Pre-treatment of biomasses using magnetised sulfonic acid catalysts

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Abstract

There is a significant interest in employing solid acid catalysts for pre-treatment of biomasses for subsequent hydrolysis into sugars, because solid acid catalysts facilitate reusability, high activity, and easier separation. Hence the present research investigated pre-treatment of four lignocellulosic biomasses, namely Switchgrass (*Panicum virgatum* L 'Alamo'), Gamagrass (*Tripsacum dactyloides*), Miscanthus (Miscanthus × giganteus) and Triticale hay (*Triticale hexaploide* Lart.) at 90°C for 2 h using three carbon-supported sulfonic acid catalysts. The catalysts were synthesized *via* impregnating p-Toluenesulfonic acid on carbon (regular) and further impregnated with iron nitrate *via* two methods to obtain magnetic A and magnetic B catalysts. When tested as pre-treatment agents, a maximum total lignin reduction of 17.73±0.63% was observed for Triticale hay treated with magnetic A catalyst. Furthermore, maximum glucose yield after enzymatic hydrolysis was observed to be 203.47±5.09 mg g^{-1} (conversion of 65.07±1.63%) from Switchgrass treated with magnetic A catalyst. When reusability of magnetised catalysts were tested, it was observed that magnetic A catalyst was consistent for Gamagrass, Miscanthus × Giganteus and Triticale hay, while magnetic B catalyst was found to maintain consistent yield for switchgrass feedstock. Our results suggested that magnetised solid acid catalyst could pre-treat various biomass stocks and also can potentially reduce the use of harsh chemicals and make bioenergy processes environment friendly.

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Introduction

Lignocellulosic biomass possesses distinctive advantage as one of the renewable sources of energy due to high carbohydrate content. In addition to being inexpensive, lignocellulosic biomass offers sustainability and a high potential to reduce greenhouse gas emissions (Perlack *et al*., 2005; Zhou *et al*., 2011). However, one of the main challenges in converting biomass into alcohols involves disruption of the complex structure of the biomass to obtain fermentable monomeric sugars (Kumar *et al*., 2009; Agbor *et al*., 2011). Usually, physico-chemical pre-treatments are required to ensure that biomass becomes accessible to enzymes for hydrolysis either *via* removal of lignin or solubilisation of hemicellulose (Mosier *et al*., 2005; Alvira *et al*., 2010). Several physical and chemical pre-treatments using heat, acids, bases, organic solvents and ionic liquids have been developed and studied extensively. Although, chemical pre-treatment techniques are attractive due to the higher reaction efficiency and excellent mass transfer capabilities (Guo *et al*., 2012), use of chemical agents leads to various environmental issues and also requires expensive unit operations on the downstream side of the process (Peña *et al*., 2014). Therefore, reusable pre-treatment agents that also minimise environmental impacts are required. One such option is to use solid acid catalyst as pre-treatment agent for biomass (Hara, 2010; Guo *et al*., 2012).

Utilising solid acid catalysts can potentially address some of these aforementioned challenges associated with liquid pre-treatments because solid acid catalysts allow for mild operating conditions and moderately high selectivity. In addition, solid acid catalysts allow for simple separation from products by vacuum filtration or magnetic separation (Lai *et al*., 2011; Guo *et al*., 2013; Peña *et al*., 2014). Further, the catalysts may be used repeatedly for the reaction without neutralisation, therefore decreasing energy consumption and waste (Zhou *et al*., 2011). Hence, there is a growing interest in developing solid catalysts for pre-treatment of biomass. Researchers have been exploring solid acid catalysts for pre-treatment of biomass streams. For example, Peña *et al*. (2014) reported glucose yield of 59% achieved from corn stover treated used propyl-sulfonic acid-functionalised nanoparticle catalyst at 160°C for 60 min followed by the addition of 2 mL of accelerase enzyme along with 2.5 g wet corn stover for 24 h hydrolysis. The study also reported that as pre-treatment temperature increased to 180°C, the yield of glucose increased reached the maximum of 90%. In a different study, macroalgae cellulose residue was treated used Dowex (TM) Dr-G8 solid catalyst followed by enzymatic hydrolysis where two enzymes were employed (45 FPU (filter paper unit)) g^{-1} of cellulase and 52 CBU (cellobiase unit) g^{-1} of β-glucosidase) to produce glucose yield at around 94% even after 5 reuses (Tan and Lee, 2015). Our group at North Carolina State University is also interested in synthesis and testing of solid acid catalysts for biomass processing. In the recent past, we explored niobium and carbon-supported sulfonic acid catalytic pre-treatment of biomasses (Ansanay *et al*., 2014, 2016). However, one of the problems associated with pre-treatment of biomass with solid

acid catalysts is separation of biomass from the catalysts as biomass and catalyst particles will be intimately mixed after pre-treatment. One possible approach to separate the catalyst from biomass is to employ magnetised catalysts and subsequently use magnetic force to separate the biomass from catalyst. However, there is little information on how these magnetic solid acid catalysts perform as pre-treatment agents for different biomass stocks. Therefore the present research was performed to systematically evaluate activated carbon-supported sulfonic acid catalysts for pre-treatment of Switchgrass (*Panicum virgatum* L 'Alamo'), Gamagrass (*Tripsacum dactyloides*), Miscanthus (Miscanthus × giganteus) and Triticale hay (*Triticale hexaploide* Lart.). Based on the surface chemistry of the solid acid catalysts, we hypothesise that activated carbon-supported sulfonic acid catalysts can pre-treat various biomasses for subsequent enzymatic hydrolysis.

Materials and methods

Lignocellulosic feedstock

Switchgrass (*Panicum virgatum* L 'Alamo'), Gamagrass (*Tripsacum dactyloides*), Miscanthus (Miscanthus × giganteus) and Triticale hay (*Triticale hexaploide* Lart.) were used as feedstocks in this research. Switchgrass was harvested in mid July 2011 from North Carolina State University Field Laboratory in Reedy Creek Road Raleigh, NC and subsamples were field cured for 3 days. Gamagrass variety was harvested towards the end of July 2012, and the postharvest samples were oven dried at 50°C for 72 h. Miscanthus was harvested from the Mountain Horticultural Crops Research and Extension Centre (Mills River, NC) in December 2011 and oven dried at 45°C for 72 h. The biomasses, Switchgrass, Gamagrass, and Miscanthus were ground to pass a 2 mm sieve. Furthermore, Triticale hay sample was collected from the field at Central Agricultural Research Centre of Montana State University. Due to the inherent properties of Triticale, the sample was ground to pass 1 mm sieve. All biomasses were placed in sealed plastic bags and stored until further use. The initial moisture contents were Switchgrass, Gamagrass, Miscanthus and Triticale hay 7.98, 6.54, 6.44 and 6.53%, respectively. In addition, the feedstocks were analysed for lignin and main carbohydrates content using standard methods (Sluiter *et al*., 2008) (Table 1).

Sulfonic solid acid catalysts preparation

Regular activated carbon-supported sulfonic acid catalyst

Catalyst used in this study was prepared by impregnating 60 g of activated carbon with p-Toluenesulfonic acid solution. p-Toluenesulfonic acid solution was prepared by mixing 67 g of p-Toluenesulfonic acid into 100 mL of deionized water. The activated carbon was soaked in the acid solution for 48 h, separated by filtration, followed by drying for 2 h at 105°C and calcination for 2 h at 250°C.

Magnetic activated carbon sulfonic acid catalyst

The magnetic activated carbon sulfonic acid catalyst was synthesized using two methods. In the first method, 30 g of activated carbon (fine) was stirred in a 50 mL deionized water solution containing 12 g of iron (III) nitrate, similar to the procedure described by Guo *et al*. (2013). The pH of the solution was adjusted to 10 by adding 3M of sodium hydroxide solution. The mixture was stirred at 200 rpm at room temperature for 24 h, after which the solid was filtered and calcined at 400°C under nitrogen flow for 3 h to obtain magnetically activated carbon. Subsequently, 20 g of magnetic carbon was mixed with an aqueous solution containing 20 mL deionized water, 13.5 g of p-Toluenesulfonic acid, and 20 mL mercaptoacetic acid for 24 h at room temperature at 200 rpm. At the end of 24-h period, 3M-sodium hydroxide solution was added until the pH of the slurry reached 7. At this stage, the solid was separated from the slurry and dried at 80°C for 12 h followed by calcination under nitrogen flow at 400°C for 3 h. Subsequently, 12 g of the solid was immersed into 20 mL of deionized water and 20 ml of hydrogen peroxide was added dropwise. The mixture was stirred at 200 rpm at room temperature for 12 h. The solid was separated and dried again at 80°C for 16 h to obtain the final product, which was named magnetic, activated carbon-supported p-Toluenesulfonic acid catalyst and named Magnetic A. In the second method of preparation, similar procedure (as above) was employed. However, granular sodium hydroxide was used instead of liquid. In addition, during the final step, 10 mL of hydrogen peroxide was added twice instead of dropwise addition. Subsequently, the mixture was dried (80°C) and calcined (16 h) to obtain of magnetic activated carbon-supported p-Toluenesulfonic acid catalyst and named Magnetic B.

Pre-treatment

Pre-treatment was performed in batch reactors placed on a hot plate capable of heating and mixing the reactor contents. Biomass and catalyst were mixed for 2 h at 90°C, stirred at 350 rpm. After pre-treatment, catalyst was separated from biomass. For regular catalyst pre-treatment, the separation was performed simple filtration followed by the solid wet biomass separation using vacuum filtration. For magnetised catalyst pre-treatment, catalysts particles were extracted *via* conventional long magnetic retriever followed by the separation of solid wet biomass using vacuum filtration. The catalyst was stored for subsequent use and pre-treated biomass was hydrolysed.

Sugar analysis

Soluble polysaccharide in the liquid hydrolysate after pre-treatment consisted of both simple sugars and sugars oligomer. Simple sugars such as glucose and xylose were measured *via* YSI 2950 Biochemistry Analyzer (YSI Incorporated, Yellow Springs, OH, USA). Typically, 1 mL of each sample was prepared in an Eppendorf tube followed by exposing the sample to the enzyme-immobilised sensor to obtain the concentrations of glucose and xylose in g L^{-1}. To determine total oligomer, all sugars oligomers

Table 1. Initial compositional analysis of four feedstock (dry basis).

Biomass/Composition	Glucan (%)	Xylan (%)	Acid soluble lignin (%)	Acid insoluble lignin (%)
'Alamo' Switchgrass	28.14±0.32	13.47±0.28	3.21±0.12	22.35±0.6
Gamagrass	30.18±0.64	12.88±0.59	2.56±0.04	22.17±0.48
Miscanthus × giganteus	37.04±0.21	11.79±0.10	1.54±0.06	21.92±0.33
Triticale hay	27.97±0.52	13.29±0.54	3.29±0.07	23.04±0.46

in the hydrolysate were expressed as monomeric sugar by adapting 4% acid hydrolysis NREL procedures (Sluiter *et al*., 2006) as below:

Liquefaction = Total oligomer + CSS (1)

Simple sugars = Glucose (2)

Carbohydrate simple sugar (CSS) = Glucose × 0.9 (3)

Total oligomer = (Glucose × 0.9) + (Xylose × 0.88) (4)

In the present context (Eqs. 1-4), liquefaction referred to a mixture of total oligomers and carbohydrate simple sugar (glucose), while total oligomers consisted of short polymers including xylose oligomer (from xylan) and glucose oligomer (from glucan).

Enzymatic hydrolysis

Enzymatic hydrolysis was performed at 50°C for 72 h (150 rpm). Biomass samples (1 g dry basis) were mixed with 20 fpu of Cellic Ctec 2 (Novozymes, NA) (activity ~ 119 fpu/mL), corresponding to 3.5% w/w (g protein enzyme g^{-1} dry biomass), and 50 mM of citric acid monohydrate buffer (pH=5.0) to bring the total volume of 20 mL. To avoid microbial growth, 40 µg mL^{-1} of tetracycline was added as an antibiotic agent. After 72 h, slurry samples were cooled down to 4°C and kept refrigerated until further analysis.

Leaching tests

To determine the extent of leaching of iron from the magnetic catalysts into the solution, leach tests for the liquid hydrolysate and pre-treated samples were performed *via* Perkin Elmer 3100 Atomic Absorption Spectroscopy. Final concentrations of iron adhered to the solid was reported in mg/g while the iron in the liquid hydrolysates was expressed in mg L^{-1}.

Statistics analysis

All experiments were performed in triplicate. The data were analysed *via* SAS (SAS Institute Inc., Cary, NC, USA) Proc GLIMMIX method with Tukey adjustment. Data were analysed to study the effect of 3 different catalysts (regular, magnetic A and magnetic B) on 4 different biomasses (Switchgrass, Gamagrass, Miscanthus × giganteus, and Triticale hay). In addition, effect of reusability of magnetic catalysts was also tested by analysing the data for magnetisation procedure (2 levels: Magnetic A and Magnetic B), feedstock (4 levels: Switchgrass, Gamagrass, Miscanthus × giganteus, Triticale hay) and reuse (2 levels: Reuse 1 and Reuse 2).

Results and discussion

Effect of regular and magnetic catalytic pre-treatment on sugar and lignin

After the pre-treatment, the magnetic catalysts were easily separated from biomass slurry *via* simple magnetic bar separators. Data for liquefaction, total oligomer and simple sugar of glucose for all biomasses tested are presented in Figure 1. It appeared that for Triticale hay regular and magnetic A catalysts facilitated solubilisation of carbohydrate (Figure 1A and B) corresponding to total sugar yields of 48.87±1.42 mg g^{-1} and 53.37±0.58 mg g^{-1} respectively. Wang *et al*. (2012) reported the use of perfluoroalkylsulfonic (PFS) and alkylsulfonic (AS) acid-functionalised magnetic nanoparticles for pre-treatment of wheat straw and attempted to solubilise hemicellulose. Their results show that after 24-h reaction at lower temperature (80°C), 3.5±0.1% and 1.0±0.2%, of monosaccharides from xylan were obtained from the two catalysts. However, at higher temperature (160°C for 2 h) xylose yields were observed to be 0.3% and 1.2% from PFS and AS catalysts respectively (Wang *et al*., 2012). In addition, Tan and Lee (2015) reported 0.77 g glucose (glucose yield of 0.77%) in the pre-treatment liquid, when 100 g of macroalgae cellulosic residue was treated using Dowex (TM) Dr-G8 solid acid catalyst.

In comparison, the catalysts synthesized in our study were able to hydrolyse cellulose (glucan). Particularly, Magnetic B catalyst when used to pre-treat Triticale hay provided the highest glucose yield of 33.62±0.08 mg g^{-1} (glucose yield of 10.82±0.02%) and maximum xylan oligomer of 1.79±0.2 mg g^{-1} in the liquid treatment, probably because smaller particles and the resulting higher surface area of Triticale (1-mm) may have allowed for effective enzymatic hydrolysis. However, the glucose yields obtained from other biomasses, such as Switchgrass, Gamagrass, and Miscanthus, using Magnetic B were substantially lower perhaps due to inherent differences in biomass structures.

The data was also analysed to investigate the effectiveness of these catalysts to disrupt lignin in the biomasses. As presented in

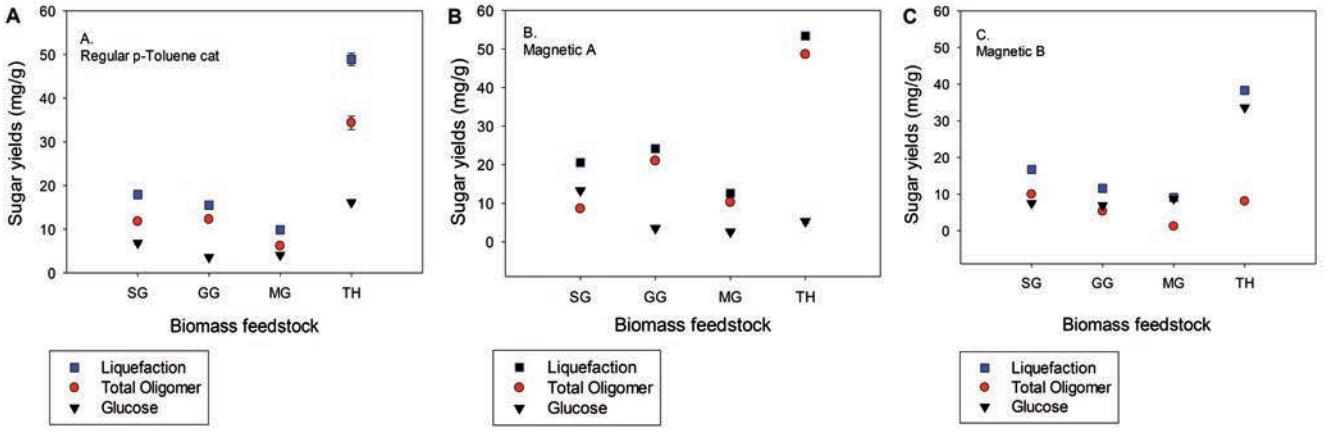

Figure 1. Sugars in the liquid after pretreatment with (A) regular catalyst, (B) Magnetic A and (C) Magnetic B catalyst. SG, Switchgrass; GG, Gamagrass; MG, Miscanthus × giganteus; TH, Triticale hay.

Table 2, the highest reduction in total lignin was found in Triticale hay treated with magnetic A catalyst (17.73±0.63%) followed by regular catalyst (15.11±0.86%) probably due to smaller particle sise. Our results are similar to Chen *et al*. (2007) who reported the use of 0.5-2% alkali to obtain a 10.16-24.06% reduction in total lignin for Triticale hay.

Effect of regular and magnetic catalysts on the enzymatic hydrolysis stage

As expected, each biomass responded to pre-treatment in different way due to inherent dissimilarities in biomass structures and compositions. The surface reaction between biomass and catalyst may have proceeded differently depending on the surface chemical and physical structure of lignin and cellulosic portion of each biomass. As presented from Figure 2, the glucose yields obtained after hydrolysis of switchgrass pre-treated with regular and magnetic B catalysts were similar (P=0.93).

However, for magnetic A, the yields were significantly higher than the yields obtained from regular and magnetic B catalysts (P<0.05). For Gamagrass there was no significant difference between the glucose yields for all three catalysts tested (P>0.1). Meanwhile, glucose yields for triticale hay treated with regular and magnetic A catalyst were not significantly different (P>0.05). Overall the maximum glucose yields (for all biomasses) ranged between 25.3±0.14% and 65.07±1.63% with Switchgrass providing with maximum glucose yields of 65.07±1.63%. The yields observed from Miscanthus were between 25.3±0.14% - 34.55±3.28%. In comparison, Panneerselvam *et al.* (2013b) reported a maximum glucose yield (after enzymatic hydrolysis) of 13-26% (60-80 mg g^{-1}) when Miscanthus × giganteus was pre-treated with 40-58 mg L^{-1} ozone using uniflow and reserve flow configurations. In addition, Miscanthus × giganteus treated with alkali followed by enzymatic hydrolysis was able to reach glucan conversion of 32.8±3.49% (Panneerselvam *et al*., 2013a). Similarly Gamagrass produced glucose yields between 160.4-174.33 mg g^{-1} (47.84±0.26% - 51.99±4.21%; Figure 2) after enzymatic hydrolysis with maximum yield that was obtained from Gamagrass treated with regular catalyst. The glucose yields obtained in our research are slightly lower than those reported by other researchers in literature. For example, Xu *et al*. (2012) reported the glucose yields of 215.5-270.5 mg g^{-1} (maximum glucan conversion of 67.7%) after enzymatic hydrolysis from many varieties of Gamagrass treated with 1% NaOH for 60 min at 121°C. It may be noted that when the liquid and pre-treated biomass samples were analysed *via* atomic absorption spectroscopy, it was found that 0.4-6 mmol L^{-1} and 4.5-7 mg g^{-1} of iron was present in liquid and pre-treated biomass respectively, suggesting that iron was leaching into the system due to agitation. Despite reports by Tejirian and Xu (2010) and Chen and Fu (2013) that iron may inhibit enzymatic hydrolysis our data suggested that Cellic Ctec2 can still performed reasonably well. We theorize that the yields could be enhanced by employing a surfactant to minimise the effects of iron on enzymatic hydrolysis as proposed by Chen and Fu (2013). In addition, the amounts of xylose also increased between 11.48±3.66 mg g^{-1} - 46.88±0.38 mg g^{-1} after enzymatic hydrolysis even without the addition of xylanase (Table 3).

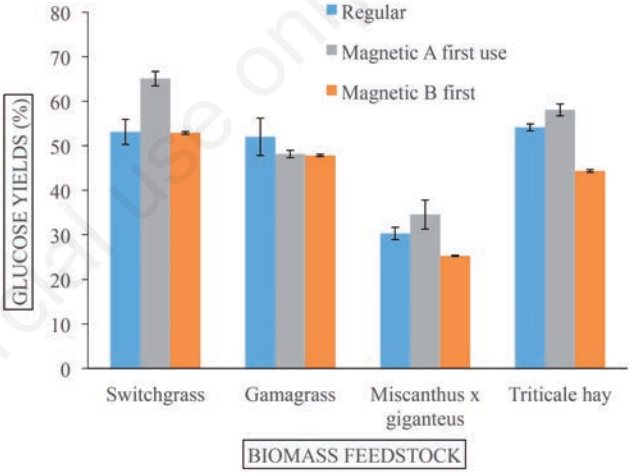

Figure 2. Glucose yields obtained after enzymatic hydrolysis of four different biomasses using three sulfonic acid catalysts.

Table 2. Total lignin reduction after pretreatment using sulfonic acid catalysts.

Biomass feedstock	Total lignin reduction (%) after pretreatment used activated carbon supported p-Toluenesulfonic acid catalysts			P-values
	Regular	Magnetic A	Magnetic B	
Switchgrass	10.02±0.95	10.75±1.84	9.50±1.02	0.972
Gamagrass	9.83±0.69	13.02±0.19	9.27±0.36	0.005
Miscanthus × giganteus	9.19±0.63	11.76±0.82	9.21±0.13	0.046
Triticale hay	15.11±0.86	17.73±0.63	12.25±0.34	0.003

Table 3. Xylose produced after enzymatic hydrolysis from four biomasses treated using p-Toluenesulfonic acid catalysts.

Biomass feedstock	Xylose produced (mg g^{-1} dry biomass)					P-values
	Regular	Magnetic A first use	Magnetic A second use	Magnetic B first use	Magnetic B second use	
Switchgrass	30.00±1.86	37.00±1.80	23.27±1.27	20.93±0.48	28.33±0.18	<0.001
Gamagrass	22.34±2.17	24.80±1.50	19.94±5.62	19.85±0.07	12.30±1.46	0.093
Miscanthus × giganteus	12.35±0.85	13.85±0.24	15.93±0.90	11.48±3.66	13.25±0.57	0.483
Triticale hay	35.60±1.42	46.88±0.38	45.53±0.29	29.80±0.23	33.27±0.70	<0.001

Effect of reusability of magnetic catalysts on sugars yields produced at enzymatic hydrolysis

The data suggested that when Magnetic A catalyst was reused twice to pre-treat biomasses, the glucose yields after hydrolysis of Gamagrass, Miscanthus × giganteus and Triticale hay were within 5% difference (Figure 3). Analysis of data using GLIMMIX procedure suggested that glucose yields (after enzymatic hydrolysis) from Gamagrass, Miscanthus × giganteus, and Triticale hay treated with magnetic A catalyst were not significantly different between first and second uses ($P>0.05$). In addition, the glucose yield for Switchgrass treated with magnetic A was found to decrease by 11.8% after first use.

The trend exhibited by Magnetic B, however was different. The data indicated that when Magnetic B catalyst was used to pre-treat biomasses, the glucose yields after hydrolysis of miscanthus, and triticale hay increased significantly when the catalyst was reused for the second time. However, the hydrolysis yields for switchgrass was similar for both reuses (53.86%, $P=0.42$). Recently, Tan and Lee (2015) reported the use of solid acid catalyst (Dowex (TM) Dr-G8) to treat macroalgae cellulosic residue at 120°C for 30 min followed by enzymatic hydrolysis for 30 h using 45 FPU g^{-1} of cellulase and 52 CBU g^{-1} of β-glucosidase. The authors observed a glucose yield of 94% even after fifth reuse of the catalyst. Although our glucose is lower when compared to Tan and Lee (2015), it may be noted that the feedstock employed by the authors, *i.e.*, macroalgae cellulosic residue did not contain lignin.

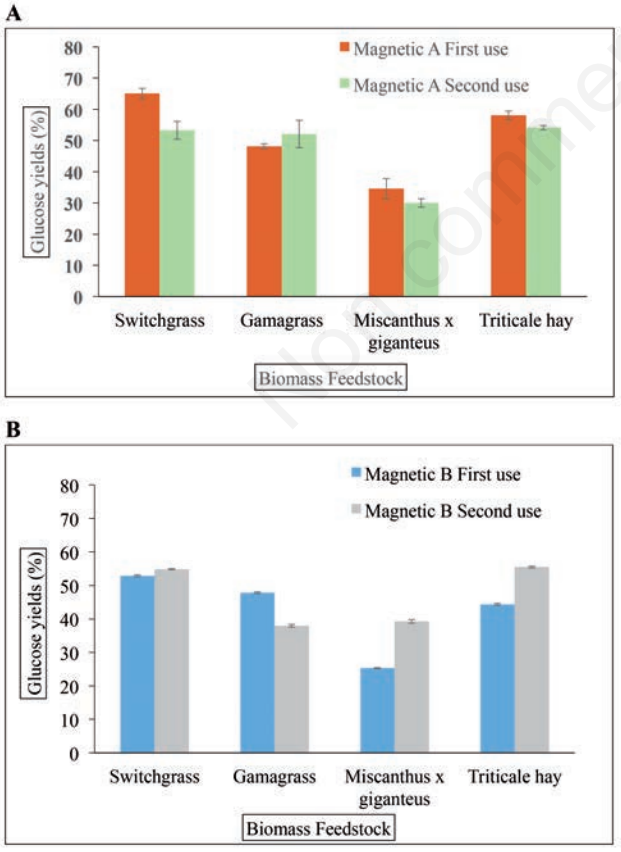

Figure 3. Glucose yields obtained from reusability studies using (A) Magnetic A and (B) Magnetic B catalysts.

In addition, the enzyme loading in our study was is lower than that of Tan and Lee (2015). Further, we also observed xylose in our research (Table 3). Overall, our results suggest that Magnetic A exhibited consistent activity for Gamagrass, Miscanthus × giganteus and Triticale hay while Magnetic B was observed to be consistent for Switchgrass. In addition, possibility that accumulated iron in wet biomass, which may also have affected the yield. Hence, additional studies on employing surfactants and other agents to minimise the effects of iron are suggested.

Conclusions

Magnetic sulfonic acid catalysts were found to serve as pre-treatment agents for real biomass streams and can provide similar yield of sugars compared with regular catalyst. Although xylose was detected in the liquid after enzymatic hydrolysis, adding xylanases might help in improving the formation of 5 carbon sugars. Although, reusability of magnetic catalysts was tested, future studies are needed to enhance the activities. Magnetic acid catalysts are expected to alleviate problems associated with separation of the catalysts from pre-treated biomass thereby making biomass pre-treatment processes more practical.

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