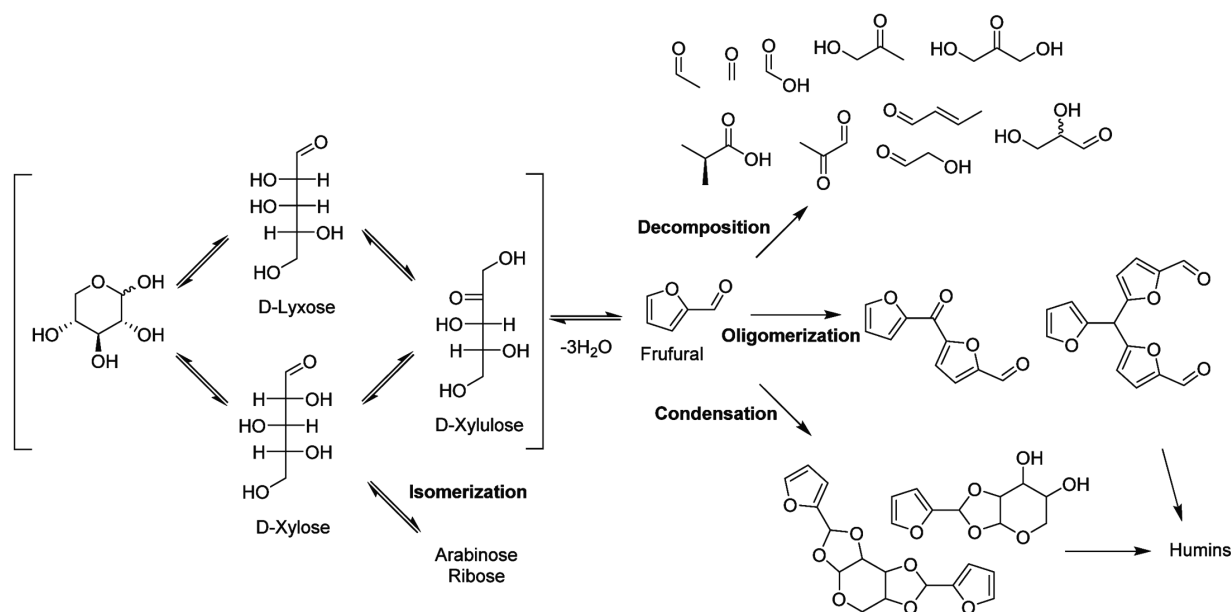


Figure 4. Byproducts formed by unwanted over-reactions of furfural [16].

Table 2. The effect of catalysts on the dehydration of D-xylose to furfural

| Entry | Catalysts | Heating method | Xylose conversion (%) ^{a)} | Furfural yield (%) ^{b)} |
|-----------------|---------------------------------------|----------------|-------------------------------------|----------------------------------|
| 1 ^{a)} | No catalyst | Conventional | 0 | 0 |
| 2 ^{a)} | SAC-wp-H ₂ SO ₄ | Conventional | 0 | 0 |
| 3 ^{a)} | SAC-wp-ClSO ₃ H | Conventional | 0 | 0 |
| 4 ^{b)} | No catalyst | Microwave | 83.8 | 41.0 |
| 5 ^{b)} | SAC-wp-H ₂ SO ₄ | Microwave | 90.8 | 49.5 |
| 6 ^{b)} | SAC-wp-ClSO ₃ H | Microwave | 99.7 | 74.0 |

^{a)} Reaction conditions: xylose (114 μ mol), catalyst (8 mg), H₂O (2 mL), MIBK (4 mL), 5 h, 180 °C.

^{b)} Reaction condition: xylose (28 μ mol), catalyst (2 mg), H₂O (0.5 mL), MIBK (1 mL), 5 h, 180 °C.

^{c)} Glycerol used as an internal standard.

3.3. Effect of catalysts on the dehydration of D-xylose to furfural

To investigate the effect of catalysts on the dehydration reaction of D-xylose, SAC-wp-ClSO₃H and some other heterogeneous acid catalysts were examined under both conventional heating and microwave-assisted method and the results were summarized in Table 2. At first, the yields of furfural were not detected under conventional heating procedure regardless catalysts used including SAC-wp-ClSO₃H and no other by-products found during the experiments (Entry 1-3). It was observed that the reaction yields were significantly improved under microwave condition even without the presence of the above catalyst, from 0% to 41% furfural yield (Entry 4). A trace of formic acid was

found in reaction media at the end of the reaction and it seemed to be formed by thermal dehydration of xylose under microwave heating conditions. Therefore, it was considered that autocatalysis by formic acid happened with no addition of catalyst. Further study on furfural synthesis without catalyst is ongoing. Although SAC-wp-H₂SO₄ is acidic in nature, it performed no activity toward the formation of furfural as the yield (49.5%) was almost similar to that of non-catalyzed conditions (Entry 5). On the other hand, when SAC-wp-ClSO₃H was used, furfural yield increased up to 74% at almost complete D-xylose conversion (Entry 6) within 5 h. The high activity of SAC-wp-ClSO₃H could be attributed to larger surface area and higher loading level of active sites on the catalyst compared to that SAC-wp-H₂SO₄ (see Table 1).

3.4. Effect of reaction parameters on the synthesis of furfural

3.4.1. Effect of reaction time

For the optimization, SAC-wp-ClSO₃H was used as catalysts for the reaction under microwave condition at 180 °C. Figure 5 illustrated the effect of reaction time on the conversion of D-Xylose and furfural yield. We found that the yield and conversion increased noticeably from 1 to 5 h indicating that there was a strong dependency between reaction time and the formation of furfural. Beyond the cited range, however, the yields of furfural dropped gradually even though the conversions were still as high as that of 5 h. This was probably due to the over-reactions of furfural under prolonged reaction time to form several by-products by undesired isomerization and over-reactions such

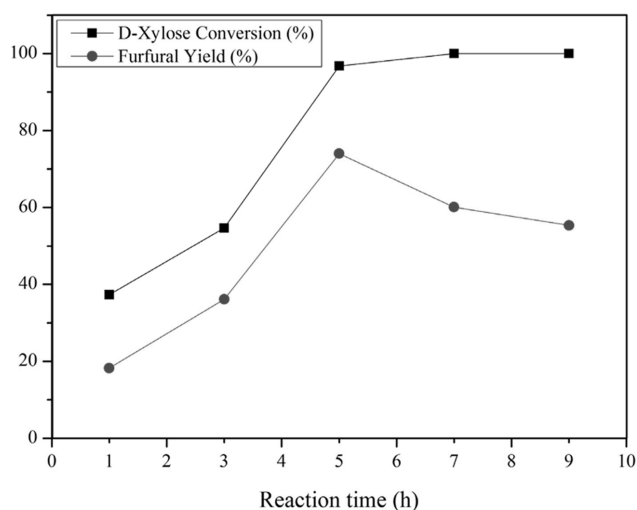


Figure 5. The effect of reaction time on the synthesis of furfural. Reaction conditions: Xylose (28 μmol), SAC-wp-ClSO₃H (2 mg), MIBK (1.0 mL), H₂O (0.5 mL), 180 °C.

as decomposition, oligomerization, and condensation. Actually, arabinose by isomerization of D-xylose was found in the aqueous phase after 3 h and insoluble humins via oligomerization and condensation were observed on the reactor wall.

3.4.2. Effect of reaction temperature

To investigate the influence of reaction temperature on the reaction, a series of the experiment were carried out in the temperature range from 150 °C to 190 °C and the results were shown in Figure 6. It was found that any temperature lower than 180 °C resulted in lower furfural yield and D-xylose conversion. Furfural was obtained with the highest yield at the temperature of 180 °C, up to 74% at an almost complete conversion of D-

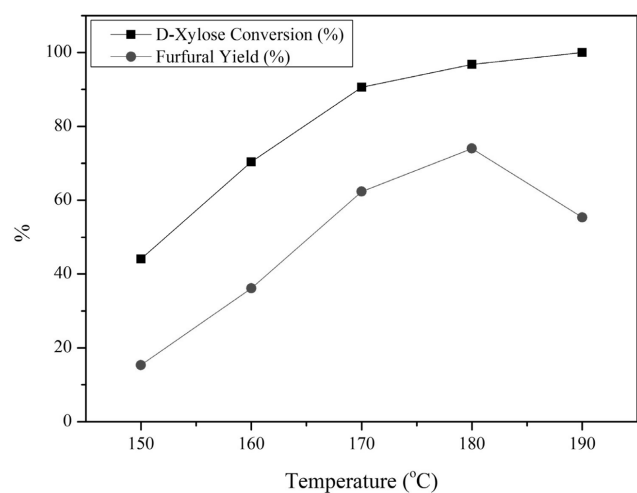


Figure 6. The effect of reaction temperature on the synthesis of furfural. Reaction conditions: Xylose (28 μmol), SAC-wp-ClSO₃H (2 mg), MIBK (1.0 mL), H₂O (0.5 mL), 5 h.

xylose. However, the temperature effect appeared to be negative at 190 °C or higher which resulted in the decrease of furfural yield, i.e. 44% at 190 °C. The result was in good agreement with literature that the stability of furfural is relatively low at a higher temperature in which side-reactions became dominated to produce more by-products along with the formation of a large amount of black humins [18,19].

3.4.3. Effect of the solvent ratio

It has been emphasized that the use of MIBK as the second reaction phase can suppress the by-product formation by over-reactions of furfural and leads to the improvement in desired product yield and selectivity. Therefore, it is important to investigate the influence of MIBK amount on the reaction. Here, different biphasic ratios (water - MIBK) and monophasic systems containing only water or MIBK were studied, and the result was illustrated in Figure 7. The experiments showed that a lot of insoluble humins were found after reaction under either monophasic environment of water or MIBK. The presence of the MIBK phase improved the catalytic efficiency prominently. The experiment showed that SAC-wp-ClSO₃H led to a D-xylose conversion of 90.7% and a furfural yield of 34.25% in pure water. As the dosage of MIBK increased from the ratio (2:1) to (1:2), the furfural yield was promoted from 48.82 to 74%, which confirmed the importance of extractive solvent during reaction time by the transfer of the produced furfural to the organic phase after its formation in the aqueous phase. However, an additional increment of MIBK dosage to 2 mL could not improve the catalytic efficiency of this biphasic system, on the contrary, the furfural yield reached only 32% in MIBK due to the lack of solubility of D-xylose and its degradation to the

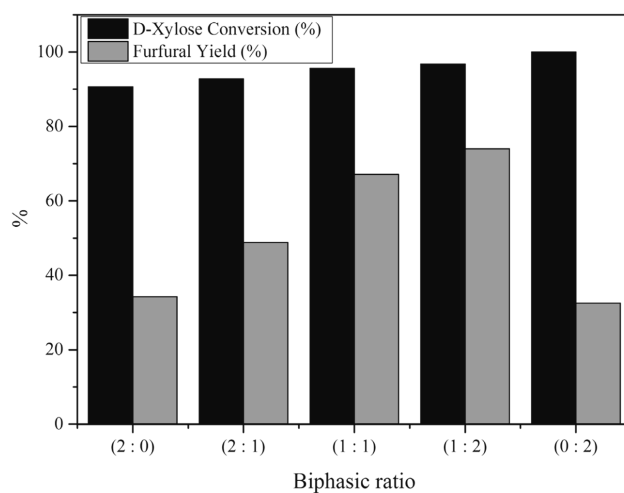


Figure 7. The effect of the ratio of H₂O/ MIBK on the synthesis of furfural. Reaction conditions: Xylose (28 μmol), SAC-wp-ClSO₃H (2 mg), MIBK, H₂O, 180 °C, 5 h.

carbonaceous material [18]. The experiments showed that the optimized mixture was water-MIBK (1:2), v/v and this ratio was chosen for the synthesis of furfural from D-xylose.

3.4.4. Effect of the substrate/catalyst ratio

Figure 8 showed the influence of catalyst amount on the reaction with respect to furfural yield. To quantify the amount of catalyst to the substrate, R-value was defined as moles of xylose per moles of SO_3H on the catalyst.

The formation of furfural was just moderate with the low substrate/catalyst molar ratio (the high amount of catalyst). In the addition of catalyst at $R = 5$, 99.5% of xylose conversion and 49% of yield was observed at a reaction temperature of 180 °C for the reaction time of 5 h. When the amount of catalyst was decreased to 10 of R-value, furfural yield was remarkably increased to 74%, whereas the xylose conversion was still kept in over 95%. It indicated that the high amounts of the acid site could cause the decomposition of furfural [20]. However, both xylose conversion and furfural yields were decreased at the R-value more than 10. In particular, as the R-values were increased from 15 to 20, isomerization was favored rather than

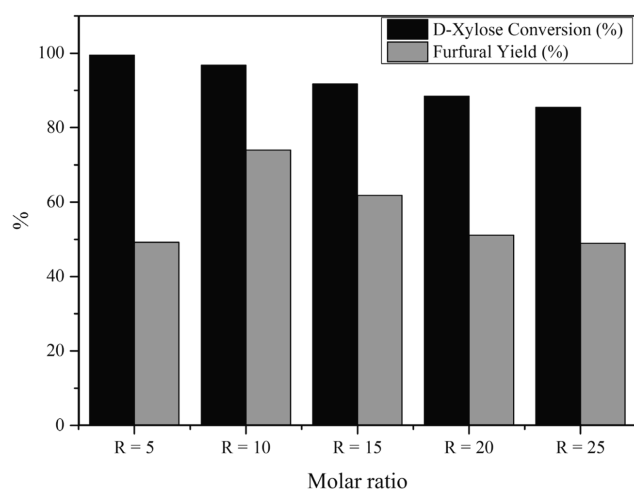


Figure 8. The effect of substrate/catalyst molar ratio (R) on the synthesis of furfural. Reaction conditions: Xylose (28 μmol), SAC-wp- ClSO_3H , MIBK (1.0 mL), H_2O (0.5 mL), 180 °C, 5 h.

Table 3. Isomerization products according to substrate/catalyst molar ratio (R)

| Ratio | Arabinose | Ribose | Lyxose |
|--------|-----------|--------|--------|
| R = 5 | 0.00 | 0.00 | 0.00 |
| R = 10 | 0.00 | 0.00 | 0.00 |
| R = 15 | 0.00 | 1.22 | 0.00 |
| R = 20 | 0.00 | 1.13 | 1.23 |
| R = 25 | 3.74 | 1.00 | 0.00 |

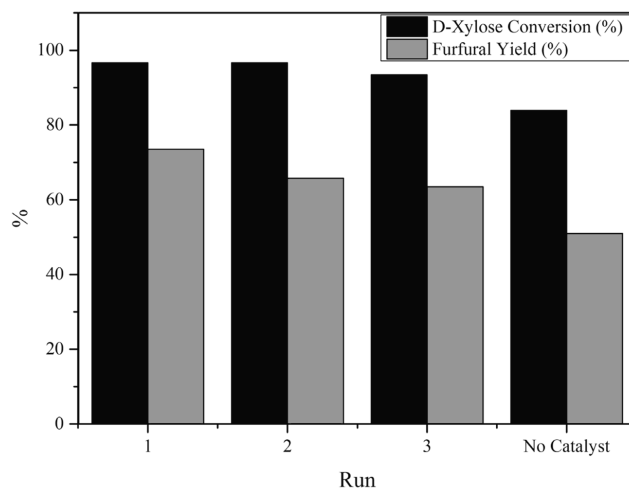


Figure 9. Recycle of SAC-wp- ClSO_3H in dehydration of xylose into furfural.

dehydration, resulting in the formation of undesired products such as arabinose, ribose, and lyxose were formed by isomerization (Table 3).

3.5. Catalyst Reusability

After the reaction, the catalysts were filtered and washed with methanol and hot water. Then the catalysts were dried in the vacuum oven for about 24 h and used for the next reaction. The conversion and yield in each run are shown in Figure 9. It was found that the furfural yield has slightly decreased from 74% in the first run to 64% in the third run. It was considered that humins formed during the reaction could decrease the activity of SAC-wp- ClSO_3H catalyst. Insoluble humins can be accumulated on the surface of the catalyst, which may block active sites of catalyst and reduce the surface area. In fact, a slight gain of catalyst weight was observed after each run, which supported that humins were attached on the catalyst. The similar phenomenon was found in the previous report by Wu *et al* [2]. Moreover, water solvent used in this reaction can be another reason why the decreasing activity of catalysts because the heterogeneous acid catalysts are hardly able to maintain the desirable acidity in highly protic and polar solvent like water due to the solvent-surface interaction and coordination abilities of the solvent [10]. Nevertheless, the reused catalysts still demonstrate the better performance than the reaction with no catalyst.

4. Conclusions

In summary, a clean and efficient catalytic system for the conversion of xylose into furfural using bio-based heterogeneous acid catalysts in a microwave-assisted biphasic system (water / MIBK) has been developed. To obtain the high yield, various

reaction parameters including the reaction temperature, time solvent ratio, and substrate/catalyst ratio were optimized to afford quantitative conversion of D-xylose in 74% of furfural yield. Either too high temperature or too long reaction time led to over-reaction of furfural into humins. Microwave and the co-solvent MIBK in biphasic system played a crucial role in accelerating dehydration of D-xylose and shifting the reaction to the right way to furfural. Particularly, the sulfonated amorphous carbonaceous (SAC) materials prepared from wood powder were successfully applied to the synthesis of furfural from D-xylose as promising bio-based heterogeneous acid catalysts that can be potential for a replacement of conventional homogeneous acid catalysts.

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