**Electronic Supplementary Information** 

# Exceptionally High Yields of Furfural from Assorted Raw Biomass over Solid Acids

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#### Materials

Zeolite, HMOR (Si/Al=10), H $\beta$  (Si/Al=19) and HUSY (Si/Al=15) were obtained from Zeolyst International, USA. Prior to use, zeolites were calcined at 823 K for 16 h in an air flow (10 mL min<sup>-1</sup>). Pseudoboehmite (Marathwada Chemical Industries Pvt. Ltd, India, grade: MCI-1524, 65-78% Al<sub>2</sub>O<sub>3</sub>), Aluminium isopropoxide (LOBA Chemical, India, 98%), fumed silica (Aldrich, USA), Silica sol, Ludox AS-40 (Aldrich, USA, 40% silica), orthophosphoric acid (Fisher Scientific, Germany, 85%), cyclohexylamine (CHA, Spectrochem, India, 99%), di-n-propylamine (DPA, Spectrochem, India, 99%), Amberlyst-15 (Fluka, USA), Nafion SAC-13 (Aldrich, USA), niobium pentoxide (Spectrochem, India, 99.95%), hemicellulose/xylan (Aldrich, USA, softwood (beechwood or oat spelt): xylose  $\geq$ 70%, glucose 15%, arabinose 10% and hardwood (birchwood): xylose  $\geq$ 90%), xylose (LOBA Chemicals, India, 99.5%), arabinose (s. d. fine, India, 100%), glucose (s. d. fine, India, 100%), furfural (LOBA Chemicals, India, 98%), 5-hydroxymethyl furfural (HMF) (Aldrich, USA 99%), toluene (LOBA Chemicals, India, 99.5%), methyl *iso*butyl ketone (LOBA Chemicals, India, 99%), *p*-xylene (LOBA Chemicals, India, 99.5%) were purchased and were used as received. All the raw biomass (bagasse, rice husk and wheat straw) were collected directly from field/farmers from various parts of India and used in the reaction without any chemical pre-treatment. The raw biomass were crushed and made into average size of 1 mm.

#### **Catalyst preparation**

Silicoaluminophosphate (SAPO) catalysts were synthesized by hydrothermal method and the details on the synthesis procedures are described here.

In a typical synthesis of SAPO-44, 7.7 g orthophosphoric acid was dissolved in 12.5 g distilled water. To this 4.6 g of pseudoboehmite was slowly added under continuous stirring. The gel thus formed was denoted as gel X. Gel Y was prepared in the following manner: 2.1 g of fumed silica was mixed with 23.5 g of water to this 3.3 g of CHA was added dropwise. Now gel Y was poured into gel X under vigorous stirring and the resulting mixture was stirred for 6 h to obtain homogeneous gel. This solution was the poured in to the Teflon lined stainless steel autoclave and the solution was left to aging (crystallization) for 176 h at 473 K under atmospheric pressure under static condition.

Afterwards the autoclave was allowed to cool to room temperature and then the solid material was filtered off. The solid thus obtained was washed with distilled water and dried at 333 K for 16 h in oven, and next in vacuum oven at 423 K for 6 h. The material thus obtained was calcined in presence of air at 823 K for 6 h.

Typically in the synthesis of SAPO-5, slurry was prepared with 12.0 g distilled water and 4.3 g aluminium isopropoxide. Dilute phosphoric acid (2.4 g phosphoric acid was mixed in 3.6 g distilled water) was added drop by drop to the slurry and stirred for 1 h to ensure homogeneity. 1.3 g CHA was added slowly to the resultant gel and continued stirring for 1.5 h. Finally, 6.4 g silica sol was added slowly and stirred for another 0.25 h. The resulting gel was transferred to the Teflon lined stainless steel autoclave and subjected to aging (crystallization) for 2.5 h at 473 K under atmospheric pressure at static condition. After cooling down the autoclave, solid materials were separated from mother liquor through filtration, washed thoroughly with distilled water and dried (333 K for 16 h in oven, 423 K, 6 h in vacuum). Material was calcined at 823 K for 6 h in presence of air.

For synthesis of SAPO-11, 2 g of pseudoboehmite and 4.7 g water were mixed properly. To this solution 3.2 g  $H_3PO_4$  was added and stirred vigorously. Stirring was continued for another 2 h after the addition of 4.7 g water to it. Afterward 0.2 g silica sol was added to the mixture with continuous stirring followed by addition of 1.4 g Di-*n*-propyl amine (DPA) was done. Next, this mixture was stirred for another 2 h. Solution thus obtained was aged (crystallization) in an stainless steel autoclave equipped with Teflon liner for 24 h at 473 K under static conditions. Afterwards, solid materials were separated from the liquid portion through filtration, washed thoroughly with water and dried (333 K for 16 h in oven, 423 K, 6 h in vacuum). At 823 K calcination was performed for 6 h under the flow of air.

In the synthesis of SAPO-46, 2.4 g of orthophosphoric acid was slowly mixed with phosphorus acid solution (1.2 g phosphorus acid + 10 g distilled water). This acid solution was added dropwise to 2.4 g of pseudoboehmite with constant stirring followed by 0.25 h continuation in stirring. Later, 10.0 g of distilled water was poured to it and stirred for 0.5 h. To it 5.7 g of DPA was added carefully and then the stirring was continued for 0.25 h. Water dispersed fumed silica (0.5 g fumed silica+4.6 g distilled water) was added to the solution with stirring for 0.25 h. The gel obtained was taken in a Teflon lined stainless steel autoclave and kept for aging (crystallization) at 473 K for 144 h. Afterwards the autoclave was allowed to cool to room temperature and then the solid material was filtered off. The solid thus obtained was washed with distilled water and dried at 333 K for 16 h in oven, and next in vacuum oven at 423 K for 6 h. The material thus obtained was calcined in presence of air at 823 K for 2 h.

#### **Catalyst characterization**

Catalysts were characterized with TGA-DTG, XRD, NH<sub>3</sub>-TPD N<sub>2</sub>-sorption and solid state MAS NMR. Prior to characterization all the samples were dried at 423 K for 16 h under evacuation. Before characterization of spent catalyst, those were calcined at 823 K for 12 h in presence of air (flow rate = 10 mL min<sup>-1</sup>).

TGA-DTG of samples was carried out on Mettler Toledo TGA/SDTA 851 series, USA instrument in nitrogen atmosphere with a heating rate of 10 K min<sup>-1</sup> from 298-1273 K.

Powder X-ray Diffraction (XRD) measurements were performed using Rigaku Miniflex diffractometer, equipped with a Ni-filtered monochromatic Cu K $\alpha$  radiation ( $\lambda = 1.5406$  Å).

Temperature Programmed Desorption (TPD) of NH<sub>3</sub> study was carried out using Micromeritics AutoChem-2920 instrument, equipped with TCD. In a Typical method first catalyst was activated at 823 K (4 K min<sup>-1</sup>) in helium flow (30 mL min<sup>-1</sup>) for 1 h and then the temperature was decreased to 323 K. Now, 10% NH<sub>3</sub> in helium gas was passed through the sample for 1 h. After this adsorption process, the system was flushed with helium gas for another 1 h at 373 K (desorption of physisorbed NH<sub>3</sub>). Then the spectra for desorption of NH<sub>3</sub> was recorded in helium flow (30 mL min<sup>-1</sup>) by increasing the temperature from 373 to 873 K at the rate of 10 K min<sup>-1</sup>.

The specific surface area and pore diameter of samples were calculated with the help of Nova 1200 and 1C Quanta Chrome instrument, USA at 77 K. All the samples were activated at 573 K for 2 h under evacuation before analysis.

Solid state <sup>29</sup>Si, <sup>27</sup>Al and <sup>31</sup>P spectra were recorded on a Bruker Avence-300 MHz spectrometer, operated at a field of 7.06 tesla. Fine powdered of sample was placed in a 4 mm zirconia rotor and spun at 10 kHz for all the nuclei.

#### **Catalytic reactions**

Before reaction all the catalysts were evacuated at 423 K for 6 h.

For hemicellulose reaction, isolated hemicellulose (softwood or hardwood) and solid acid catalyst were mixed with 60 mL of water + toluene solvent (1:1 v/v, 1:2 v/v, and 1:4 v/v) in an autoclave. Reactor was heated at desired temperature under slow stirring (100 rpm). When temperature of reactor was reached just 5 K below the desired temperature, stirring was increased to 800 rpm and this time was considered as a start time of reaction. After completion of reaction autoclave was cooled to room temperature in a flowing air. Solid was separated from reaction mixture by centrifugation and aqueous and organic layers were separated from each other by separating funnel.

In catalyst recycle study (for isolated hemicellulose), after each run, catalyst was separated from reaction mixture as mentioned above and washed thoroughly with distilled water to remove any adsorbed water soluble products. The catalyst (wet, without drying) thus obtained was used directly in the next reaction.

For real substrate reaction, 0.67 g raw biomass (bagasse or rice husk or wheat straw) and 0.05 g SAPO-44 were mixed with 60 mL water + toluene (1:2 v/v) in a Parr autoclave and reaction was carried out as per the procedure described for isolated hemicellulose reaction. Typically bagasse (I) contains 30% hemicellulose, so we have taken 0.67 g bagasse (I) in 20 mL water to maintain 1 *wt*% hemicellulose (with respect to water) in the reaction system. Also for other substrates, bagasse (II and III), rice husk (I, II and III) and wheat straw we have taken the same amount of substrate (0.67 g) in the reaction despite of their different hemicellulose composition.

For raw biomass, catalyst + unreacted solid was separated from the reaction mixture and washed with distilled water properly. First solid was dried properly (Lab oven: 333 K, 16 h; vacuum oven: 423K, 6 h) and further it was

subjected to calcination at 823 K for 12 h in presence of air (flow rate =  $10 \text{ mL min}^{-1}$ ) to remove all the unreacted part of biomass. Finally this calcined catalyst was used in recycle runs.

## Analysis of reaction mixture

After separation of solvent phase, aqueous layer sample was centrifuged (1.5 mL tube) and then filtered through 0.22  $\mu$ m syringe filter prior to analysis. Aqueous layer containing water soluble products (sugars, furfural) were analysed by HPLC (Agilent, 1200 Infinity Series), equipped with Pb<sup>2+</sup> column (300 mm × 7.8 mm, 353 K) and refractive index detector (Agilent, 1200 Infinity Series, cell temperature of 313 K). Millipore water was used as a mobile phase with 0.6 mL min<sup>-1</sup> flow rate. Organic layer samples were filtered through 0.22  $\mu$ m syringe filter and then analysed on a Varian gas chromatograph (CP3800), equipped with HP-5 column (50 m × 0.22  $\mu$ m ID) and flame ionisation detector (FID).

#### Calculations

Hemicellulose molecular weight was taken as 132 considering loss of 18 (due to water removal) from xylose/arabinose (molecular weight of 150) during polymerization to form hemicellulose.

So 132 g hemicellulose will form 150 g xylose + arabinose (considering 100% conversion and selectivity).

% yield of xylose + arabinose = [Weight of xylose + arabinose (HPLC) / Weight of xylose + arabinose (theoretical)] × 100

Molecular weight of furfural is 96. So, 96 g furfural yield is possible from 150 g xylose + arabinose (considering 100% yield and selectivity).

% yield of furfural = [Weight of furfural (GC [org] + HPLC [water]) / Weight of furfural (theoretical)]  $\times$  100

Calculation for oligomer yield was done using calibration curve drawn for pre-isolated oligomer. For isolation of oligomer, hemicellulose reactions were carried out at 383 K for 2 h in water in the absence of any catalyst. Solid part was separated from the liquid through centrifugation to remove unreacted hemicellulose. The soluble oligomer was collected from the liquid through evaporation of water and then the solids obtained were oven dried at 333 K for 16 h and further in vacuum at 423 K for 6 h to complete removal of water. The isolated oligomer was identified as pure (without any other sugars) with the help of HPLC and further calibration curve was drawn. In our earlier report also we have proved the formation of oligomers with the help of LC-MS analysis.<sup>1</sup>

Hemicellulose conversion was calculated based on solid charged and recovered (weight basis).

% Hemicellulose conversion = [(Total solid charged in the reaction – Solid recovered after reaction) / (Weight of initial hemicellulose charged in the reactor)]  $\times$  100

# Calculations for real biomass reaction

Product yields were calculated based on the hemicellulose present in the respective raw biomass (bagasse or rice husk or wheat straw). For example when the reactions were carried out with following charge, 0.67 g bagasse (I), 60 mL solvent and 0.05 g catalyst; bagasse (I) contains 30% hemicellulose, which means 0.201 g hemicellulose is present in the system. So the product yield calculations are done using 0.201 g hemicellulose.

Catalyst	Weak acid amount (373-523 K) (mmol g <sup>-1</sup> )	Strong acid amount (623- 773 K) (mmol g⁻¹)	Total acid amount (mmol g <sup>-1</sup> )
Fresh SAPO-44	0.7	0.5	1.2
Spent SAPO-44 (isolated hemicellulose)	0.6	0.5	1.1
Spent SAPO-44 (bagasse) <sup>[a]</sup>	0.6	0.6	1.2
Spent SAPO-44 (rice husk) <sup>[a]</sup>	0.7	0.4	1.1
Spent SAPO-44 (wheat straw) <sup>[a]</sup>	0.6	0.5	1.1
Fresh SAPO-46	0.4	0.4	0.8
Fresh SAPO-5	0.8	0	0.8
Fresh SAPO-11	0.3	0	0.3
Fresh HUSY (Si/Al = 15)	0.1	0.5	0.6
Fresh HMOR (Si/Al =10)	0.5	0.7	1.2
Fresh H $\beta$ (Si/Al = 19)	0.2	0.7	0.9

Table S1. Studies on solid acid catalyst acid amount with NH<sub>3</sub>-TPD analysis

[a] SiO<sub>2</sub> (ash) corrected value.



Fig. S1. Partition coefficient calculation for furfural distributed in different solvent system.



**Fig. S2.** Recycle study of SAPO-44 catalyst used in isolated hemicellulose conversion to furfural. Reaction conditions: softwood hemicellulose (0.2 g), SAPO-44, water + toluene = 60 mL (1:2 v/v), 443 K, 10 h.



Fig. S3a <sup>1</sup>H NMR spectral data for isolated furfural from reaction mixture (bagasse).



Fig. S3b <sup>13</sup>C NMR spectral data for isolated furfural from reaction mixture (bagasse).



Fig. S4. Images for real (raw) biomass used for furfural synthesis.

Region/country	2009 (MMT) <sup>2</sup>	2010 (MMT) <sup>2</sup>	2011 (MMT) <sup>2</sup>
Worldwide total	1.67×10 <sup>9</sup>	1.69×10 <sup>9</sup>	1.80×10 <sup>9</sup>
Americas total	9.30×10 <sup>8</sup>	9.46×10 <sup>8</sup>	9.75×10 <sup>8</sup>
Asia total	6.17×10 <sup>8</sup>	6.19×10 <sup>8</sup>	7.07×10 <sup>8</sup>
Africa total	9.31×10 <sup>7</sup>	8.98×10 <sup>7</sup>	9.07×10 <sup>7</sup>
Oceania total	3.27×10 <sup>7</sup>	3.35×10 <sup>7</sup>	2.73×10 <sup>7</sup>
Australia + New Zealand total	3.02×10 <sup>7</sup>	3.15×10 <sup>7</sup>	2.52×10 <sup>7</sup>
Europe total	5.15×10 <sup>3</sup>	5.32×10 <sup>3</sup>	5.20×10 <sup>3</sup>
India	2.85×10 <sup>8</sup> (17% w.r.t	2.92×10 <sup>8</sup> (17% w.r.t.	3.42×10 <sup>8</sup> (19% w.r.t.
	worldwide total)	worldwide total)	worldwide total)

Table S2a. Distribution of sugarcane production in tones per year in various regions

Table S2b. Distribution of rice (paddy) production in tones per year in various regions

Region/country	2009 (MMT) <sup>2</sup>	2010 (MMT) <sup>2</sup>	2011 (MMT) <sup>2</sup>
Worldwide total	6.85×10 <sup>8</sup>	7.01×10 <sup>8</sup>	7.23×10 <sup>8</sup>
Americas total	6.19×10 <sup>8</sup>	6.34×10 <sup>8</sup>	6.54×10 <sup>8</sup>
Asia total	3.78×10 <sup>7</sup>	3.69×10 <sup>7</sup>	3.76×10 <sup>7</sup>
Africa total	2.35×10 <sup>7</sup>	2.59×10 <sup>7</sup>	2.61×10 <sup>7</sup>
Oceania total	4.23×10 <sup>6</sup>	4.31×10 <sup>6</sup>	4.37×10 <sup>6</sup>
Australia + New Zealand total	8.17×10 <sup>4</sup>	2.09×10 <sup>5</sup>	7.38×10 <sup>5</sup>
Europe total	6.52×10 <sup>4</sup>	1.97×10 <sup>5</sup>	7.23×10 <sup>5</sup>
India	1.36×10 <sup>8</sup> (20% w.r.t	1.44×10 <sup>8</sup> (21% w.r.t	1.58×10 <sup>8</sup> (22% w.r.t
	worldwide total)	worldwide total)	worldwide total)

Table S2c. Distribution of wheat production in tones per year in various regions

Region/country	2009 (MMT) <sup>2</sup>	2010 (MMT) <sup>2</sup>	2011 (MMT) <sup>2</sup>
Worldwide total	6.87×10 <sup>8</sup>	6.52×10 <sup>8</sup>	7.01×10 <sup>8</sup>
Americas total	3.01×10 <sup>8</sup>	2.90×10 <sup>8</sup>	3.15×10 <sup>8</sup>
Asia total	2.28×10 <sup>8</sup>	2.04×10 <sup>8</sup>	2.26×10 <sup>8</sup>
Africa total	1.09×10 <sup>8</sup>	1.14×10 <sup>8</sup>	1.09×10 <sup>8</sup>
Oceania total	2.56×10 <sup>7</sup>	2.17×10 <sup>7</sup>	2.50×10 <sup>7</sup>
Australia + New Zealand total	2.21×10 <sup>7</sup>	2.26×10 <sup>7</sup>	2.78×10 <sup>7</sup>
Europe total	2.21×10 <sup>7</sup>	2.26×10 <sup>7</sup>	2.78×10 <sup>7</sup>
India	8.07×10 <sup>7</sup> (12% w.r.t	8.08×10 <sup>7</sup> (12% w.r.t	8.69×10 <sup>7</sup> (12% w.r.t
	worldwide total)	worldwide total)	worldwide total)



**Fig. S5.** XRD patterns for fresh and recovered bagasse (with SAPO-44 catalyst) from reaction mixture. The assigned peaks were corresponds to SAPO-44 catalyst phase remained with recovered bagasse after reaction.

# Hydrophilicity-hydrophobicity

In this study mainly we described the superior hydrophilicity of SAPO's compared to zeolite, HMOR. To check the hydrophilicity of the catalysts (SAPO-44, SAPO-5, SAPO-11, SAPO-46 and HMOR), we immersed those in water + toluene mixture (1:1 v/v) at *RT*. Fig. S6 shows the photographs taken for all the catalysts immersed in the solvent. It is clear from the photographs that compared to SAPO catalysts; HMOR was well dispersed in both water and toluene layer indicating that it has a lower hydrophilic character than the SAPO catalysts. This ensures us that this characteristic may play an important role in deciding the yields of furfural since even after furfural is extracted into organic layer it can be in contact with HMOR catalyst to undergo further reactions. In view of SAPO-44 tend to remain in aqueous layer (Fig. S6) it is predicted that it has more hydrophilic character and thus can show higher yields for furfural.



**Fig. S6.** Study on hydrophilicity property of various solid acid catalysts; upper layer stands for toluene and lower later stands for water.

## TGA-DTG study and its extension to determine hydrophilicity of catalysts

In case of activated samples, SAPO-44 and HMOR catalysts were activated at 423 K under vacuum for 6 h. For water adsorption study, both the activated samples were kept in a closed desiccator containing water for 48 h at 308 K. Under such condition, water was distributed in closed container and this vapor was adsorbed on the sample. Just before TGA-DTG analysis, samples were taken out from desiccator and weighed.



Fig. S7a. TGA-DTG profile for activated SAPO-44.



Fig. S7b. TGA-DTG profile for water adsorbed SAPO-44.



Fig. S7c. TGA-DTG profile for activated HMOR.



Fig. S7d. TGA-DTG profile for water adsorbed HMOR.

# Table S3. Studies on SAPO-44 surface area and pore size

Catalyst	Surface area (m <sup>2</sup> g <sup>-1</sup> )	Pore size (nm)
Fresh SAPO-44	369	0.45
Spent SAPO-44 (isolated hemicellulose)	359	0.48
Spent SAPO-44 (bagasse)	351	0.46



Fig. S8a. <sup>29</sup>Si MAS NMR spectra for fresh and spent SAPO-44 (used in isolated hemicellulose reaction).



Fig. S8b. <sup>27</sup>AI MAS NMR spectra for fresh and spent SAPO-44 (used in isolated hemicellulose reaction).



Fig. S8c. <sup>31</sup>P MAS NMR spectra for fresh and spent SAPO-44 (used in isolated hemicellulose reaction).

# References

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