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Design of a selective solid acid catalyst for the optimization of glucose production from *Oryza sativa* straw†

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A selective, green and fast method for the production of glucose from rice (*Oryza sativa*) straw is demonstrated. Aq. ammonia based pretreatment techniques played a crucial role in the removal of lignin and xylan from rice straw which in-turn accelerated glucan hydrolysis and improved the selectivity of glucose production. The cellulose isolated from rice straw is further hydrolyzed to glucose using a solid acid catalyst (activated carbon supported phosphotungstic acid, ~40 wt% HPW/AC). Microwave irradiation of cellulose from rice straw for a short duration of 5 min at 100 °C yielded 11.2 wt% glucose relative to 8 wt% glucose produced from a hydrothermal hydrolysis process (3 h, 150 °C) with a substrate to catalyst wt/wt ratio of 1. Thus an effective biomass pretreatment (aq. ammonia–dil. H_2SO_4) method and an accelerated selective biomass hydrolysis process is developed.

1. Introduction

The production cost for obtaining bioethanol from rice (*Oryza sativa*) straw is the highest (23–26 \$/GJ) relative to soy (11–15 \$/GJ), palm (8–23 \$/GJ), and poplar (14–17 \$/GJ). It is however, comparable to that of fossil fuels (20–30 \$/GJ). Optimization of the biomass conversion process is a major factor apart from labour costs and agricultural productivity in biofuel production.[1] Rice straw is an abundantly available agricultural waste in Asian countries like India, China and Vietnam.[2] The present rice straw based bioethanol production process cost (1.19 \$/L) in Vietnam could be lowered to 0.45 \$/L (plant size, 200 ML per year) by improving the pretreatment, enzyme hydrolysis, enzyme activity and productive utilization of residual biomass.[3]

Typical composition of rice straw comprise of: cellulose (32–47%), hemicellulose (19–27%), lignin (5–24%) and ash (10–17%). High cellulose content of rice straw makes it a promising feedstock for bioethanol production for transportation application.[4]

Pretreatment of rice straw is necessary to remove the lignin, hemicellulose and mineral content and to isolate cellulose which upon hydrolysis yields readily fermentable glucose. The state of the art processes developed for the pretreatment of rice straw as well as the subsequent hydrolysis of pretreated rice straw to glucose are summarized in Table 1.

As could be noted from Table 1, even though diverse strategies were developed for effective delignification and hemicellulose removal, essentially enzymatic hydrolysis was most widely used for the conversion of pretreated rice straw to glucose except the work of Rehman *et al.*, where H_2SO_4 is used for the hydrolysis.[19,20] But use of mineral acids as catalyst pose problems like product separation, reactor corrosion, poor catalyst recyclability, requirement of waste effluent treatment.[21] To overcome the afore mentioned issues, state of the art solid acid catalysts were developed for the hydrolysis of cellulose to glucose which was reviewed by Huang and Fu.[21] Even though sulfonated carbon, polymer and magnetic solid acid based catalysts were developed, most of their applications were tested only on commercial cellulose but not on real lignocellulosic biomass. Jiang *et al.*, have developed a sulfonated carbon catalyst for the hydrolysis of corn cob to glucose with an yield of 34 wt% under microwave irradiation (100 W, 140 °C) for 20 h.[22] The main drawbacks of the process were the use of fumed H_2SO_4 at 120 °C for 10 h for preparing the sulfonated carbon catalyst and also the longer hydrolysis reaction times. Our approach is novel – employing a green solid acid catalyst (H_3-$PW_{12}O_{40} \cdot nH_2O$/activated carbon) as a substitute to either enzymes or mineral acids and using microwave irradiation for faster production of glucose. The use of heteropoly acid catalyst have several advantages including the fact that there are currently several industrial processes being operated using these solid acid catalysts.[21] Moreover, in the suggested process the glucose production is accelerated with the use of microwave irradiation. Profitable bioethanol production from rice straw could be achieved by improving the biomass conversion process

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Table 1 Strategies for the conversion of rice straw to monosaccharides

Pretreatment method	Hydrolysis conditions	Yield of mono saccharides	Reference
Electron beam irradiation (50–500 kGy) followed by alkali pretreatment (3% NaOH, 5 h, 120 °C, 1 bar); lignin content decreased from 19.5 to 6.4% and cellulose content increased from 39.5 to 71.1%	Enzymatic (Celluclast 1.5 L and novozyme-188) hydrolysis at 50 °C for 24–72 h	77 wt% total sugars (glucose (65 wt%), xylose and others)	5
Electron beam irradiation (50–500 kGy) followed by acid pretreatment (3% dil. H_2SO_4, 1 h, 120 °C); hemicellulose content decreased from 26.7 to 8.7%, lignin content decreased from 19.5 to 18.1% and cellulose content increased from 39.5 to 68.1%	Enzymatic (cellulase and glucosidase) hydrolysis at 50 °C for 24–72 h	80 wt% total sugar yield (glucose selectivity – 92.7%)	6
Alkaline (NaOH 1% w/v) pretreatment for 48 h at 30 °C; solid recovery – 57.6%	Enzymatic (cellulase, xylanase and β-glycosidase) hydrolysis at 150 rpm, 50 °C for 72 h	Conversion of pretreated rice straw to reducing sugars – 92.6%	7
Hot compressed water, HCW, (140–240 °C; 10–30 min) pretreatment was effective for the removal of xylan but not lignin. Upon HCW treatment, xylan content decreased from 19% to <2% whereas lignin content increased from 18 to 40% and glucan content increased from 36 to 54%	Enzymatic (acremonium cellulase, novozyme 188, Optimash BG) hydrolysis at 45 °C for 72 h at a pH of 5	Glucose yield – 85 wt%	8
Organosolv (75% (v/v) aq. ethanol, 1% w/w H_2SO_4, 180 °C, 30 min, 5% solid loading); 60% lignin removal	Enzymatic hydrolysis (cellulase and β-glucosidase), pH = 4.8, 45 °C, 72 h; 140 rpm	Glucose yield – 46.2%	9
HNO_3 (0.65%, 158.8 °C, 5.86 min) pretreatment dissolved hemicellulose and yielded 86.5% xylose; moreover, the nitrate was found to be potential nutrient for improving fermentation efficiency	Enzymatic (Cellic C-Tec, novozymes, derived from *Trichoderma reesei*) hydrolysis at a pH 4.8, solid loading 10% w/v, 50 °C for 72 h at 170 rpm	Glycose yield – 83% (47.7 g L^{-1})	10
$(NH_4)_2CO_3$ (20%, 80 °C, 12 h) pretreatment is effective in dissolving the amorphous components (lignin and hemi cellulose); 23.9% lignin removal and 92.3% glucan recovery	Enzymatic (Cellic C-Tec, novozymes, derived from *Trichoderma reesei*) hydrolysis at a pH 4.8, solid loading 5% (w/v), 50 °C for 72 h at 200 rpm	Glucose yield – 72.2%	11
Ionic liquid (cholinium argininate, [Ch][Arg]) pretreatment at 60 °C for 6 h; incubation under nitrogen and stirring; 72% lignin removal	Enzymatic (cellulase) hydrolysis at a pH – 4.8, 50 °C, 200 rpm	Glucose yield – 81% xylose yield – 26%	12
CO_2 added ammonia explosion (14.3% ammonia conc.; 2.2 MPa CO_2 loading, 165.1 °C, 69.8 min) pretreatment; ammonia induced swelling and removed lignin whereas CO_2 caused increase in the pore size. 60% lignin removal; 80% carbohydrate recovery	Enzymatic (novozymes) hydrolysis; 50 °C, 24 h	Glucose yield 93.6%	13
Na_2CO_3 (0.5 M, 180 °C, 120 min) pretreatment; lignin, xylan and mineral content removed in one step process; lignin decreased from 15.5 to 8.4% and xylan decreased from 23.8 to 6.3%; glucan content increased from 40.3 to 80.1%	Enzymatic (cellulase, β-glucosidase) hydrolysis at a pH of 4.8, at 45 °C for 72 h at 100 rpm in an incubator	Glucose yield 43.5 g L^{-1}	14
Sodium sulfite, 12% – formaldehyde (1 : 1 mole ratio) at 160 °C for 1 h; selective removal of lignin (75%); sulfonation generates hydrophilic groups in the side chain of hydrophobic lignin polymer. HCHO addition raises the pH and facilitates sulfomethylation at C5 position of lignin aromatic ring	Enzymatic (cellulase, xylanase and β-glucosidase) hydrolysis at 50 °C, 180 rpm, 48 h, pH – 4.8	Glucose yield 88.8%	15
Na_2CO_3–Na_2SO_3 (0 : 1) pretreatment (12%, 140 °C, 60 min); presence of higher Na_2CO_3 facilitated hemicellulose degradation, delignification (53.4%) and conserved polysaccharide (91.4%)	Enzymatic (cellulase, xylanase, glucosidase) hydrolysis at pH – 4.8, 50 °C, 180 rpm, 48 h	Glucose yield 82.7%	16
Popping (220 °C, 1.96 MPa) pretreatment increased conversion efficiency of cellulose to glucose. The chemical composition remained unchanged but a two fold increase in surface area is observed	Enzymatic (cellulase and xylanase) hydrolysis; 37 °C; 48 h	0.394 g glucose per g biomass	17

Table 1 (Contd.)

Pretreatment method	Hydrolysis conditions	Yield of mono saccharides	Reference
Dil. H_2SO_4 (142 °C, 1.2%, 11.6 min) followed by aqueous ammonia pretreatment (20.93%, 42.7 °C, 48 h); glucan content increased from 39 to 80% as a result of removal of XMG (xylan, mannan and galactan) as well as lignin and ash	Enzymatic (cellulase, β-glucosidase) hydrolysis; pH – 4.8, 50 °C, 60 min	Glucose yield 87.24%	18
Sonication (20 kHz, 750 W, 20% amplitude, 80 °C, 50 min) assisted H_2SO_4 based simultaneous pretreatment and saccharification (SPS)	H_2SO_4 (10 wt%) based simultaneous pretreatment and saccharification	31.8 g reducing sugar/100 g dry rice straw	19 and 20

(pretreatment, hydrolysis and fermentation). The current work is an attempt towards developing efficient pretreatment and green hydrolysis strategies for the conversion of rice straw to glucose which is a precursor to bioethanol.

2. Experimental

2.1. Materials

Rice straw is collected from the fields of South Korea after the harvest. $H_3PW_{12}O_{40} \cdot nH_2O$ (HPW), HCl, H_2SO_4, NH_3 and activated carbon (Norit® CA1 from wood, chemically activated, powder) are purchased from Sigma Aldrich Ltd., Israel. All reagents are used as received without further purification. Double distilled water is used as a solvent.

2.2. Pretreatment of rice straw

The rice straw is subjected as received to three different methods of pretreatment namely, soaking in aqueous ammonia (SAA), soaking in aqueous ammonia (SAA) and subsequent hot water (SAA–hot water) treatment and soaking in aqueous ammonia with a subsequent H_2SO_4 treatment (SAA–H_2SO_4). Typical process of SAA comprise of soaking a known amount of rice straw in 15 wt% ammonia (solid : liquid ratio = 1 : 12) for 12 h at 80 °C. The other two pretreatment methods, namely, SAA–hot water and SAA–H_2SO_4 comprise of two stages with the reaction conditions as shown below:

SAA–hot-water pretreatment: 1st stage (SAA) – 15 wt% ammonia, 80 °C, 12 h, and solid : liquid ratio = 1 : 12; 2nd stage – hot-water, 5.0 mL min^{-1} of flow rate, 190 °C, 2.3 MPa.

SAA–H_2SO_4 pretreatment: 1st stage (SAA) – 15 wt% ammonia, 80 °C, 12 h, and solid : liquid ratio = 1 : 12; 2nd stage – dilute sulfuric acid treatment: sulfuric acid (0.2 wt%), 5.0 mL min^{-1} of flow rate, 170 °C, 2.3 MPa.

Solid analysis of sugar and lignin is performed following the NREL Chemical Analysis and Testing Standard procedures.[24] Detailed description of the estimation of the acid soluble and acid insoluble lignin could be found elsewhere.[25]

2.3. Preparation of activated carbon (AC) supported tungstophosphoric acid ($H_3PW_{12}O_{40} \cdot nH_2O$, HPW)

Conventional wet impregnation method is used for supporting heteropoly acid (HPW) on activated carbon.[26] Typical catalyst preparation method comprise of taking 4 g of HPW in 70 mL water in a 250 mL beaker and subjecting the same for stirring using a magnetic stirrer at room temperature. To the aqueous solution of the heteropoly acid, 6 g of activated carbon is added and the content is stirred for 72 h after which the supernatant is separated from the solid component through filtration. The residual solid (∼40 wt% HPW/activated carbon) is dried in an air oven at 100 °C overnight.[23] The catalyst thus obtained is characterized using SEM-EDAX (FEI Megallon 400 L microscope equipped with energy dispersive X-ray spectroscope) to evaluate the distribution of the active component (heteropoly anions) on the activated carbon surface and also by using FT-IR (Bruker Tensor 27) spectroscopy to confirm the retention of the Keggin type poly anion structure typical of heteropoly acid. The loading of the amount of HPW on the activated carbon support is evaluated using UV-Vis spectroscopy. Aq. HPW exhibits a characteristic absorption band at 256 nm due to charge transfer from bridge oxygen to tungsten in W–O–W, which was used as a measure for the quantification of HPW loaded on activated carbon (Fig. S1†).[27] The amount of the HPW in the filtrate obtained in the impregnation process is subtracted from the initial amount of HPW taken, which resulted in the actual amount of HPW loaded on the support to be 39 ± 1 wt%.

2.4. Hydrolysis of pretreated rice straw

The pretreated (SSA–hot water & SSA–H_2SO_4) rice straw is subjected to hydrolysis in a modified domestic microwave oven (MDMWO, 2.45 GHz, 1100 W at 100% power),[28] commercial microwave oven (MARS, CEM),[29] and a hydrothermal reactor (cylindrical stainless steel reactor lined inside with poly tetra fluoro ethylene to resist corrosion by the acid catalyst).[30] The biomass hydrolysis reaction is carried out using either conventional mineral acid (HCl, 3 M) or the solid acid catalyst (activated carbon supported tungstophosphoric acid, 40 wt% HPW/AC), under identical reaction conditions. The systematic procedure adopted for the conversion of rice straw to glucose is depicted in Scheme 1.

Preliminary studies on the acid (HCl) hydrolysis of pretreated rice straw are carried out in a modified domestic microwave oven (MDMWO) with stirring facility (Fig. S2†). Typical hydrolysis batch in a MDMWO comprise of taking 0.5 g (pretreated biomass) and 20 mL 3 M HCl in a 100 mL round bottom flask and irradiating the contents for 5–10 min at 100% power.

The unreacted biomass after the acid (HCl) hydrolysis is separated from the hydrolyzate through filtration, washed with
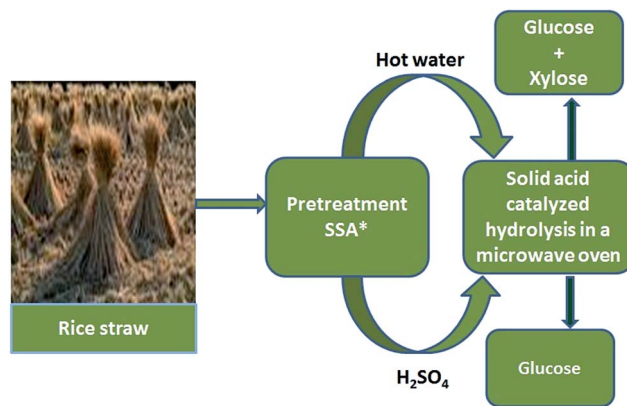
*SSA- Soaked in aqueous Ammonia

Scheme 1 Schematic representation of conversion of rice straw to monosaccharides.

water and dried in an air oven over night at 373 K and weighed. The wt% conversion of the biomass to products is deduced from the difference in the initial (before exposure to microwave irradiation) and final (after exposure to microwave irradiation) weights of the biomass.[31,32]

Typical hydrolysis batch in a commercial microwave oven comprise of taking 0.125 g pretreated rice straw, 3 M HCl, 5 mL in the reaction vessel (XP-1500 plus control vessel) and irradiating the contents at 100 °C, 300 W for 1–5 min. The rice straw (pretreated) hydrolysis reaction is also evaluated using the designed solid acid catalyst (0.125 g) in the place of the mineral acid with other conditions being the same. For comparison, the acid hydrolysis of pretreated rice straw is carried out in a conventional hydrothermal reactor by taking 0.5 g biomass, 20 mL HCl (3 M) and placing the reactor in a pre-heated air oven (150 °C) for 3 h. The biomass hydrolysis reaction in the presence of solid acid catalyst is carried out by taking 0.5 g pretreated rice straw, 0.5 g 40 wt% HPW/AC, 20 mL H_2O with other reaction conditions being the same as mentioned before. After the hydrolysis reaction, the residual solid mass is separated from the hydrolyzate through filtration using Whatman® (150 mm ϕ). The hydrolyzate thus obtained in each instance is qualitatively (^{13}C NMR) and quantitatively (HPLC) analyzed for the fermentable sugars. ^{13}C NMR spectra were recorded on a Bruker Avance DPX 300 using D_2O as solvent at room temperature. HPLC analysis is carried out on a Shimadzu system with a refractive index detector (RID-10A). Chromatographic separation was carried out using a strong cation-exchange column (Aminex HPX-87H, 300 × 7.8 mm).

3. Results and discussion

3.1. Delignification of rice straw

Presence of lignin and hemicellulose in the rice straw hinders the accessibility of cellulose (exposure of cellulose surface) component by the acidic catalytic sites. Pretreatment of biomass not only solubilizes the amorphous content (lignin and hemicellulose) but also reduces the crystallinity of cellulose *via* pore enlargement and increase in the internal surface area.[5] Among several pretreatment (biological, chemical, physical,

mechanochemical) methods, alkali (ammonia, lime and NaOH) based pretreatment was found to be effective for agricultural residues.[33] Alkali pretreatment is superior to other approaches, as it causes swelling of the biomass, increases the internal surface area and essentially removes the enzyme inhibitor, lignin.[34] Soaking the rice straw in aq. ammonia was reported to be better than $(NH_4)_2CO_3$ pretreatment for the enzymatic digestibility of the rice straw (76.5 *vs.* 72.2%).[11]

In the present study, rice straw was subjected to three different pretreatments which are essentially based on aq. NH_3, namely, (1) soaking in aq. NH_3, (2) soaking in aq. NH_3 followed by hot water treatment and (3) soaking in aq. NH_3 followed by treatment with dil. H_2SO_4. Among the three methods, the later was found to be more effective for the removal of lignin and xylan from the rice straw yielding higher cellulose content.

Typical composition of the rice straw before and after delignification was shown in Table S1.† Detailed mass balance of the untreated rice straw and the rice straw subjected to the three pretreatments is shown in Fig. 1.

A steady increase in the glucan (cellulose) content from 30.6 wt% to 70.6 wt% is achieved through modification of the pretreatment methods from only aq. ammonia pretreatment to aq. ammonia pretreatment followed by dil. H_2SO_4 treatment. Thus the pretreatment process facilitates generating cellulose rich biomass.

While soaking in aq. NH_3 removed lignin from 18.7 to 9.7 wt%, subsequent treatment with dil. H_2SO_4 essentially enhanced xylan removal from 14.4 to 6.9 wt%. While lignin removal from rice straw accelerates the cellulose hydrolysis, xylan removal improves the selectivity of glucose production. The lignin recovered in the pretreatment process of biomass is usually regarded as a biorefinery waste. On the contrary, such lignin could be converted to value added phenolic compounds *via* pyrolysis. This further improves the cost effectiveness of the rice straw based bioethanol production process.[36]

3.2. Hydrolysis of pretreated rice straw

3.2.1. Hydrolysis of pretreated rice straw in a modified domestic microwave oven (MDMWO). The pretreated (SAA–hot water) rice straw was hydrolyzed using HCl in a MDMWO for 5
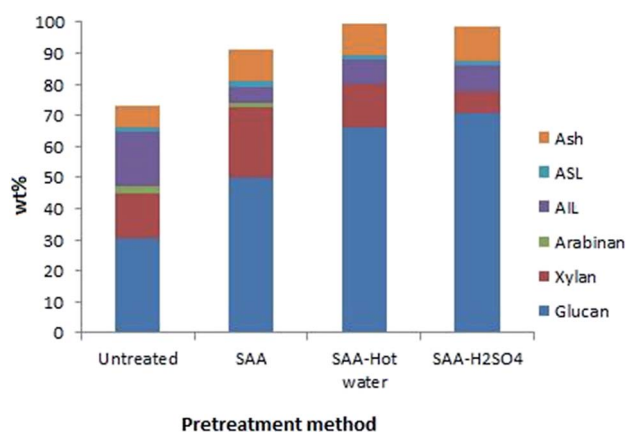

Fig. 1 Mass balance of the untreated and pretreated rice straw (ASL-acid soluble lignin; AIL-acid insoluble lignin).
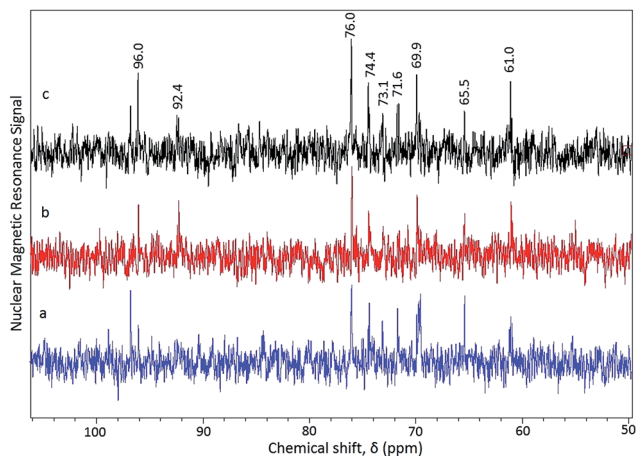
Fig. 2 ^{13}C NMR spectra of hydrolyzate from pretreated (SAA–hot water) rice straw (a) step 1, 5 min; (b) step 2, 5 min; (c) single step, 10 min.

Fig. 3 ^{13}C NMR spectra of hydrolyzate from pretreated (SAA–H$_2$SO$_4$) rice straw (a) step 1, 5 min; (b) step 2, 5 min; (c) single step, 10 min.

min and a conversion value of 29 wt% to monosaccharides was observed. NMR (^{1}H and ^{13}C) is a potential analytical tool for studying the biomass hydrolysis process, especially, the reaction products and by-products.[29] Usually, hydroxy methyl furfural (HMF), levulinic acid and formic acid are the by-products that are formed during the conversion of biomass to glucose and these molecules could be easily identified using NMR analysis.[23] The ^{13}C NMR spectra of the hydrolyzate indicated the presence of both glucose and xylose (Fig. 2(a)).

Assignment of the signals to respective carbon nuclei of a monosaccharide was based on our previous studies.[23,29] The unreacted biomass separated from the hydrolyzate through filtration was again subjected to hydrolysis using HCl in a MDMWO for 5 more minutes. A biomass conversion value of 30.4 wt% and the hydrolyzate contained both xylose and glucose (Fig. 2(b)). Thus microwave irradiation of the biomass for 10 min (in two consecutive steps each for 5 min) lead to a conversion value of 59.4 wt%. On the contrary, direct irradiation of the pretreated (SAA–hot water) rice straw for 10 min in one stretch lead to a biomass conversion value of only 28.1 wt% with the hydrolyzate comprising of both xylose and glucose (Fig. 2(c)). Thus microwave irradiation in two stages is advantageous for higher conversion of the pretreated biomass. The source of xylose in the hydrolyzate is the xylan (13.8 wt%) content present in the pretreated (SAA–hot water) rice straw. Hot water treatment following the SAA is not effective for the removal of xylan even though the lignin content is effectively removed.

Unlike SAA–hot water treated rice straw, the hydrolyzate of pretreated rice straw showed exclusive presence of glucose (Fig. 3). Pretreated (SSA–H$_2$SO$_4$) rice straw is hydrolyzed for 5 min in HCl under MDMWO yielding a biomass conversion value of 19 wt% and the ^{13}C NMR spectra of the hydrolyzate showed exclusive presence of glucose (Fig. 3(a)). This selectivity towards glucose is in line with the potential of dil. H$_2$SO$_4$ to remove the xylan components during pretreatment.

The unreacted biomass is separated by filtration and reirradiated for 5 min resulting in a biomass conversion value of 35
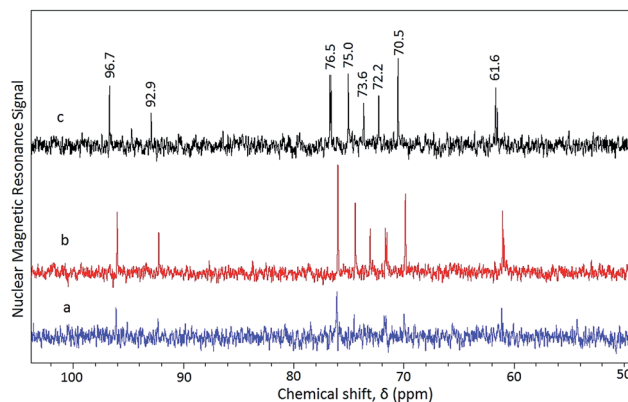
wt% and exclusive presence of glucose is observed in the ^{13}C NMR spectra of hydrolyzate (Fig. 3(b)). Thus a total of 54 wt% biomass conversion could be achieved in a two step microwave irradiation based hydrolysis process unlike a single step continuous irradiation of the pretreated biomass yielding only 26 wt% conversion. Contrary to the SAA–hot water pretreated rice straw, SAA–H$_2$SO$_4$ pretreated rice straw yielded glucose selectively. The signals at 61.6 (C6), 70.5 (C4), 73.6, 72.2 (C2), 75.0 (C3), 76.5 (C5), 92.9 (C1, α) and 96.7 (C1, β) are characteristic of glucose.[32] Also the absence of signal at 65.5 (C5, β) which is a finger print for xylose presence indicate absence of xylose in the hydrolyzate. The absence of xylose in the hydrolyzate from SAA–H$_2$SO$_4$ pretreated rice straw signify the effectiveness of dil. H$_2$SO$_4$ treatment in the reduction of xylan content from 14.4 to 7 wt% (Fig. 1).

Further optimization studies of biomass hydrolysis in commercial microwave oven as well as hydrothermal reactor were carried out using SAA–H$_2$SO$_4$ pretreated rice straw.

3.2.2. Hydrolysis of pretreated (SSA–H$_2$SO$_4$) rice straw in a commercial (MARS) microwave oven. The pretreated rice straw (SSA–H$_2$SO$_4$) was hydrolyzed using mineral acid (HCl, 3 M) at 100 °C for 1, 2 and 5 min. In a short duration of 1 min of irradiation, selective hydrolysis of biomass to glucose is obtained with a conversion of 15.7 wt%. The ^{13}C NMR of the hydrolyzate (Fig. 4(a)) showed exclusive presence of glucose. The signals at 61.6 (C6), 70.5 (C4), 72.2, 73.6 (C2), 75.0 (C3), 76.6 (C5), 92.9 (C1, α), 96.7 (C1, β) are indicative of glucose.

As the time of irradiation is increased from 1 min to either 2 or 5 min no trace of glucose is seen in the hydrolyzate as evident from the absence of signals in the region of 50–100 ppm (Fig. 4(a) and (b)). Instead, signals typical of levulinic acid were observed in the hydrolyzate obtained from 2 min (Fig. 4(b)) and 5 min (Fig. 4(c)) irradiation.

The signals at 30.2 and 39.9 ppm are characteristic of two methylene groups, one adjacent to the carbonyl and the other adjacent to the carboxyl groups. The signals at 31.2, 181.3 and 215.0 ppm correspond to methyl, carboxyl and carbonyl groups. In addition to levulinic acid, the presence of formic acid in the hydrolyzate is confirmed from the observation of the signal at 171.7 ppm.[35] The presence of levulinic and formic acids in the
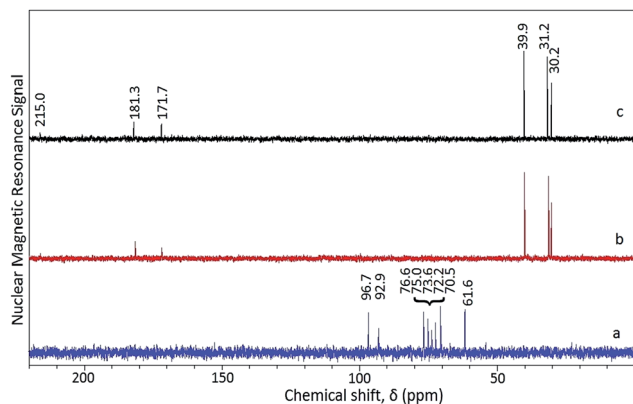
Fig. 4 ^{13}C NMR spectra of hydrolyzate from pretreated (SAA–H_2SO_4) rice straw irradiated in microwave oven (MARS) for (a) 1 min; (b) 2 min; and (c) 5 min using HCl as catalyst.

Fig. 5 ^{13}C NMR spectra of hydrolyzate from pretreated (SAA–H_2SO_4) rice straw hydrolyzed using solid acid catalyst in (a) microwave oven (MARS) and (b) hydrothermal reactor.

hydrolyzate obtained in the case of pretreated rice straw irradiated for 5 min in the presence of HCl is further confirmed from ^1H NMR spectrum (Fig. S3†). The presence of a singlet signal at 2.4 ppm (3H, s) and two triplets at 2.62 (2H, t) and 2.98 (2H, t) ppm confirm the presence of levulinic acid. In addition, the appearance of a singlet signal (1H, s) at 8.3 ppm is characteristic of formic acid (Fig. S3†). Thus irradiation time of 1 min at 100 °C using HCl (3 M) is optimum for the selective conversion of pretreated rice straw to glucose. But, the use of a mineral acid as catalyst for biomass conversion has several environmental as well as operational hazards. Recently, Wang *et al.*, provided a comprehensive account of the use of solid acid catalysts for the production of glucose from cellulose. Even though, there were several additional reports on the conversion of cellulose (commercial) to glucose using solid acid catalysts, there were limited studies on the application of solid acid catalysts for the hydrolysis of real biomass feedstock.[37] Keeping this in view, further hydrolysis studies of the pretreated rice straw were carried out using the solid acid catalyst (40 wt% HPW/AC) in the place of mineral acid (HCl). Interestingly, upon 5 min irradiation of the pretreated rice straw using solid acid catalyst at 100 °C, the biomass could indeed be hydrolyzed exclusively to glucose and no reaction by-products like levulinic acid or formic acid were formed. The ^{13}C NMR spectra of the hydrolyzate obtained using solid acid catalyst showed exclusive presence of glucose (Fig. 5(a)).

The signals at 61.4 (C6), 70.3 (C4), 72.2 (C2), 73.4 (C2), 75.0 (C3), 76.4 (C5), 92.7 (C1, α), 96.5 (C1, β) were indicative of the presence of glucose. The amount of glucose in the hydrolyzate was found to be 11.2 wt% using HPLC analysis. Irradiation of the pretreated rice straw for lower reaction time (1 and 2 min) did not result in the glucose production. Even though Onda *et al.*, reported a much higher glucose yield (40.5 wt%) from the hydrolysis of cellulose using sulfonated carbon catalyst, reaction conditions require 48 h of ball milling of cellulose as well as longer hydrothermal reaction time (24 h) at 150 °C. Moreover, the catalyst is based on a mineral acid (H_2SO_4) for generating the acid sites of activated carbon surface which is not environmentally friendly.[38]
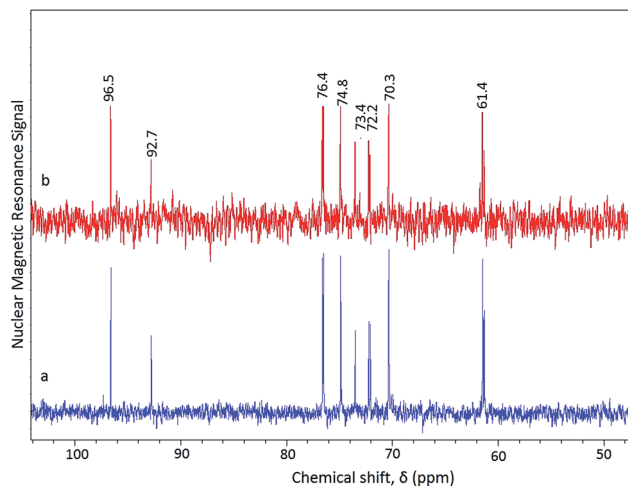
Apart from microwave irradiation, conventional hydrothermal method has also been evaluated for the conversion of pretreated rice straw using solid acid as catalyst. Hydrolysis of pretreated rice straw under hydrothermal conditions (150 °C, 3 h) using ~40 wt% HPW/AC resulted in the selective production of glucose. The hydrothermal reaction product showed similar ^{13}C NMR peak pattern (Fig. 5(b)) to that obtained in a microwave reactor (Fig. 5(a)).

Apart from glucose (characteristic signals in the region of 50–100 ppm), no other signals typical of common by-products like levulinic acid and formic acid were observed indicating the selective nature of the solid acid catalyst for the conversion of pretreated rice straw to glucose. The yield of glucose in the hydrolyzate from the hydrothermal reaction was found to be 8 wt% using HPLC analysis.

It is clear that the yield of glucose is higher and also the reaction time is shorter and the reaction temperature is lower in the microwave irradiation based biomass hydrolysis compared to the conventional hydrothermal reaction. Thus under modest reaction conditions (100 °C, 5 min), glucose could be produced from the pretreated rice straw using the solid acid catalyst offering a green pathway for biomass conversion. The hydrolyzate obtained under microwave irradiation (MARS) is further analyzed by UV-Vis analysis for possible leaching of the heteropoly acid into the medium during the reaction. No absorption band characteristic of HPW is observed in the hydrolyzate indicating the stability of the HPW/AC catalyst (Fig. S1†).

Under similar microwave reaction conditions, use of mineral acid catalyst lead to the formation of levulinic acid. The appearance of the reaction product of the hydrolysis of pretreated rice straw using solid acid catalyst *vs.* mineral acid could be seen in Fig. 6. Deep brown colouration (Fig. 6(b)) is typical of levulinic acid formation (with HCl as catalyst) whereas the reaction product using solid acid catalyst is transparent and colourless (Fig. 6(c)) as expected of a glucose solution.
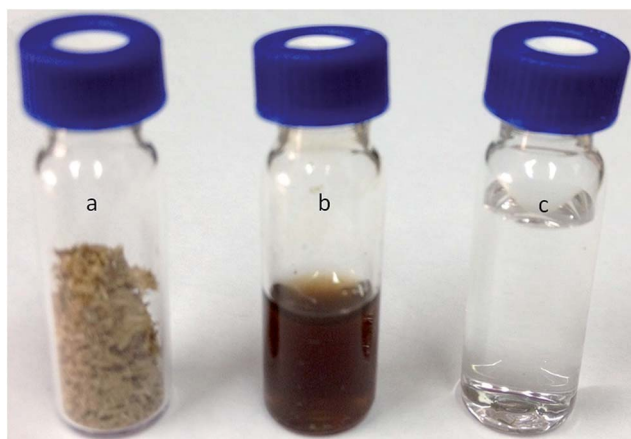
Fig. 6 Pictorial representation of (a) pretreated rice straw (SAA–H_2SO_4), (b) hydrolyzate using HCl as catalyst and (c) hydrolyzate using solid acid catalyst under MW (MARS) irradiation.

3.3. Characterization of the solid acid catalyst, ∼40 wt% HPW/AC

FT-IR spectra of the solid acid catalyst (∼40 wt% HPW/AC) before and after the biomass hydrolysis reaction in a microwave oven (MARS) is shown in Fig. 7.

The presence of four consecutive bands in the region of 800–1100 cm^{-1} is a finger print of the Keggin type polyanion and they are a result of the four kinds of metal-oxygen bonds present in the heteropoly anion $[PW_{12}O_{40}]^{3-}$.[26] Interestingly, similar features were also observed in the case of the spent catalyst indicating that the structure of the active component at the molecular level remained unperturbed even after microwave irradiation.

The solid acid catalyst, before and after the biomass hydrolysis reaction under microwave irradiation (MARS), was further characterized using SEM-EDAX with elemental mapping. The morphology of the ∼40 wt% HPW/AC could be seen in the SEM (Fig. 8).
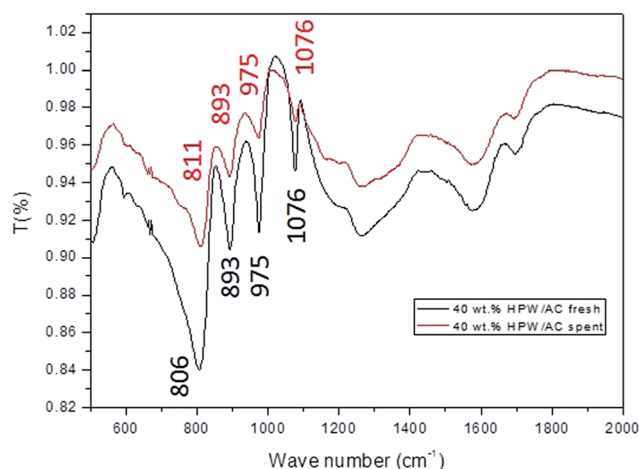

Fig. 7 FT-IR spectra of (a) fresh and (b) spent catalyst (∼40 wt% HPW/AC) used for the hydrolysis of rice straw under micro wave irradiation.
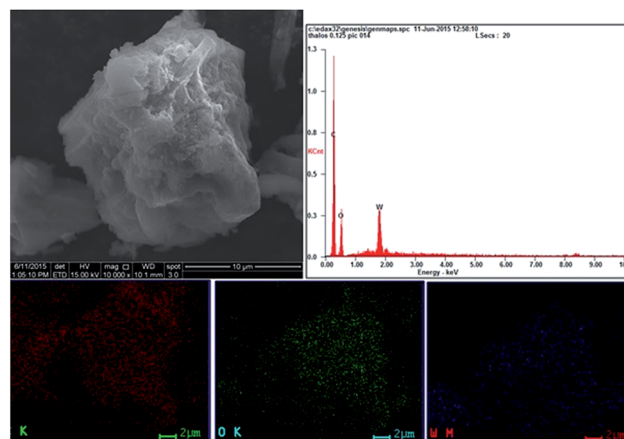

Fig. 8 E-SEM, EDAX and the elemental mapping (C, O, W) of ∼40 wt% HPW/AC catalyst.

Activated carbon particle of irregular shape could be viewed upon which the active component $H_3PW_{12}O_{40}$ is homogeneously distributed. The homogeneous distribution of the heteropoly acid could be observed from the elemental mapping in Fig. 8. As expected W (in blue colour) and oxygen (green) were distributed upon carbon (red colour) surface. Interestingly, even in the spent catalyst similar elemental distribution is observed (Fig. S4†) indicating that the poly anion, $[PW_{12}O_{40}]^{3-}$ is strongly adhered to the activated carbon surface which remained bound to the surface even after the biomass hydrolysis reaction.

This result (SEM-EDAX) is in concurrence with the FT-IR (Fig. 7) analysis of the solid acid catalyst. Thus the solid acid catalyst designed is potential (active and selective) for the conversion of pretreated rice straw to glucose. Owing to the industrial demand for green solid acid catalysts for biomass conversion stringent efforts are being carried out not only for glucose production but also for a variety of catalytic reactions. Pesaresi et al., developed Cs-doped silico tungstic acid catalyst for the production of biodiesel via transesterification of C4 and C8 glycerides.[39] Fraile et al., developed a sulfonated carbon catalyst for the esterification of palmitic acid with methanol.[40] Ngee et al., designed a novel sulfated mesoporous niobium oxide catalyst for the conversion of a variety of sugars (fructose, sucrose, cellobiose and inulin) into a valuable fuel precursor, 5-hydroxy methyl furfural (5-HMF).[41] Pent et al., reported a sulfonated two-dimensional covalent organic frame work synthesized from the condensation of 1,3,5-triformyl phloroglucinol and 2,5-diaminobenzenesulfonic acid (THF-DABA), which efficiently catalyzed the conversion of fructose to 5-HMF (97% yield).[42]

Effective pretreatment of rice straw, ease of synthesis of the catalyst (HPW/AC), environmental friendliness, stability of the catalyst under microwave irradiation conditions, fast and selective production of glucose from pretreated rice straw were the salient features of the current process.

4. Conclusions

Abundantly available biomass, rice straw, is pretreated by soaking in aqueous ammonia followed by treating with dil. H_2SO_4.

Reaction with aq. NH$_3$ facilitated the removal of lignin whereas treatment with dil. H$_2$SO$_4$ effectively removed hemicellulose (xylan). The pretreated rice straw was further hydrolyzed using two different class of catalysts: conventional mineral acid and solid acid catalyst. Use of solid acid catalyst (~40 wt% tungsto phosphoric acid/activated carbon) under microwave irradiation (5 min, 100 °C) yielded 11.2 wt% glucose exclusively. No by-products like levulinic and formic acids which were obtained in the case of mineral acid were observed when solid acid catalyst is used. For comparison, conventional hydrothermal method (150 °C, 3 h) of heating was also used for the hydrolysis of pretreated rice straw which resulted in the selective production of glucose (8 wt%). Microwave based hydrolysis using solid acid catalyst is particularly advantageous owing to shorter reaction time, lower reaction temperature, higher and selective glucose yield. The structural integrity of the solid acid catalyst is retained even after the microwave irradiation.

Acknowledgements

References

1 J. V. Eijck, B. Batixzirai and A. Faaij, *Appl. Energy*, 2014, **135**, 115–141.

2 L. D. Escribà and M. Porcar, *Biofuels, Bioprod. Biorefin.*, 2010, **4**, 154.

3 N. Q. Diep, K. Sakanishi, N. Nakagoshi, S. Fujimoto and T. Minowa, *J. Renewable Energy*, 2015, **74**, 456.

4 P. Binod, R. Sindhu, R. R. Singhania, S. Vikram, L. Devi, S. Nagalakshmi, N. Kurein, R. K. Sukumaran and A. Pandey, *Bioresour. Technol.*, 2010, **101**, 4767.

5 D. Y. Kim, B. M. Lee, Y. J. Lee, P. H. Kang and J. P. Jeun, *J. Korean Soc. Appl. Biol. Chem.*, 2014, **57**(5), 591.

6 B. M. Lee, J. Y. Lee, P. H. Kang, S. K. Hong and J. P. Jeun, *Appl. Biochem. Biotechnol.*, 2014, **174**, 1548.

7 E. Cabrera, M. J. Munoz, R. Martin, I. Caro, C. Curbelo and A. B. Diaz, *Bioresour. Technol.*, 2014, **167**, 1.

8 G. Yu, S. Yano, H. Inoue, S. Inoue, J. Wang and T. Endo, *Appl. Biochem. Biotechnol.*, 2014, **174**, 2278.

9 H. Amiri, K. Karimi and H. Zilouei, *Bioresour. Technol.*, 2014, **152**, 450.

10 I. Kim, B. Lee, J. Y. Park, S. A. Choi and J. I. Han, *Carbohydr. Polym.*, 2014, **99**, 563.

11 I. Kim, B. Lee, D. Song and J. I. Han, *Bioresour. Technol.*, 2014, **166**, 353.

12 X. D. Hou, J. Xu, N. Li and M. H. Zong, *Biotechnol. Bioeng.*, 2015, **112**(1), 65.

13 Y. L. Cha, J. Yang, J. W. Ahn, Y. H. Moon, Y. M. Yoon and G. D. Yu, *Bioprocess Biosyst. Eng.*, 2014, **37**, 1907.

14 S. M. Salehi, K. Karimi, T. Behzad and N. Poornejad, *Energy Fuels*, 2012, **26**, 7354–7361.

15 F. Gu, W. Wang, L. Jing and Y. Jin, *Bioresour. Technol.*, 2013, **142**, 218.

16 L. Yang, J. Cao, J. Mao and Y. Jin, *Ind. Crops Prod.*, 2013, **43**, 711.

17 S. G. Wi, I. S. Choi, K. H. Kim, H. M. Kim and H. J. Bae, *Biotechnol. Biofuels*, 2013, **6**, 166.

18 S. B. Kim, S. J. Lee, J. H. Lee, Y. R. Jung, L. P. Thapa, J. S. Kim, Y. Um, C. Park and S. W. Kim, *Biotechnol. Biofuels*, 2013, **6**, 109.

19 M. S. U. Rehman, I. Kim, K. H. Kim and J. I. Han, *Int. J. Environ. Sci. Technol.*, 2014, **11**, 543.

20 M. S. U. Rehman, M. A. Umer, N. Rashid, I. Kim and J. I. Han, *Ind. Crops Prod.*, 2013, **49**, 705.

21 Y. B. Huang and Y. Fu, *Green Chem.*, 2013, **15**, 1095.

22 Y. Jiang, X. Li, X. Wang, L. Meng, H. Wang, G. Peng, X. Wang and X. Mu, *Green Chem.*, 2012, **14**, 2162.

23 V. B. Kumar, I. N. Pulidindi and A. Gedanken, *J. Renewable Energy*, 2015, **78**, 141.

24 NREL, Chemical Analysis and Testing Laboratory Analytical Procedures (CAT), National Renewable Energy Laboratory, Golden.

25 T. H. Kim, *Korean J. Chem. Eng.*, 2012, **29**(1), 82.

26 I. N. Pulidindi, Development and exploitation of carbon materials from plant sources, Ph. D. Thesis, Indian Institute of Technology, Madras, 2009.

27 M. Sliwa, K. Samson, M. Ruggiero-Mikolajczyk, A. Zelazny and R. Grabowski, *Catal. Lett.*, 2014, **144**, 1884.

28 I. N. Pulidindi, B. B. Kimchi and A. Gedanken, *J. CO$_2$ Util.*, 2014, **7**, 19.

29 A. Victor, I. N. Pulidindi and A. Gedanken, *J. Environ. Manage.*, 2015, **162**, 215.

30 A. Victor, I. N. Pulidindi and A. Gedanken, *RSC Adv.*, 2014, **4**, 44706.

31 I. N. Pulidindi, R. H. Mariana, M. Patricia and A. Gedanken, *J. Fundam. Renewable Energy Appl.*, 2014, **4**(2), 143, DOI: 10.4172/2090-4541.1000143.

32 I. N. Pulidindi, B. B. Kimchi and A. Gedanken, *J. Renewable Energy*, 2014, **71**, 77.

33 D. J. Seo and A. Sakoda, *Biomass Bioenergy*, 2014, **71**, 47.

34 A. Das, T. Paul, A. Jana, S. K. Halder, K. Ghosh, C. Maity, P. K. D. Mohapatra, B. R. Pati and K. C. Mondal, *Ind. Crops Prod.*, 2013, **46**, 217.

35 A. Szabolcs, M. Molnár, G. Dibó and L. T. Mika, *Green Chem.*, 2013, **15**, 439.

36 K. A. Jug, S. H. Woo, S. R. Lim and J. M. Prak, *Chem. Eng. J.*, 2015, **259**, 107.

37 J. Wang, J. Xi and Y. Wang, *Green Chem.*, 2015, **17**, 737.

38 A. Onda, T. Ochi and K. Yanagisawa, *Green Chem.*, 2008, **10**, 1033–1037.

39 L. Pesaresi, D. R. Brown, A. F. Lee, J. M. Montero, H. Williams and K. Wilson, *Appl. Catal., A*, 2009, **360**, 50.

40 J. M. Fraile, E. Garcia-Bordeje and L. Roldan, *J. Catal.*, 2012, **289**, 73.

41 E. L. S. Ngee, Y. Gao, X. Chen, T. M. Lee, Z. Hu, D. Zhao and N. Yan, *Ind. Eng. Chem. Res.*, 2014, **53**, 14225.

42 Y. Peng, Z. Hu, Y. Gao, D. Yuan, Z. Kang, Y. Qian, N. Yan and D. Zhao, *ChemSusChem*, 2015, **8**, 3208.