THF co-solvent enhances hydrocarbon fuel precursor yields from lignocellulosic biomass†

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A novel single phase co-solvent system using tetrahydrofuran (THF) promotes hydrolysis of maple wood to sugars, sugar dehydration, and lignin extraction simultaneously and achieves higher overall yields of the fuel precursors furfural, 5-hydroxymethylfurfural (HMF), and levulinic acid (LA) than previously reported from biomass. In a one-pot reaction, we obtained yields of 86% furfural, 21% HMF, and 40% LA in the liquid phase and over 90% extraction of lignin as a solid powder. The co-solvent reaction also produced a glucan-rich residue that is highly digestible by enzymes for biological conversion to ethanol or further thermochemical reaction to additional HMF and levulinic acid. These findings enable an integrated conversion platform in which THF is both a co-solvent and final co-product to enhance production of fuel precursors for catalytic upgrading to renewable liquid hydrocarbons fuels.

We present here the application of tetrahydrofuran (THF) as a unique co-solvent to enhance yields of the hydrocarbon fuel precursors furfural, 5-hydroxymethylfurfural (HMF), levulinic acid (LA), and glucose directly from raw maple wood. Wood and other types of lignocellulosic biomass are the most abundant sources of organic carbon on Earth and present the only option to economically and sustainably replace fossil resources for production of liquid fuels for transportation on a large scale.[1,2] Furfural, HMF, and LA are promising platform chemicals[3–5] produced from acid-catalyzed dehydration of biomass sugars that can serve as precursors to gasoline, jet fuel, diesel-range alkanes, and fuel blending components compatible with the existing fuel infrastructure (so-called "drop-in" fuels) while also providing energy densities well suited to heavy duty vehicles and aircraft.[6–9]

In this context, we define a fuel precursor (FP) as any biomass sugar monomer or sugar dehydration product that can be biologically, chemically, or catalytically converted into fuels and fuel products. Continued efforts to improve the synthesis of furans from sugar streams[10,11] and their catalytic upgrading to fuel products have made this pathway increasingly viable as an industrially relevant biofuels platform. However, the natural resistance of lignocellulosic biomass to breakdown to monomeric sugars and low yields of their dehydration products are the major obstacles to low cost fuels that must be overcome for biomass drop-in fuels to have impact.[12] Thus, effective strategies are needed that can efficiently fractionate raw biomass and achieve high product yields directly from biomass without expensive catalysts or solvents or complex process configurations.

THF is a promising green solvent that is relatively non-toxic and miscible with water over a wide range of reaction conditions. Unlike other miscible solvents and ionic additives used to enhance FP production,[13,14] THF is low boiling (66 °C), forms an azeotrope with water, and can be synthesized directly from furfural at high selectivities through catalytic decarbonylation to furan followed by ring hydrogenation.[5] In previous work, THF demonstrated exceptional properties for extracting furfural and HMF from water mixtures and was successfully used in biphasic reactions to increase their yields from sugar streams and less-recalcitrant biomass.[10,15,16] However, biphasic systems are physically limited by the presence of two discernible liquid phases so high initial solids concentrations cannot be achieved, and saturation of the aqueous phase with salts is needed to partition THF from water. Instead of a two phase approach, we show here, for the first time, that THF in a one-pot monophasic reaction can significantly increase fuel precursor yields compared to traditional water-only strategies while promoting deconstruction of biomass beyond what has been possible in biphasic systems.

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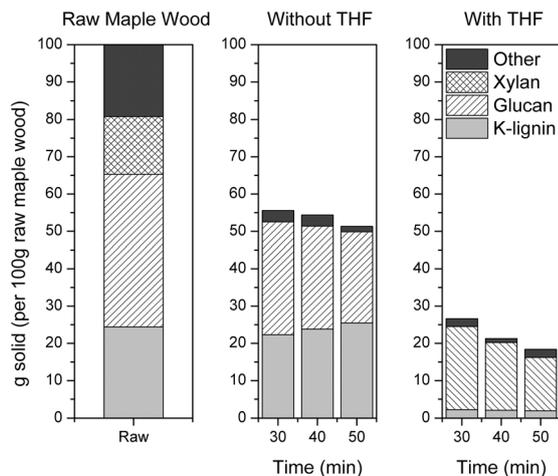†Electronic supplementary information (ESI) available. See DOI: 10.1039/c3gc41214h

Fig. 1 Composition of raw maple wood and solids remaining after reaction with and without THF based on 100 g of initial solids. THF dissolved over 90 wt% of the lignin and degradation products that otherwise accumulated in the non-solvent case. Reaction conditions: 5 wt% maple wood and 1 wt% H_2SO_4 in batch reactions at 170 °C. The THF co-solvent solution was at a 1 : 1 solvent–water ratio.

Fig. 2 SEM images of the maple wood residue after 40 min reaction with (A) no THF and (B) with 1 : 1 THF co-solvent.

We selected raw maple wood as a highly recalcitrant model lignocellulosic feedstock for both co-solvent and non-solvent reactions to establish the advantages of this novel application of THF. Consecutive batch reactions at 170 °C were performed using dilute sulfuric acid (1 wt%), which is an abundant and inexpensive strong acid that can be used in low enough amounts at high solids concentrations so that it can be economically neutralized in the waste stream for disposal.[17a] From the mass and composition of the remaining solids (per 100 g basis of raw maple wood) presented in Fig. 1, we observed a significantly higher degree of biomass solubilization in the presence of THF than without. For the reactions containing a 1 : 1 (vol.) mixture of THF and water, over 90 wt% of the acid-insoluble Klason lignin (K-lignin) initially present in maple wood was removed into the liquid phase by 10 min, producing a solid residue that was highly glucan-rich (>85 wt% glucan). In contrast, the composition of the remaining solids from reactions without THF showed that K-lignin content was only slightly reduced at 30 min but then quickly increased over time due to formation of pseudo-lignin[17b] and other acid-insoluble degradation products (Fig. 1). The THF co-solvent also appeared to catalyze the hydrolysis reaction as the disappearance of glucan from the solids was faster compared to reactions with just water (Fig. 1).

We were able to easily recover the low-boiling THF from the post-reaction liquor by room temperature vacuum distillation. The removal of THF rapidly precipitated the dissolved lignin in the liquor as a sticky solid residue that could be collected by pouring out the remaining liquid. Further washing of the solid precipitate with diethyl ether followed by oven-drying produced a brown lignin-rich powder largely free of sugars, proteins, and ash (as shown in Fig. S1 in the ESI†). The lignin recovered from the co-solvent reaction readily re-dissolved in THF for
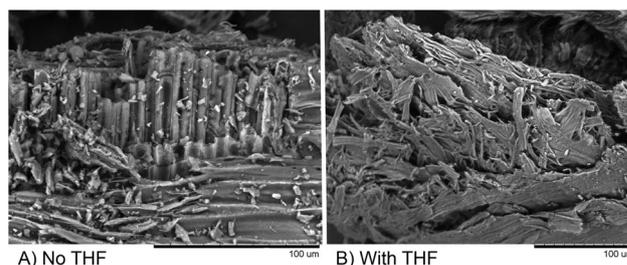
catalytic upgrading into valuable aromatics and polymers.[18] FT-IR absorbance spectra (as shown in Fig. S2 in the ESI†) in the fingerprint region of the lignin product extracted by THF matched that of the K-lignin residue that remains from concentrated sulphuric acid extraction (72 wt% H_2SO_4 for 1 h) of raw maple wood very well. Unlike THF-extracted lignin, acid-extracted K-lignin residue contained a small amount of acid-insoluble ash, was darker in color, and did not readily dissolve in either THF or DMSO. Based on previous characterization studies of hard wood lignin,[19] a stronger absorbance band representing carbonyl stretching of unconjugated β-ketones and conjugated acid/esters (Fig. S2†) indicated a greater oxidation of the lignin structure extracted by THF. Characterization in progress by 2D NMR will provide additional insights on the specific changes in the molecular weight and chemical reactivity of the THF isolated lignin to determine suitable paths for catalytic upgrading.

As shown in Fig. 2, SEM images of the solid biomass residues that remained after 40 min of reaction for both the co-solvent and non-solvent case showed remarkable differences in the macro surface structure of maple wood. In the reactions with THF (Fig. 2), the fibrous structure was nearly completely disrupted, and cell walls collapsed in contrast to the non-solvent case (no THF, Fig. 2) where these features were still clearly visible. Removal of hemicellulose and lignin at the high severity conditions applied in the co-solvent reaction and disruption of the surface structure are characteristic of solids that can be more easily hydrolyzed to fermentable glucose with lower enzyme doses than solids from most other pretreatment systems.[20,21] The results of an enzyme assay of these samples using the commercial cellulase cocktail Accellerase® 1500 is shown in Fig. 3. As shown, the glucose yield achieved from the enzymatic hydrolysis of THF pretreated maple wood (with THF, Fig. 3) was much greater than that for dilute acid-pretreated maple wood (no THF, Fig. 3) and raw untreated maple wood (raw, Fig. 3). In fact, even at a low enzyme loading of 15 mg protein per g glucan, the resulting 72 h glucose yield from the THF pretreated maple wood residue matched that of Avicel® cellulose (95–98% glucan). Thus, the solids could be ideal for biological conversion by such routes as Simultaneous Saccharification and Fermentation (SSF) or Consolidated Bioprocessing (CBP) to produce ethanol after a washing step to remove traces of solvent and inhibitors. Currently, work on applying THF
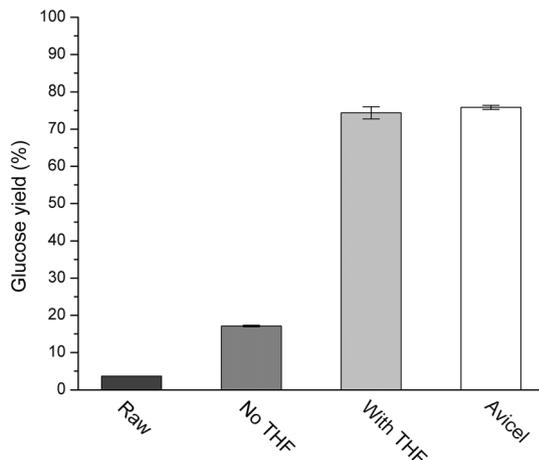
Fig. 3 Comparison of glucose yields between raw and reacted maple wood samples to Avicel® cellulose after 72 h enzymatic hydrolysis at 15 mg protein g^{-1} glucan loading of Accellerase® 1500 cellulase.

co-solvent as a fractionation and pretreatment strategy to enhance the release of sugar monomers is underway.

Table 1 compares the highest yields of furfural, LA, and HMF obtained from THF co-solvent and non-solvent reactions of raw maple wood chips. Most notably, at 40 min reaction, THF improved furfural yields from 62% to 87% of theoretical compared to the non-solvent case and greatly improved HMF production. Evidence from the concentration profiles of the sugars and sugar products (as shown in Fig. S3 in the ESI†) indicate that THF catalyzed both the hydrolysis of maple wood polysaccharides and the dehydration of C5 and C6 sugars to improve fuel precursor yields. Varying the solvent–water ratio in the co-solvent reactions (Table 1, runs 2–4) showed that overall product yields were lower for a 1 : 3 mixture, the highest furfural yields were realized with 1 : 1 and 3 : 1 solutions, and higher yields of LA (32%) and HMF (21%) were obtained from the 3 : 1 mixture. By carrying the reaction out to 60 min with the 3 : 1 mixture (Table 1, run 5), the LA yield was further increased (40%) with additional biomass solubilisation, but furfural yields began to drop (86%). As HMF readily hydrolyses to form LA and formic acid

in the presence of a strong Brønsted acid,[5] LA is the primary product from C6 sugars in these reactions. However, we have found that certain strong Lewis acids can increase HMF selectivity, providing an exciting area of future study for various co-production schemes.

Although higher than 3 : 1 mixtures may increase co-production yields further, excessively high solvent ratios are likely to be detrimental to process competitiveness due to increased recovery costs, heating requirements, and reduced solids loading. As raw biomass often contains significant moisture levels (*e.g.*, 50 wt% for wood), a 1 : 1 or less mixture is desirable to maximize product concentrations and keep thermal loads as low as possible. In any event, THF as a miscible co-solvent significantly enhanced production of furfural, HMF, and LA over the non-solvent case, achieving yield improvements comparable to our previously reported biphasic reactions with maple wood and MIBK.[22] By optimizing reaction conditions for the production of furfural (Table 1, run 3), the least thermally-stable fuel precursor, we achieved a maximum overall FP recovery of 87% and 92% (of theoretical) from the C5 and C6 sugars from maple wood, respectively (Material balance shown by Fig. S4 in the ESI†).

At longer reaction times (Table 1, runs 6 and 7), higher LA yields were obtained at the expense of significant furfural losses in both cases. However, furfural losses were greatly reduced in the co-solvent reaction, providing the initial evidence that THF helped to protect furfural from degradation in the catalytically-active phase. Yet, effective co-production of these fuel precursors was still limited by rapid furfural losses despite increasing the solvent–water ratio. These furfural losses can be attributed to condensation reactions between furfural and intermediate sugar products,[23] the slow conversion of furfural to formic acid,[24] and formation of solid resins and other degradation products.[25] Furthermore, since amorphous hemicellulose is more acid-labile than crystalline cellulose, xylan is hydrolyzed and dehydrated much sooner than glucose from cellulose during acid-catalyzed reactions.[21] Consequently, achieving high overall yields of fuel precursors from both hemicellulose and cellulose fractions in one vessel is challenging.[27] Thus, to maximize overall FP yields in a single

Table 1 Acid-catalyzed production of furfural, LA, and HMF from maple wood in batch reactions with and without THF addition[a]

Run #	Solvent content[c]	Substrate	Acid catalyst	Time (min)	Reaction temp. (°C)	Yields (of theoretical)		
						Furfural (%)	HMF (%)	LA (%)
1	None[d]	Maple wood[b]	1 wt% H_2SO_4	40	170	62	2.4	7.2
2	1 : 3 THF–water	Maple wood[b]	1 wt% H_2SO_4	40	170	76	4.9	8.3
3	1 : 1 THF–water	Maple wood[b]	1 wt% H_2SO_4	40	170	87	13	11
4	3 : 1 THF–water	Maple wood[b]	1 wt% H_2SO_4	40	170	87	21	32
5	3 : 1 THF–water	Maple wood[b]	1 wt% H_2SO_4	60	170	86	21	40
6	None[d]	Maple wood[b]	1 wt% H_2SO_4	120	170	39	2.6	32
7	1 : 1 THF–water	Maple wood[b]	1 wt% H_2SO_4	120	170	69	7.6	40
8[e]	None	Maple wood[f]	1.5 wt% H_2SO_4	40	200	—	—	75

[a] All reactions performed using a 1 L Parr reactor and reported yields are % of theoretical maximum. [b] 5 wt% total solids loading. [c] The ratio of solvent to water by volume is as described. [d] These reactions were control reactions without solvent. [e] Production of LA from pretreated maple wood after hemicellulose extraction. [f] 10 wt% total solids loading.

phase system, preservation of the least stable species is paramount, and separate stages to independently target production of furfural and levulinic acid will be beneficial.

To illustrate this point, we subjected cellulose-enriched maple wood in a non-solvent reaction at a higher reaction temperature of 200 °C to favor the formation of LA. For this reaction, we used maple wood that had been pretreated hydrothermally to first remove most of the hemicellulose fraction. The reaction contained 10 wt% solids at a 1.5 wt% sulfuric acid concentration to mimic a more concentrated product stream that would result from a prior co-solvent reaction optimized for furfural production. As shown (Table 1, run 8), we achieved a high LA yield of 75% without the need for THF if reaction temperatures and acid concentrations were increased to specifically target LA production. However, since hydrothermally pretreated material contained more lignin than results from THF treatment, future study using THF reacted residue will confirm these results.

Fig. 4 illustrates an integrated approach to apply these exciting results in a biorefinery. We propose the direct injection of high-pressure (HP) steam (Fig. 4, item 2) as an efficient heating method for this system. The Pandia reactor shown (Fig. 4, item 1) uses a conveying screw to keep residence times and temperatures reasonably uniform and handle high solids concentrations. Water-volatile species, such as furfural and THF, can be flashed off (Fig. 4, item 3) or stripped off by steam into an azeotropic distillation unit for furfural purification, THF recovery, and water recycle (Fig. 4, item 4, dotted lines represent recycle streams). The furfural azeotrope (b.p. 97.9 °C) contains about 65% water and can be further purified by a dehydration column. The THF azeotrope (b.p. 65 °C) contains only a small amount of water (4.6 wt%), and since additional drying is unnecessary, its recovery is not energy intensive.[26] Removal of THF from the liquid phase causes lignin to precipitate so that it can be collected as a bottom product. Mild

catalytic upgrading (Fig. 4, item 5) of furfural can regenerate any THF losses and produce aromatic gasoline components. Solvent extraction or reduced-temperature vacuum distillation can be used to recover HMF to limit unwanted reactions or the concentrated aqueous solution can be sent directly to a second reactor (Fig. 4, item 6) for LA production. The glucan-rich solids remaining from the co-solvent reactions could either be sent to the second reactor or enzymatically hydrolyzed to fermentable glucose.

Hydrogenation is the most versatile and advocated option to upgrade furfural, HMF, and levulinic acid to hydrocarbon fuel products. At the high yields obtained in the co-solvent reaction, the diversity of potential products from these fuel precursors greatly improves their marketability. Furfural can be catalytically upgraded to furfuryl alcohol (FAlc), tetrahydrofurfuryl alcohol, and dihydropyran.[6,28,29] Methylfuran (MF) and methyltetrahydrofuran (MTHF, P-series fuel) are hydrogenated products of FAlc which have excellent properties for application as gasoline blendstock.[27] Aldol-condensation and dimerization of furfural adducts followed by hydrodeoxygenation can produce alkanes[28] up to tridecanes.[30] Dimethylfuran (DMF) is a promising fuel product from HMF that is also suitable as a gasoline component.[8] LA, from the hydrolysis of HMF, is a valuable chemical precursor to levulinate esters, γ-valerolactone (GVL), MTHF, and other fuel-related products.[5] LA's high boiling point (245 °C) makes it difficult to separate by distillation, so maintaining a concentrated product stream, such as with our proposed strategy, will improve separation economics.

THF as a single phase co-solvent can meet the challenge of increasing FP yields from lignocellulosic biomass that are vital to successful conversion to hydrocarbon, aka "drop-in," fuels compatible with the existing infrastructure. We have shown that when THF is used as a water-miscible co-solvent, biomass deconstruction, sugar dehydration, and lignin removal are simultaneously promoted, resulting in the highest reported overall FP yields obtained from biomass. Application of other more environmentally-friendly homogeneous or heterogeneous catalysts in our ongoing studies can allow for improved selectivity to furfural and HMF. By integrating this co-solvent system with recent developments in catalytic conversion of these precursors to hydrocarbon fuels, the economic production of sustainable biofuels may be realized.

Fig. 4 Conceptual process flow diagram for an integrated biorefinery to produce fuel precursors, THF, and lignin products from lignocellulosic biomass using THF as a single-phase co-solvent. Process key: (1) high solids screw-type Pandia reactor, (2) high pressure (HP) boiler, (3) flash of volatiles and liquid–solid separation, (4) azeotropic distillation to recover furfural, THF, and water, (5) catalytic upgrading of furfural to THF, and (6) LA production from concentrated sugar solution and cellulose-enriched material. Dotted lines represent recycle and recovery streams.

Experimental

The acid-catalyzed reactions in this study were carried out in solvent and non-solvent water solutions. The co-solvent solution consisted a mixture of THF (>99% purity, Fisher Scientific, Pittsburgh, PA) and deionized (DI) water. Concentrated sulfuric acid (72 wt%, Ricca Chemical Company) was diluted in solution to obtain the indicated acid loadings for each run. The reactions were then carried out in a high-pressure continuously stirred 1 L Parr reactor (Parr Instrument Company, Moline, IL). The reactor temperature was directly measured by
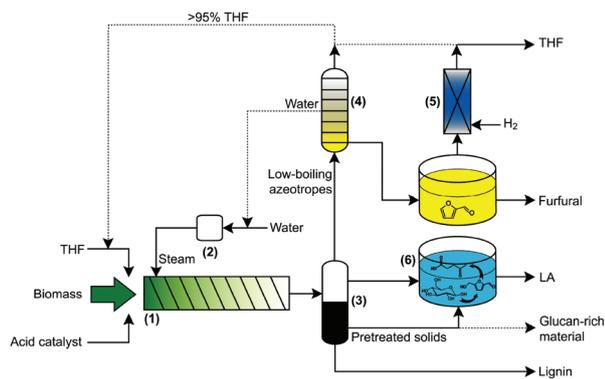
an in-line thermocouple (Omega, K-type). All reaction temperatures were maintained by convective heating with a fluidized sand bath (Techne, Princeton, NJ). Mixing was performed by twin 6-blade impellers operating at 200 rpm driven by a top mounted electric motor. At the conclusion of a run, the reactor was cooled by quickly lowering it into a large room temperature water bath. All liquid containing receptacles were made of glass to prevent the loss of furfural and THF that was observed when plastics were used.

Maple wood reactions were carried out using air-dried (<5% moisture content) maple wood chips obtained in upper New York State by Mascoma Corporation (Lebanon, NH). The chips were milled to below 1 mm particle size. Maple wood composition was measured according to the established National Renewable Energy Laboratory (NREL) procedure (version 8-03-2012) in triplicates with a resulting composition of 40.9 ± 0.3 wt% glucan, 15.5 ± 0.2% xylan, 2.1 ± 0.1% mannan, 24.4 ± 0.3% K-lignin, and 17.1% other material. The latter was not further characterized in this study but was expected to consist of minor saccharides, ash, sugar acids, and protein. Because arabinan and galactan were not present in significant quantities (<0.3%), it may be appropriate to treat all maple wood pentosans as xylan and all hexosans as only glucan and mannan. For each run, the biomass was allowed to pre-soak overnight at 4 °C. Contents were then equilibrated to room temperature prior to reaction. Samples were analyzed by HPLC (Agilent 1200 system equipped with a Bio-Rad Aminex® HPX-87H column and RI detector) with an eluent (5 mM sulfuric acid) flow rate of 0.6 ml min^{-1}. Since the HPX-87H column cannot distinguish between xylose, mannose, and galactose sugars, we also equipped our HPLC with an Aminex® HPX-87P column for quantification of xylose and solids composition. Since the HPX-87P column is incompatible with acids, we elected not to use this column for fuel precursor analysis. The solids were then separated from the reaction liquor by vacuum filtration at room temperature through glass fiber filter paper (Fisher Scientific, Pittsburgh, PA). Mass and density of the liquid fraction were measured to calculate accurate yields by the equations below. Due to the difference in density between the solvent and non-solvent solutions, densities were determined by weighing 25 ml of the reacted liquid in a volumetric flask after each reaction. Calculation of the fuel precursor yields is given by eqn (1) where the molar equivalents (θ_{FP}) of furfural (eqn (2)), LA (eqn (3)), and HMF (eqn (4)) are individually calculated for their respective sugar sources.

$$\%\text{FP yield} =$$
$$\theta_{FP}\frac{\text{FP}_{prod.}(\text{g L}^{-1}) \times \text{mass of liquor}_{prod.}(\text{g})}{\text{maple wood}_{init.}(\text{g}) \times \text{density of liquor}_{prod.}(\text{g L}^{-1})}100\%$$
$$(1)$$

$$\theta_{furfural} = \frac{1.375}{\text{fraction of total xylan}_{init.}} \quad (2)$$

$$\theta_{LA} = \frac{1.396}{\text{fraction of total hexosan}_{init.}^{a}} \quad (3)$$

$$\theta_{HMF} = \frac{1.286}{\text{fraction of total hexosan}_{init.}^{a}} \quad (4)$$

^{a}Total hexosan = glucan + mannan.

Analysis of the lignin product was performed using an Agilent Cary 630 FT-IR with ZnSe ATR solids analyser (32 scans at 2 cm^{-1} wavenumber resolution). FT-IR spectra were overlaid after baseline correction and absorbances were scaled proportionately by Resolutions Pro software (Agilent) to allow for comparison of relative peak heights. SEM images were taken on a Hitachi TM-1000 Tabletop Scanning Electron Microscope and were generated at the Microscopy Core/Center for Plant Cell Biology at the institute for Integrative Genome Biology at UC Riverside.

Enzymatic hydrolysis of maple wood and Avicel® cellulose (PH-101, Sigma-Aldrich) was performed in 50 mM citrate buffer using Accellerase® 1500 cellulase cocktail (BCA protein – 82 mg ml^{-1}, DuPont Industrial Biosciences, Palo Alto, CA). Samples were prepared based on 1 wt% glucan loading and 15 mg protein per g glucan in 125 ml shake flasks and were incubated at 50 °C and 150 rpm for 72 h.

Acknowledgements

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