



Cite this: *Green Chem.*, 2017, **19**, 2129

Received 23rd February 2017,
Accepted 13th April 2017

DOI: 10.1039/c7gc00574a

rsc.li/greenchem

Carbon dioxide as a pH-switch anti-solvent for biomass fractionation and pre-treatment with aqueous hydroxide solutions†

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Rice husks (or rice hulls) pre-treated with aqueous potassium hydroxide solutions showed excellent glucose yields during enzymatic saccharification. CO₂ addition to the hydroxide solutions precipitated the dissolved rice husk silica as a nanoporous powder, while Ca(OH)₂ addition regenerated the hydroxide solution and precipitated the dissolved lignin. Fractionation of the biomass was thus achieved using CO₂ addition as a reversible pH-switch, and the hydroxide could be repeatedly recycled while maintaining biomass pre-treatment and fractionation efficacy.

Inedible lignocellulosic biomass represents a prime candidate for biofuel production.¹ However, the inherent recalcitrance of this biomass to (bio)chemical processing necessitates chemical pre-treatment.² This pre-treatment adds significantly to the cost,^{2a} and techno-economic analysis has demonstrated that other chemical constituents present in the biomass (beyond carbohydrates) ideally need to be utilised as value-added materials for such processes to be economically viable.³ Bio-based products achieved *ca.* 10% penetration into the USA chemical market in 2015, and by 2025 this is expect to rise to *ca.* 22%;⁴ full use of the chemical constituents of biomass are required from both economic and sustainability standpoints.

Rice husks (or rice hulls) are an agricultural crop waste; they are produced on a massive scale worldwide,⁵ and are readily supplied in easily handled *ca.* 8 mm by 2 mm pieces.⁶ As a lignocellulosic biomass, they are composed (on a dry basis) of *ca.* 38 wt%, cellulose, 24 wt% hemicellulose, 20 wt% silica and 19 wt% lignin.⁷ The cellulose and hemicellulose represent sources of fermentable sugars,^{2a} lignin is a potential source of aromatic feedstock chemicals⁸ and silica has numerous applications,⁹ *e.g.* from solar technology to toothpaste.

High silica content in biomass is associated with significantly reduced digestibility,¹⁰ excessive teeth wear,¹¹ and even machine wear during up-stream mechanical process.^{5b} As such, rice husks can be considered 'zero calorie' waste, since their high silica content (15–25 wt%)^{5b,7,12} is *ca.* 40 fold higher than the typical limit for livestock feed.

Due to a lack of viable alternatives, rice husks are typically disposed of or burned.¹² The resulting silica-rich ashes cause extensive environmental problems.^{9,13} Attempts to use the rice husk ash for other applications, *e.g.* as water glass for construction, are hindered by the relatively low purity of the silica, containing inorganic contaminants such as metals and phosphates.¹⁴

Carbon dioxide (CO₂) is the main waste product of combustion, and as a greenhouse gas its emission is of great environmental concern. CO₂ in the form of supercritical liquid has been employed in many applications, such as a solvent for extracting herbal ingredients in the food industry,¹⁵ anti-solvent for protein formulation in biosciences¹⁶ and solvent/anti-solvent for chemical reactions¹⁷ and material synthesis,¹⁸ to name a few.

CO₂ has recently been employed in biomass processing, *e.g.* through CO₂-explosion,¹⁹ supercritical CO₂ extraction from biomass²⁰ and the supercritical CO₂-driven precipitation of dissolved cellulose²¹ and lignin.²² CO₂ has also been reacted with bases to form 'switchable ionic liquids', which can be employed for, *e.g.* cellulose dissolution²³ and biomass fractionation.²⁴ Notably, these processes typically involve high pressures and temperatures, and have been reviewed elsewhere.²⁵

The pre-treatment of recalcitrant lignocellulosic biomass with aqueous alkaline solutions represents a method to significantly improve downstream treatments. For example, pre-treatment of switchgrass with aqueous sodium hydroxide (NaOH) improves the resulting enzymatic sugar yield.²⁶ This results in a lignin-rich alkaline solution ('black liquor') that can be reused for further biomass pretreatment.²⁷ The effectiveness of NaOH solutions can be further supplemented by addition of CaO.²⁸ Alkaline treatment enhances yields from downstream (bio)chemical processes primarily due to partial lignin removal and significant structural modifications.²⁸

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† Electronic supplementary information (ESI) available: Materials and methods, and Fig. S1–4. See DOI: 10.1039/c7gc00574a



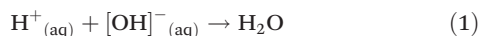
Aqueous alkaline solutions are also able to pre-treat rice husks effectively prior to chemical (*e.g.* acid) or biochemical (*e.g.* cellulase) saccharification,⁷ largely due to their ability to remove silica, in addition to lignin removal and structural changes. A recent cation study has investigated concentrated alkali solutions for pre-treating rice husks, with cations ranging from the relatively small lithium cation up to the relatively large tetrahexylammonium cation.⁶ Excessive interactions with cellulose were found to be detrimental, while the above noted biomass alterations were still key. Lithium hydroxide solutions (with *ca.* 11 to 23 equivalents of water) were found to be optimum, although sodium and potassium hydroxide solutions maintained 70–95% of the activity while also being more viable economically.⁶

We have therefore employed aqueous sodium hydroxide (NaOH) and potassium hydroxide (KOH) in this study, and investigated using CO₂ to achieve fractionation of the rice husks, enhance enzymatic digestibility, recycle of the hydroxide and isolation of CO₂ as a solid product. The full Materials and methods section can be found in the ESI.[†]

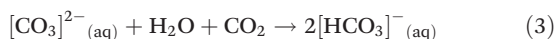
While the chemistry behind the reaction with [OH][−] to CO₂ to form [CO₃]^{2−} and [HCO₃][−] is standard chemistry, we carried out the experiments firstly to ensure that the inter-conversions happen in a timely manner, and secondly to ensure that it is possible at the high concentrations^{6,7} required for effective rice husk pre-treatment. The back-conversion of carbonates to [OH][−], while simultaneously removing CO₂ as a solid, was also investigated. This involved the addition of calcium hydroxide (Ca(OH)₂), to yield calcium carbonate (CaCO₃) as an innocuous by-product. Ca(OH)₂ is abundantly available, *e.g.* it is the main product upon heating food waste such as egg shells and mollusc shells.²⁹

Proof-of-concept pH switches

A solution of NaOH (0.34 M) was titrated using HCl (Fig. 1). As expected, it was initially highly alkaline and displayed only one step in its titration curve, as shown by eqn (1).



CO₂ is readily available in solid form as dry ice. The stoichiometric quantity of CO₂ (two CO₂ per [OH][−]) was weighed out as dry ice. This dry ice was then added slowly to the NaOH solution, in order to achieve the two-step reaction shown in eqn (2) and (3);



Titration of the solution with HCl demonstrated a two-step curve (Fig. 1) indicative of a mixture of Na₂CO₃ and NaHCO₃. Conversion was therefore near-quantitative; it should be noted that this was all performed at room temperature and open to the atmosphere, hence a small amount of CO₂ was lost. Addition of an excess of CO₂ resulted in a single titration

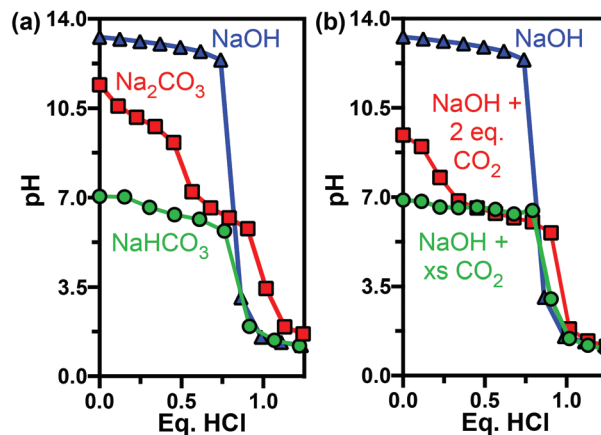


Fig. 1 Titration curves for (a) 0.34 M of (▲) NaOH, (■) Na₂CO₃ and (●) NaHCO₃ compared with (b) 0.34 M NaOH, and this solution after the addition of (■) two equivalents of CO₂ and (●) more than two equivalents of CO₂ (as dry ice), highlighting complete conversion from NaOH to NaHCO₃.

process entirely consistent with complete conversion to NaHCO₃ (Fig. 1).

The conversion of NaHCO₃ back to NaOH was also investigated, using solid Ca(OH)₂. The solubility of Ca(OH)₂ in water is relatively low (<2 g L^{−1}), hence an excess of solid Ca(OH)₂ was added in order to achieve the metathesis shown in eqn (4);



Metathesis was observed to be extremely rapid with associated heat generation. Some of the Ca(OH)_{2(s)} dissolved and a finer white precipitate was formed. The isolated solid was confirmed to be composed of a mixture of CaCO₃ and excess Ca(OH)₂, while the titration curve of the treated solution was virtually identical to that of pure NaOH. These observations confirmed the facile inter-conversion between [OH][−] and [HCO₃][−] made possible by CO₂ and Ca(OH)₂, respectively. This could be achieved using both NaOH and KOH.

Solutions more concentrated than 0.34 M [OH][−] are required for effective biomass pre-treatment (at room temperature). With increasing alkali concentration, the direct addition of dry ice eventually became unfeasible due to the relative quantity of solid to liquid. However, by placing the dry ice in a sealed container at room temperature, and allowing the evolved CO₂ to bubble through the hydroxide solution *via* an immersed tube, efficient and complete conversion to [HCO₃][−] could be reproducibly achieved, within an hour for *ca.* 5 M [OH][−] samples.

Inherent recalcitrance and the need for fractionation

The direct addition of as-received rice husks to a standard cellulase-based enzymatic broth yielded no detectable sugar



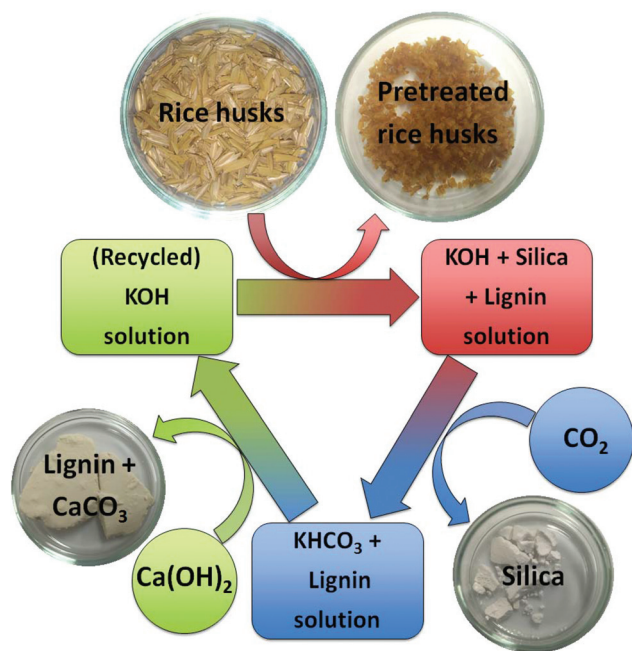


Fig. 2 Three-step rice husk pre-treatment, fractionation and recycling process.

release, confirming the extreme recalcitrance of the rice husks. Stirring the rice husks in water for three days before subjecting them to enzymatic hydrolysis resulted in only extremely low sugar yields (22 ± 1 mg glucose per g of rice husks).

Following biomass pre-treatment, the dilution or addition of a solvent to the treatment solution is commonly employed to assist in separation.³⁰ The direction addition of CO_2 was benchmarked against the addition of methanol as an anti-solvent, and the enzymatic hydrolysability of the rice husks evaluated. However, one-pot treatment in the alkali solution then CO_2 or methanol addition could not raise the enzymatic glucose yields above 19 ± 5 mg g⁻¹, largely due to visible silica deposition over the surface of the pre-treated rice husks. This demonstrated that the pre-treated biomass had to be isolated prior to any attempt to recycle the hydroxide solution, and prompted the three-fold fractionation and recycle route displayed in Fig. 2. These three steps are discussed separately below, and full descriptions of each process can be found in the Materials and methods section in the ESI.[†] A combined mass-balance figure and flow chart can be found in the ESI as Fig. S1.[†]

Step 1: Pre-treatment and fractionation

Semi-optimised conditions involved the room temperature pre-treatment of 2.5 wt% rice husk in 2.4 M KOH for 2 h, followed by physical separation of the undissolved material from the supernatant. Longer treatment (up to 8 h) reduced the glucose yield, as shown in the ESI in Fig. S2;[†] this is attributed to gradual removal of the alkaline soluble hemicellulose fraction.

Higher glucose yields were achieved after 48 h or more pre-treatment, but only *ca.* 17% higher than that obtained after 2 h pre-treatment. Precipitation issues in Step 2 (discussed below) necessitated the use of KOH over NaOH, and a KOH concentration not exceeding 2.4 M.

After 2 h pre-treatment, *ca.* 72% of the initial mass of rice husk was recovered. The composition of the recovered, pre-treated rice husks was found to be (on a dry basis) *ca.* 80 wt% holocellulose, *ca.* 7 wt% silica and *ca.* 13 wt% lignin. This is from an initial composition of 62 ± 6 wt% holocellulose, 20 ± 2 wt% silica and 19 ± 2 wt% lignin.

The pre-treated rice husks (shown dried in the photo insert in Fig. 2) were physically isolated by filtration, rinsed three times with water and enzymatically hydrolysed. Treatment of the rice husks in this manner could reproducibly yield *ca.* 329 ± 6 mg glucose per g of the starting mass of the rice husks (or 354 mg per g on a dry basis), confirming effective disruption of the rice husk. Acid hydrolysis optimised for non-silica containing lignocellulosic biomass³¹ could only release 172 ± 3 mg g⁻¹ from the same batch of rice husks,⁷ highlighting the superiority of the hydroxide route in pre-treating the silica-rich rice husks. Similar KOH-treatments of rice husks could not be found in the literature, but KOH treatment of entire rice plants followed by cellulase hydrolysis resulted in 405 ± 4 mg reducing sugars per g of dry rice plant; this is consistent with the higher carbohydrate content of the plant.³²

Step 2: CO_2 -treatment and silica recovery

Addition of CO_2 as an anti-solvent to the pre-treatment liquor was semi-optimised; use of NaOH was found to be less than optimal due to the significantly lower solubility of NaHCO_3 . The higher solubility of KHCO_3 avoided this and prompted its further use, although only at a maximum concentration of 2.4 M. This is equivalent to 22.5 mol H_2O per mol KOH, or *ca.* 96 mol% H_2O .

Addition of sufficient CO_2 to 2.4 M KOH could convert the system to $[\text{HCO}_3]^-$, and addition of CO_2 to the dark brown pre-treatment liquor also resulted in the precipitation of a significant quantity of white flakes. The white precipitate was completely soluble in tetramethylammonium hydroxide, and ICP-MS analysis found only Si and K; after one recycle of the KOH solution using $\text{Ca}(\text{OH})_2$ (Step 3, discussed later) the precipitated silica was consistently *ca.* 80 wt% Si, 17 wt% K and 3 wt% Ca. Silica gel prepared by the alkaline dissolution of rice husk ash followed by neutralisation typically contains Na, K and Ca;³³ mineral leaching steps can extensively remove these contaminants.³⁴ Significantly, the other contaminants common to rice husk ash such as iron, magnesium, manganese, sulfur and extensive phosphate¹⁴ were all below detection limits. TGA analysis of the dried precipitate revealed *ca.* 2 wt% mass loss consistent with water of hydration, and *ca.* 6 wt% consistent with carbonate decomposition. Stirring in 0.1 M HCl for 18 h resulted in the removal of all residual



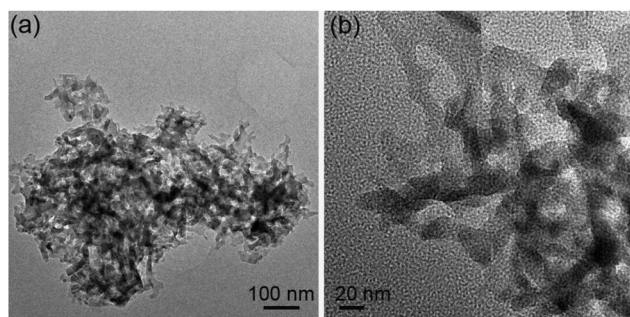


Fig. 3 (a) Low- and (b) high-magnification TEM images showing the 3D porous structure of the CO₂-precipitated rice husk silica particles.

carbonates, as well as the K and Ca, to yield *ca.* 100% pure silica (confirmed by TGA and ICP-MS) as a fine white powder, as shown in the photo insert in Fig. 2.

The resulting CO₂-precipitated, acid-washed silica could be readily re-suspended in water. Transmission electron microscopy (TEM) characterisation showed that the acid-washed silica was composed of 3D, porous nanostructures in the size range of 400–800 nm (Fig. 3a). High-magnification TEM observations showed that these structures were made up by relatively uniform ribbon-like components of ~20 nm in diameter that had formed into 3D networks (Fig. 3), rendering the sample highly porous. The entire structure was amorphous in nature, and qualitatively similar to colloidal/precipitated silica.³⁵

Step 3: KOH regeneration, lignin removal and recycle

The regeneration of alkali metal hydroxides from alkali metal carbonates using Ca(OH)₂ (the so-called ‘causticisation reaction’) is a well-studied reaction, and used on a huge scale in the Kraft pulping industry.³⁶ As an equilibrium process, it typically has a maximum efficiency of *ca.* 90% (in the absence of sulfides).^{36b} Addition of Ca(OH)₂ powder to the 2.4 M KHCO₃ solution, post-rice husk treatment and CO₂ addition, resulted in facile metathesis to reform *ca.* 2.4 M KOH. Although a relatively large amount of powder was required, the liquid–solid separation was easily accomplished.

Having completed the whole cycle shown in Fig. 2, recycle was easily achieved. One solution was therefore utilised in six complete recycles. A fixed biomass loading was used (2.5 wt% rice husks) and the KOH solution (initially 40 mL) was not treated in any manner between cycles beyond what is shown in Fig. 2, *i.e.* additional KOH or water was not added, nor made more concentrated by water evaporation. However, due to some natural volume reduction through the cycles, each (re) cycle was performed on a slightly smaller scale.

Each cycle involved the addition of excess Ca(OH)₂ powder, and recovery of a CaCO₃/Ca(OH)₂ powder. Additionally, as the cycles progressed the CaCO₃/Ca(OH)₂ powder was noted to be off-white (photo insert in Fig. 2). Ca(OH)₂ will dissolve in

dilute HCl to form a clear solution, while dissolution of the recovered CaCO₃/Ca(OH)₂ in dilute HCl resulted in significant brown solid remaining and the solution being dark brown–yellow (ESI, Fig. S3†). UV-Vis analysis of the solution confirmed the characteristic presence of acid-soluble lignin in the solution, and the solid was determined to be acid-insoluble lignin, as per NREL guidelines.³¹ The acid-soluble and acid-insoluble lignin were present in a *ca.* 20 : 80 ratio by mass, and the total lignin recovered corresponded to 64 ± 4% (by mass) of the lignin that was removed from the rice husks.

The lignin content of the liquor was therefore monitored as a function of recycle stage and number. Fig. 4(a) displays UV-Vis spectra of the KOH solution after pre-treating rice husks, displaying the two peaks at *ca.* 300 nm and *ca.* 325 nm that are characteristic of lignin dissolved in aqueous alkaline solution.^{7,37} After regeneration of the CO₂-treated sample with excess Ca(OH)₂ powder, the recovered KOH-solution clearly had a lower lignin content. Fig. 4(b) displays the absorbance across the six recycles. The lignin absorbance peak doubled after the second recycle, but gradually reached a plateau with repeated recycling, indicating that the lignin level in the liquor was approaching saturation, although it was still gradually increasing post-CO₂-treatment.

Therefore, lignin was being extracted from the rice husks by the KOH solution and accumulating through the recycles, with some precipitated by Ca(OH)₂ treatment of the lignin-containing KHCO₃ solution; this potentially reached a self-limiting value by the 6th cycle.

Evaluation of pre-treatment effectiveness as a function of recycles

The percentage of lignin remaining in the pre-treated rice husks was quantified using a standard procedure,³¹ and was

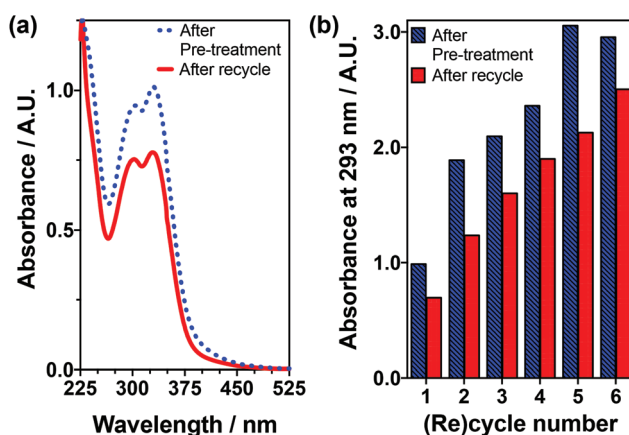


Fig. 4 (a) UV-Vis spectra of 2.4 M KOH (---) after pre-treating 2.5 wt% rice husks for 2 h, highlighting the dissolving lignin, and (—) after being recycled once, highlighting reduced lignin content after Ca(OH)₂ treatment. (b) Absorbance at 293 nm as a function of (re)cycle number, (blue, dashed) directly after pre-treatment of rice husks and (red, solid) after Ca(OH)₂ re-generation. All solutions were diluted 30-fold with fresh 2.4 M KOH before measurement.



found to be within consistent within error ($32 \pm 13\%$ removed) across the recycles, with no systematic trend. UV-Vis analysis with a fresh KOH solution demonstrated that the lignin content of the alkaline solution doubled after stirring for 120 h instead of 2 h (ESI, Fig. S4†) but this only correlated with a *ca.* 17% increase in the overall glucose hydrolysis yield (*cf.* ESI, Fig. S2†), *i.e.* removal of *ca.* 32% of the lignin was sufficient.

The quantity of silica removed was also largely insensitive of recycle number, with $59 \pm 5\%$ consistently removed. However, the amounts of (crude) silica precipitated by CO_2 addition varied with recycle number; this is shown graphically in Fig. 5 as % of silica relative to the amount initially present in the rice husks. From the 3rd to 6th recycles, *ca.* 59% silica was dissolving while *ca.* 40% of the introduced silica (*ca.* 68% of the dissolved silica) was recovered at the CO_2 addition stage. Therefore Si is likely still accumulating in the system, as was found to be the case for lignin. Some $\text{Ca}(\text{OH})_2$ was also potentially carried onto the next cycle, although it has been noted that combinations of NaOH and $\text{Ca}(\text{OH})_2$ can be more effective at biomass pre-treatment than NaOH alone.²⁸

Finally, the enzymatic hydrolysis of the pre-treated rice husks was evaluated as a function of recycle number; the resulting glucose yields per gram of starting rice husk *vs.* recycle number is plotted in Fig. 5. The highest glucose yield was obtained for the pristine KOH solution (*ca.* 325 mg g^{-1}), while the yields from cycles 2 to 6 were lower but relatively consistent (*ca.* 275 mg g^{-1}). The silica yield and glucose yield show a degree of correlation, with the pristine KOH able to achieve the best pre-treatment and fractionation; the accumulation of residual components (silica, lignin and hemicellulose) in the solution had a initial minor detrimental effect upon both the pre-treatment and fractionation processes, but was nevertheless consistent across 5 subsequent recycles.

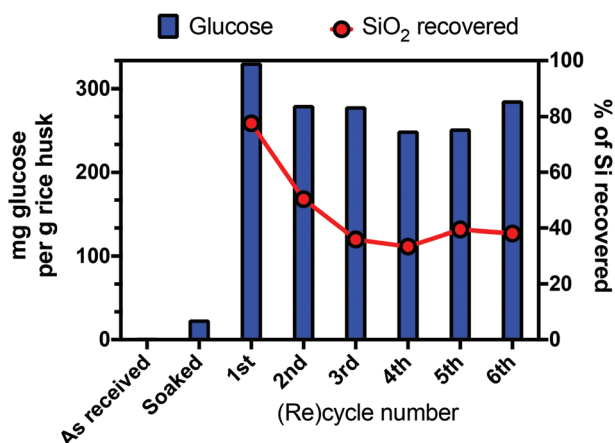


Fig. 5 Glucose yield by enzymatic hydrolysis (after 48 h, bar chart) and the % of introduced silica recovered by CO_2 addition (symbols), across six rounds of KOH pre-treatment (2.4 M KOH, 2 h pre-treatment time). As received rice husks yielded no glucose, while soaking in water for 72 h only boosted the glucose yield to *ca.* 22 mg g^{-1} .

The fate of the hemicellulose in the rice husks was not evaluated in this preliminary study. However, hemicellulose is typically soluble in aqueous alkaline solutions, even at room temperature.³⁸ Therefore it is expected to have been partially removed during pre-treatment, and likely accumulated in the hydroxide solution. Hemicellulose can be precipitated by more extensive acidification than we employed here,³⁹ and further work is required in order to ensure isolation of the hemicellulose can be achieved.

Several variables were fixed this preliminary study, such as a biomass loading of 2.5 wt% during pre-treatment at *ca.* 293 K, and 20 mg pre-treated wet biomass per ml enzymatic broth during enzymatic hydrolysis with 25 FPU g^{-1} cellulase (as per a recommended protocol³¹). High concentrations of KOH were used to ensure effective pre-treatment at room temperature. Moving to higher temperatures during pre-treatment involves additional energy expenditure, but could allow equivalent pre-treatment effectiveness at shorter times, with higher biomass loadings and with lower KOH concentrations. Higher loadings during the enzymatic hydrolysis stage are expected to be viable.

Envisaging how this process could be expanded to operate on an industrial scale, CO_2 capture from a combustion stream could be realised, providing water evaporation issues are resolved. Alternatively, the CO_2 could be employed in a closed cycle, *e.g.* after release from the CaCO_3 either thermally or by acid. Addition of acid to the CaCO_3 -lignin composite would release CO_2 as a gas (for re-use), and the acid-insoluble lignin could be isolated as a solid. However, it would produce calcium waste which would be difficult to be reused, and could introduce issues with corrosion. Conversely, thermal processes such as the combustion of lignin (as a black liquor) for energy release and inorganic chemical recovery,^{36a} and calcination to recover CaO ,^{36b} are both industrial processes that are performed in parallel in the paper pulping industry. If the two are combined, then the exothermic combustion of lignin would assist in the calcination reaction of CaCO_3 , would result in CO_2 release from both the lignin and CaCO_3 , and ultimately achieve recovery of both $\text{Ca}(\text{OH})_2$ (as CaO) and CO_2 for further use. A further fractionation possibility is the lower temperature gasification of lignin^{36a} followed by higher temperature calcination of the CaCO_3 , allowing the lignin to be utilised as a source of chemicals (*e.g.* syngas) rather than energy.

Washing of the pre-treated rice husks prior to enzymatic hydrolysis is undesirable on a large scale, but was required due to residual $[\text{OH}]^-$; the use of CO_2 at this stage to moderate the pH is also being investigated.

To conclude, we have demonstrated that CO_2 can be introduced (as a solid or as a gas) as a pH-switch anti-solvent to aid in biomass pre-treatment, fractionation, and the recycle of the alkaline pre-treatment solution. Enzymatically-hydrolysable cellulose, high-purity nanostructured silica and lignin can all be isolated *via* a three-step cycle. The regenerated pre-treatment media and solid carbon dioxide (as CaCO_3) can also be isolated, *via* the application of $\text{Ca}(\text{OH})_2$. After five rounds of pre-treatment using recycled solutions there was no significant loss in the activity of the KOH solution.



Acknowledgements

This work was supported by the Australian Research Council through Project DE130100770. Part of this research used the facilities at the Electron Microscope Unit at UNSW. Open access for this article was funded by King's College London.

References

- W. X. Teh, M. M. Hossain, T. Q. To and L. Aldous, *ACS Sustainable Chem. Eng.*, 2015, **3**, 992–999.
- (a) H. Jørgensen, J. B. Kristensen and C. Felby, *Biofuels, Bioprod. Biorefin.*, 2007, **1**, 119–134; (b) S. Behera, R. Arora, N. Nandhagopal and S. Kumar, *Renewable Sustainable Energy Rev.*, 2014, **36**, 91–106.
- D. Klein-Marcuschamer, B. A. Simmons and H. W. Blanch, *Biofuels, Bioprod. Biorefin.*, 2011, **5**, 562–569.
- J. S. Golden, R. B. Handfield, J. Daystar and T. E. McConnell, *An Economic Impact Analysis of the U.S. Biobased Products Industry: A Report to the Congress of the United States of America*, 2015.
- (a) Q. Zhao, R. C. M. Yam, B. Zhang, Y. Yang, X. Cheng and R. K. Y. Li, *Cellulose*, 2008, **16**, 217–226; (b) L. Ludueña, D. Fasce, V. A. Alvarez and P. M. Stefani, *BioResources*, 2011, **6**, 1440–1453; (c) A. M. Sousa, L. Visconte, C. Mansur and C. Furtado, *Chem. Chem. Technol.*, 2009, **3**, 321–326.
- B. B. Y. Lau, T. S. K. Yeung, R. J. Patterson and L. Aldous, *ACS Sustainable Chem. Eng.*, 2017, DOI: 10.1021/acssuschemeng.7b00647.
- B. B. Y. Lau, E. T. Luis, M. M. Hossain, W. E. S. Hart, B. Cencia-Lay, J. J. Black, T. Q. To and L. Aldous, *Bioresour. Technol.*, 2015, **197**, 252–259.
- M. M. Hossain and L. Aldous, *Aust. J. Chem.*, 2012, **65**, 1465–1477.
- S. Chandrasekhar, K. G. Satyanarayana, P. N. Pramada, P. Raghavan and T. N. Gupta, *J. Mater. Sci.*, 2003, **38**, 3159–3168.
- P. J. Van Soest, *Anim. Feed Sci. Technol.*, 2006, **130**, 137–171.
- J. Hummel, E. Findeisen, K. H. Sudekum, I. Ruf, T. M. Kaiser, M. Bucher, M. Clauss and D. Codron, *Proc. R. Soc. London, Ser B*, 2011, **278**, 1742–1747.
- E. D. Foletto, E. Gratieri, L. H. Oliveira and S. L. John, *Mater. Res.*, 2006, **9**, 335–338.
- A. Kumar, K. Mohanta, D. Kumar and O. Parkash, *Int. J. Emerg. Technol. Adv. Eng.*, 2012, **2**, 86–90.
- H. K. Tchakoute, C. H. Ruscher, S. Kong, E. Kamseu and C. Leonelli, *J. Sol-Gel Sci. Technol.*, 2016, **78**, 492–506.
- M. Raventos, S. Duarte and R. Alarcon, *Food Sci. Technol. Int.*, 2002, **8**, 269–284.
- M. A. Winters, B. L. Knutson, P. G. Debenedetti, H. G. Sparks, T. M. Przybycien, C. L. Stevenson and S. J. Prestrelski, *J. Pharm. Sci.*, 1996, **85**, 586–594.
- S. V. Dzyuba and R. A. Bartsch, *Angew. Chem., Int. Ed.*, 2003, **42**, 148–150.
- (a) N. Elvassore, M. Baggio, P. Pallado and A. Bertucco, *Biotechnol. Bioeng.*, 2001, **73**, 449–457; (b) C. Aymonier, A. Loppinet-Serani, H. Reveron, Y. Garrabos and F. Cansell, *J. Supercrit. Fluids*, 2006, **38**, 242–251.
- Y. Z. Zheng, H. M. Lin and G. T. Tsao, *Biotechnol. Prog.*, 1998, **14**, 890–896.
- L. Soh and J. Zimmerman, *Green Chem.*, 2011, **13**, 1422–1429.
- X. F. Sun, Y. L. Chi and T. C. Mu, *Green Chem.*, 2014, **16**, 2736–2744.
- A. A. Myint, H. W. Lee, B. Seo, W. S. Son, J. Yoon, T. J. Yoon, H. J. Park, J. Yu, J. Yoon and Y. W. Lee, *Green Chem.*, 2016, **18**, 2129–2146.
- Q. H. Zhang, N. S. Oztekin, J. Barrault, K. D. Vigier and F. Jerome, *ChemSusChem*, 2013, **6**, 593–596.
- I. Anugwom, V. Eta, P. Virtanen, P. Maki-Arvela, M. Hedenstrom, Y. B. Ma, M. Hummel, H. Sixta and J. P. Mikkola, *Biomass Bioenergy*, 2014, **70**, 373–381.
- (a) M. Y. He, Y. H. Sun and B. X. Han, *Angew. Chem., Int. Ed.*, 2013, **52**, 9620–9633; (b) A. R. C. Morais, A. M. D. Lopes and R. Bogel-Lukasik, *Chem. Rev.*, 2015, **115**, 3–27.
- J. L. Xu, J. J. Cheng, R. R. Sharma-Shivappa and J. C. Burns, *Energy Fuels*, 2010, **24**, 2113–2119.
- J. Xu, X. Zhang and J. J. Cheng, *Bioresour. Technol.*, 2012, **111**, 255–260.
- X. M. Zhang, J. L. Xu and J. J. Cheng, *Energy Fuels*, 2011, **25**, 4796–4802.
- (a) A. Buasri, N. Chaiyut, V. Loryuenyong, P. Worawanitchaphong and S. Trongyong, *Sci. World J.*, 2013, 460923; (b) N. Viriya-Empikul, P. Krasae, B. Puttasawat, B. Yoosuk, N. Chollacoop and K. Faungnawakij, *Bioresour. Technol.*, 2010, **101**, 3765–3767.
- A. Brandt, M. J. Ray, T. Q. To, D. J. Leak, R. J. Murphy and T. Welton, *Green Chem.*, 2011, **13**, 2489–2499.
- A. Sluiter, B. Hames, R. Ruiz, C. Scarlata, J. Sluiter, D. Templeton and D. Crocker, *Determination of structural carbohydrates and lignin in biomass*, National Renewable Energy Laboratory, 2008.
- G. D. Saratale and M. K. Oh, *RSC Adv.*, 2015, **5**, 97171–97179.
- S. R. Kamath and A. Proctor, *Cereal Chem. J.*, 1998, **75**, 484–487.
- U. Kalapathy, A. Proctor and J. Shultz, *Bioresour. Technol.*, 2000, **73**, 257–262.
- M. M. Hessien, M. M. Rashad, R. R. Zaky, E. A. Abdel-Aal and K. A. El-Barawy, *Mater. Sci. Eng., B*, 2009, **162**, 14–21.
- (a) M. Naqvi, J. Yan and E. Dahlquist, *Bioresour. Technol.*, 2010, **101**, 8001–8015; (b) M. Mahmoudkhani and D. W. Keith, *Int. J. Greenhouse Gas Control.*, 2009, **3**, 376–384.
- W. E. S. Hart, J. B. Harper and L. Aldous, *Green Chem.*, 2015, **17**, 214–218.
- T. Yokoyama, J. F. Kadla and H. M. Chang, *J. Agric. Food Chem.*, 2002, **50**, 1040–1044.
- Q. Luo, H. Peng, M. Zhou, D. Lin, R. Ruan, Y. Wan, J. Zhang and Y. Liu, *BioResources*, 2012, **7**, 5817–5828.

