Supplementary Material (ESI) for Green Chemistry

Electronic Supplementary Information (ESI)

A green solid-acid-based process for the conversion of hemicellulose

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Experimental procedure

Softwood (Oat spelt; xylose ≥ 70%, arabinose 10%, glucose 15%) and hardwood (Birch wood, xylose ≥ 90%) derived hemicellulose (xylan) are purchased from Aldrich, USA. Bagasse (hemicellulose 30%) with particle size <1 mm was obtained from sugar industry and used without any further treatment. Other compounds are purchased from Loba Chemicals, India. All the chemicals are used as received. Before reaction, all the catalysts are evacuated at 150^{o}C for 6 h.

Hydrolysis experiments. Typically in a Parr autoclave 0.6 g hemicellulose/bagasse and 0.3 g catalyst are added to 60 mL water. Reactor is flushed with nitrogen gas and pressurized to 5 MPa. Reactor is heated to desired reaction temperature (130-170^{o}C) for required time and samples were taken intermediately to follow the reaction.

Analysis. The reaction mixture is analyzed using High Performance Liquid Chromatograph (HPLC, Shimadzu) equipped with carbohydrate Pb^{2+} column (supelcogel) maintained at 80^{o}C and Refractive Index Detector (RID). The eluting solvent was water.

Calculations. For the calculation of xylose+arabinose yield, molecular weight of hemicellulose is considered 132. Hemicellulose are mainly a polymer of xylose units. Xylose has a molecular formula of $C_5H_{10}O_5$ with molecular weight of 150. However, while forming the polymer of these xylose units loss of water (H_2O) with molecular weight of 18 is known (as in hydrolysis reaction of hemicellulose we are adding water and forming xylose as the product). Because of this we have deducted 18 out of 150 and have made the molecular weight of hemicellulose 132 which is taken for calculation purpose. The other component of hemicellulose, arabinose again has a molecular formula of $C_5H_{10}O_5$ with molecular weight of 150. While glucose might be present in hemicellulose the percentagewise it is not more than 15% so for simplicity of calculations we have taken molecular weight of 132 of hemicellulose for the yields calculations. For the calculation of furfural yield, molecular weight of furfural is 96. Thus from 132 g of hemicellulose, either 150 g of xylose or 96 g of furfural formation is possible. Yield is then calculated accordingly.

Since separation of glucose and oligomer peaks is difficult, yield calculations for the glucose are not done.

For the calculation of oligomers (dimers to pentamers including merged glucose peak) response factor of xylose is used (from standard preparation) since no oligomer standards are available.

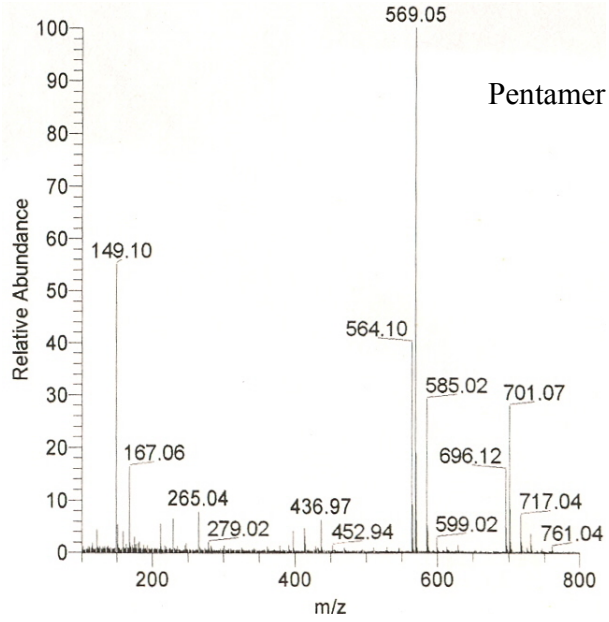
Calculations for bagasse reaction: Reactions are carried out with following charge, 0.6 g of bagasse, 60 mL water and 0.3 g catalyst. Bagasse contains only 30% hemicellulose and as results indicate only hemicellulose are converting under the reaction conditions

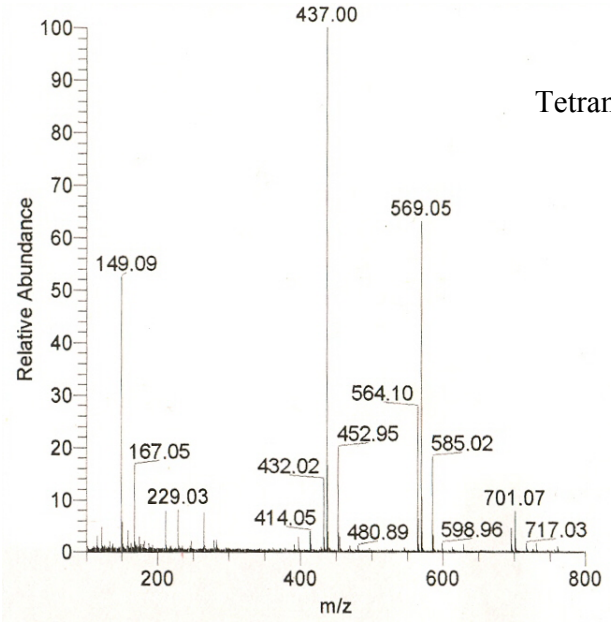
employed hence product yield calculations are done using 0.18 g hemicellulose (30% of bagasse charge of 0.6 g).

Conversion of hemicellulose is calculated by 2 methods.

First, based on difference between total solid charged and recovered after the reaction (weight basis) and Second, based on total products formed (analysis basis).

Characterization





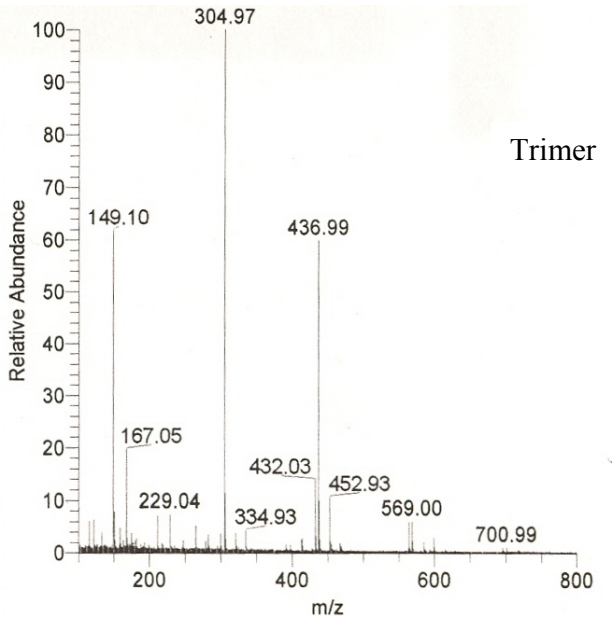


Figure S1 LC-MS analysis of oligomers formed in the hydrolysis reaction. In all cases, M+Na peak is observed. For e.g. Pentamer ($C_{25}H_{42}O_{21}$) has molecular weight 678, M+Na gives peak for m/z=701. Tetramer ($C_{20}H_{34}O_{17}$) has molecular weight 546. M+Na gives peak for m/z=569. Trimer ($C_{15}H_{26}O_{13}$) has molecular weight 414, M+Na gives peak for m/z=437. Contamination of other ions is due to difficulty in the separation of peaks.

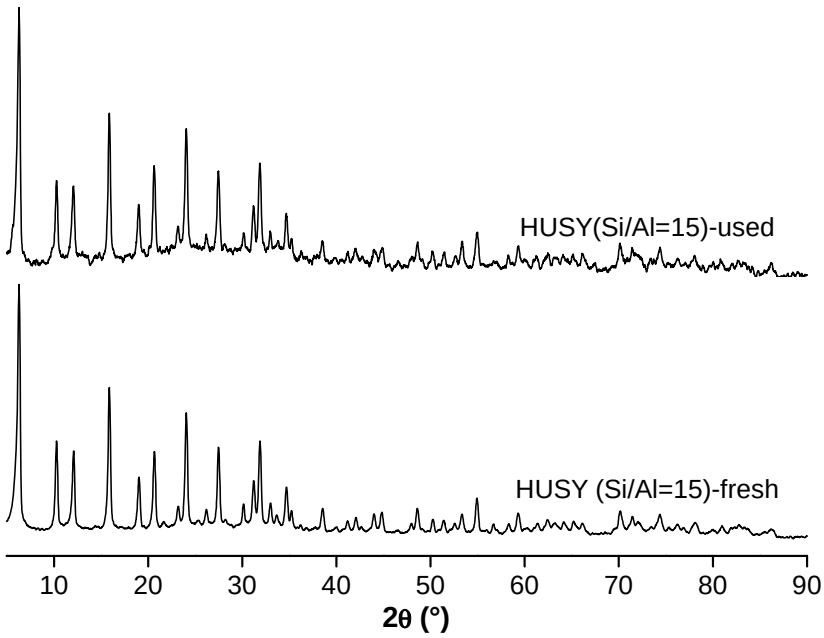


Figure S2 XRD pattern for HUSY (Si/Al=15) catalyst.

Reaction results

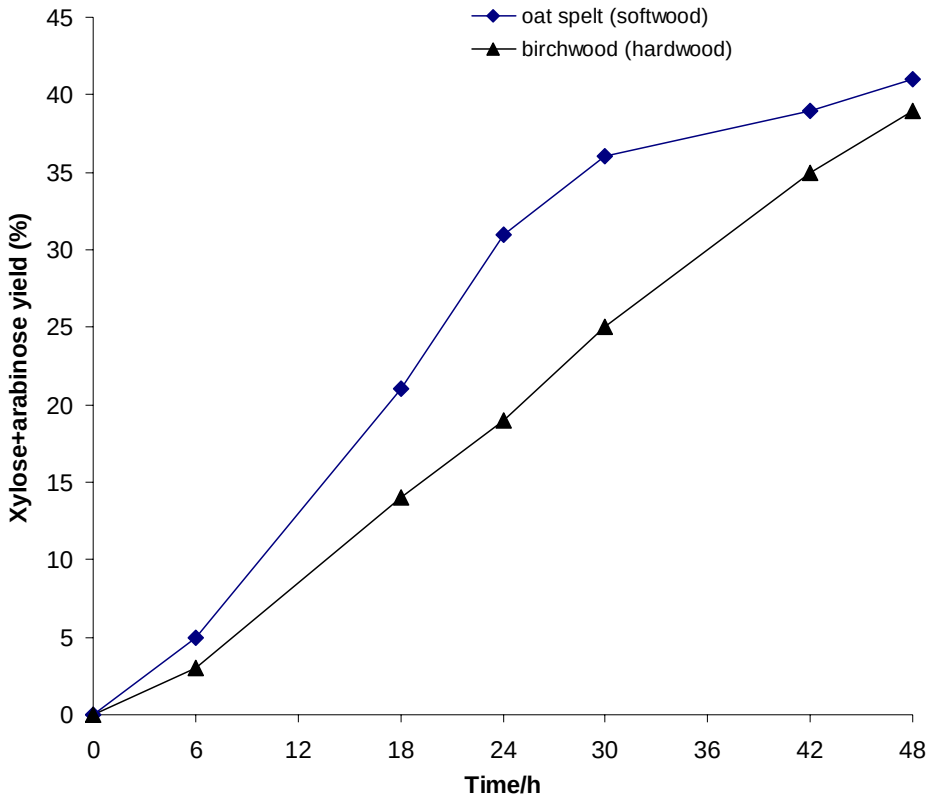


Figure S3 Effect of source of hemicellulose on the conversion. Reaction conditions: Xylan (softwood or hardwood) 0.6 g; HUSY (Si/Al=15) 0.3 g; water 60 mL; 130^{o}C; N_2 pressure 5 MPa.