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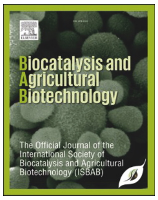

Biocatalytic reduction of 5-hydroxymethylfurfural to 2,5-furandimethanol using coconut (*Cocos nucifera* L.) water

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ABSTRACT

The hexose dehydration product and important renewable feedstock 5-hydroxymethylfurfural can be biocatalytically reduced to 2,5-furandimethanol in 96% yield using coconut (*Cocos nucifera* L.) water as the biocatalyst at room temperature. The dimer of 5-hydroxymethylfurfural 5,5'-[oxybis(methylene)]bis[2-furaldehyde] can also be reduced to the corresponding diol 5,5'-[oxybis(methylene)]bis-[2-furanmethanol] using coconut (*Cocos nucifera* L.) water in 95% yield under similar conditions. This biocatalytic system could be reused in four cycles without an appreciable loss in activity.

1. Introduction

Biocatalytic chemical transformations have attracted interest in recent years due to a number of key features such as versatility, mild reaction conditions, high turnover numbers, chemoselectivity, regioselectivity and enantioselectivity important in synthetic organic chemistry (Gröger, 2018), (Castro and Knubovets, 2003), (Drauz et al., 2012). These biocatalytic transformations are known with enzymes, yeast and plant extracts. In recent times numerous researchers have considered the use of plant extracts for organic transformations due to their ready availability or relatively low cost and eco-friendly nature in addition to the benefits of common biocatalytic systems (Bohman et al., 2009), (Bordón et al., 2015). The extracts from several widespread plants such as carrot (Daucus carota) (Acharya et al., 2018), (de Souza de Oliveira et al., 2013) fruits of *Ligustrum lucidum* (Aimar et al., 2014), cassava (*Manihot esculenta* Cranz.) (Machado et al., 2008), and coconut (*Cocos nucifera* L.) are reported as sources of reductase activity with alcohol dehydrogenase systems. The use of coconut (*Cocos nucifera* L.) water as a biocatalyst was first reported by Fonseca et al., in 2009, where they found that the juice of the common coconut species *C. nucifera* is effective in selectively reducing a broad variety of aliphatic and aromatic carbonyl compounds, showing substantial regio and enantioselectivity in the products (Fonseca et al., 2009). In these studies they have reported the reduction of a number of aliphatic, aromatic aldehydes as well as ketones, including benzaldehyde, cyclohexanone, furfural, acetophenone and 2-butanone. In addition they have noted that esters are hydrolyzed to carboxylic acids and nitrobenzene is reduced to azoxybenzene with coconut water (Fonseca et al., 2009). In another example Misra et al. have shown that aromatic electron rich aldehydes can be reduced to their corresponding alcohols using *Cocos nucifera* L. and *Borassus flabellifer* L. juices (Misra et al., 2012). Furthermore these vegetable juices were effective in decarboxylation of substituted cinnamic acids to the corresponding vinyl aromatics as well (Misra et al., 2012). The catalytic reduction is one of the most important conversions in organic synthesis and biocatalytic reduction is a widely studied biochemical conversion due to their wide applications and potential in chemical and pharmaceutical industry (Huisman and Collier, 2013), (Chadha et al., 2016). Additionally, peroxidase activity is also known with coconut water, where Rodrigues and co-workers have used coconut water as a biocatalyst for the oxidative coupling-cyclization of *p*-hydroxy phenylpropanoids (Rodrigues et al., 2017).

The 5-hydroxymethylfurfural (HMF) is a new generation versatile C6 platform chemical that can be obtained by dehydration of many abundant C6 carbohydrates (van Putten et al., 2013), (Amarasekara, 2012). The catalytic upgrading of this leading biobased furan to more stable derivatives like 2,5-furandimethanol (FDM), 2,5-diformylfuran (Amarasekara et al., 2008a) and furan 2,5-dicarboxylic acid is a high priority current research interest. There are a number of noble metal catalyst based hydrogenation approaches for the reduction of HMF to the corresponding diol, however all these methods require the use of hydrogen gas at high pressure, temperature and expensive metal catalysts, therefore biocatalytic systems operating at room temperature and mild conditions in aqueous medium is an attractive proposition (Tang et al., 2017). The HMF formed as a by-product in acid catalyzed cellulose

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depolymerization step in the cellulosic ethanol process can be toxic to most genetically engineered yeast variants used in the ethanol industry (Amarasekara, 2013). Therefore, the biocatalytic reduction of HMF to the more stable FDM can be seen as a way of detoxification of the cellulose hydrolyzate sugar solution prior to the fermentation and an industrially important transformation as well.

As far as we are aware there are only four reports on the biocatalytic reduction of HMF. He and co-workers reported the use of recombinant *E. coli* CCZU-K14 whole cells at pH 6.5 and 30 °C with glucose as a co-substrate in the presence of D-xylose, L-glutamic acid, β-cyclodextrin, cetyltrimethyl ammonium bromide and magnesium salts for the reduction of 5-hydroxymethylfurfural to 2,5-furandimethanol (He et al., 2018). Furthermore, they reported that new *E. coli* CCZU-K14 is highly tolerant to 5-hydroxymethylfurfural (up to 400 mM) (He et al., 2018). In another example Li and co-workers described the use of a new HMF tolerant yeast strain *Meyerozyma guilliermondii* SC1103 for the biocatalytic reduction of HMF to FDM using its resting cells (Li et al., 2017). In these experiments glucose was used as a co-substrate at pH 4.0–10.0 medium and produced FDM in 86% yield while achieving selectivities more than 99% (Li et al., 2017). In the third example, the vegetable *Brassica oleracea* variety *Italica*, more commonly known as broccoli, was used in fresh or in lyophilized form for the reduction of HMF to FDM (Petri et al., 2018). In these experiments 100 g of freshly picked vegetable matter suspended in 250 mL of deionized water was required for the reduction of 2 mmol of HMF giving FDM in 91% yield after 48 h, whereas the experiments in phosphate buffer (pH 7) produced a 76% yield of FDM (Petri et al., 2018). In the most recent example, synthesis of FDM from HMF was reported with the acclimatized *Meyerozyma guilliermondii* SC1103 cells entrapped in calcium alginate beads (Xu et al., 2018). Furthermore, the catalytic activitiy of the cells as well as their HMF-tolerant level increased upon immobilization and FDM was obtained in 82–85% yields in 99% selectivity (Xu et al., 2018).

Our interest in the development of catalytic methods for the preparation of HMF as well as its ether-dimer and further transformations of these renewable feedstocks has led us to study the biocatalytic methods for the reduction of HMF to 2,5-furandimethanol (Amarasekara et al., 2008b), (Amarasekara et al., 2007), (Amarasekara et al., 2017). In this publication we report the use of coconut (*Cocos nucifera* L.) water as an effective bio catalytic agent for this industrially important transformation as shown in Fig. 1. In addition, we report the use of coconut water for the reduction of the HMF dimer 5,5'-[oxybis(methylene)]bis [2-furaldehyde] to the corresponding diol 5,5'-[oxybis(methylene)] bis-[2-furanmethanol] as well (Fig. 2).

2. Experimental

2.1. Materials and instrumentation

5-Hydroxymethylfurfural (>99%) was purchased from Aldrich Chemical Co. The dialdehyde 5,5'-[oxybis(methylene)]bis[2-furaldehyde] (OBFA, **3**) was prepared from D-fructose by heating at 110 °C in DMSO with Dowex 50W X8 solid acid catalyst in 76% following our earlier published procedure (Amarasekara et al., 2017). The coconut water was obtained from freshly opened mature coconut (*Cocos nucifera* L.) purchased from local market in Houston, Texas and was used after filtration thorough Whatman number 1 filter paper. ^{1}H NMR Spectra were recorded in $CDCl_3$ on a Varian Mercury plus spectrometer at 400 MHz and chemical shifts are given in ppm downfield from TMS (δ = 0.00). The LC-MS identification and quantification were performed on an Agilent 6130B Single Quadrupole LC-MS System equipped with Electrospray ionization source (ESI) coupled to Agilent 1100 Series LC System equipped with a quaternary pump, auto sampler, column thermostat and degasification system (Agilent Technologies Inc.). The analytical column used was a Luna 5 μm C18(2) 100 Å, 150 × 4.6 mm, NP:00F-4252-E0 (Phenomenex Inc.). The solvent for the mobile phase was 0.1% formic acid in acetonitrile: water 90:10 (v/v). The injection sample volume was 5.0 μL. The SCAN parameters were; positive mode, mass range 40 to 850 m/z, fragmentor 150, gain 3.0. The spray chamber parameters were: gas temperature 300 °C, drying gas flow 11.0 L/min, nebulizer gas 50 psig, Vcap (+) and (−) 3000 V. The concentrations of HMF, 2,5-furandimethanol (FDM), 5, 5'-[oxybis(methylene)]bis[2-furaldehyde] (OBFA) and 5,5'-[oxybis(methylene)]bis-[2-furanmethanol] (OBFM) in reaction mixtures at different time intervals were calculated using standard curves prepared with pure authentic samples of HMF, FDM, OBFA and OBFM.

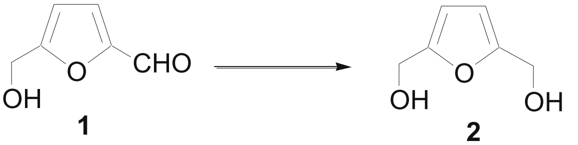

Fig. 1. Biocatalytic reduction of 5-hydroxymethylfurfural (HMF, **1**) to 2,5-furandimethanol (FDM, **2**) using coconut (*Cocos nucifera* L.) water.

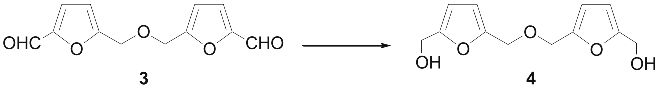

Fig. 2. Biocatalytic reduction of 5, 5'-[oxybis(methylene)]bis[2-furaldehyde] (OBFA, **3**) to 5,5'-[oxybis(methylene)]bis-[2-furanmethanol] (OBFM, **4**) using coconut (*Cocos nucifera* L.) water.

2.2. Procedure for biocatalytic reduction of 5-hydroxymethylfurfural (HMF) to 2,5-furandimethanol (FDM) using coconut (Cocos nucifera L.) water

5-Hydroxymethylfurfural (64 mg, 0.51 mmol) was suspended in 50.0 mL of coconut water in a 250 mL Erlenmeyer flask and the closed mixture was stirred at 300 rpm at 23 °C, using a 12 mm Teflon coated siring bar and a IKA C-Mag HS Digital stirring hot plate (Model no: 3581201) for 96 h. The aliquots (1.00 mL) were withdrawn from the reaction mixture at 0, 3, 10, 24, 36, 48, 60, 72 and 96 h; diluted with 1.0 mL of methanol before chromatographic analysis. The concentrations of HMF and FDM in the reaction mixture at different time intervals were determined using LC-MS as described in section 2.1. The experiments were carried out in duplicate and the changes in amounts of HMF and FDM with time are shown in Fig. 3. The product was further confirmed by isolation of the product by extraction of the reaction mixture to ethylacetate (3 × 10 mL) after 96 h, evaporation of the solvent under reduced pressure to give a white solid, m.pt. 76–77 °C, Lit. 76–78 °C (Goswami et al., 2008). ^{1}H NMR ($CDCl_3$) δ 4.58 (4H, s), 5.34 (2H, bs), 6.23 (2H, s).

2.3. Procedure for biocatalytic reduction of 5, 5'-[oxybis(methylene)]bis [2-furaldehyde] (OBFA, 3) to 5,5'-[oxybis(methylene)]bis-[2-furanmethanol] (OBFM, 4) using coconut (Cocos nucifera L.) water

5, 5'-[Oxybis(methylene)]bis[2-furaldehyde] (23 mg, 0.10 mmol) was suspended in 50.0 mL of coconut water in a 250 mL Erlenmeyer flask and the closed mixture was stirred at 300 rpm at 23 °C, using a 12 mm Teflon coated siring bar and a IKA C-Mag HS Digital stirring hot plate (Model no: 3581201) for 96 h. The aliquots (1.00 mL) were withdrawn from the reaction mixture at 0, 3, 10, 24, 36, 48, 60, 72 and 96 h; diluted with 1.0 mL of a mixture; water: acetonitrile: methanol (4:3:3) before chromatographic analysis. The concentrations of OBFA and OBFM in the reaction mixture at different time intervals were determined using LC-MS as described in section 2.1. The experiments were carried out in duplicate and the changes of amounts of OBFA and OBFM with time are shown in Fig. 4. The product was further confirmed by extraction of the reaction mixture to ethyl acetate (3 × 10 mL) after 96 h, evaporation of the solvent under reduced pressure to give a white

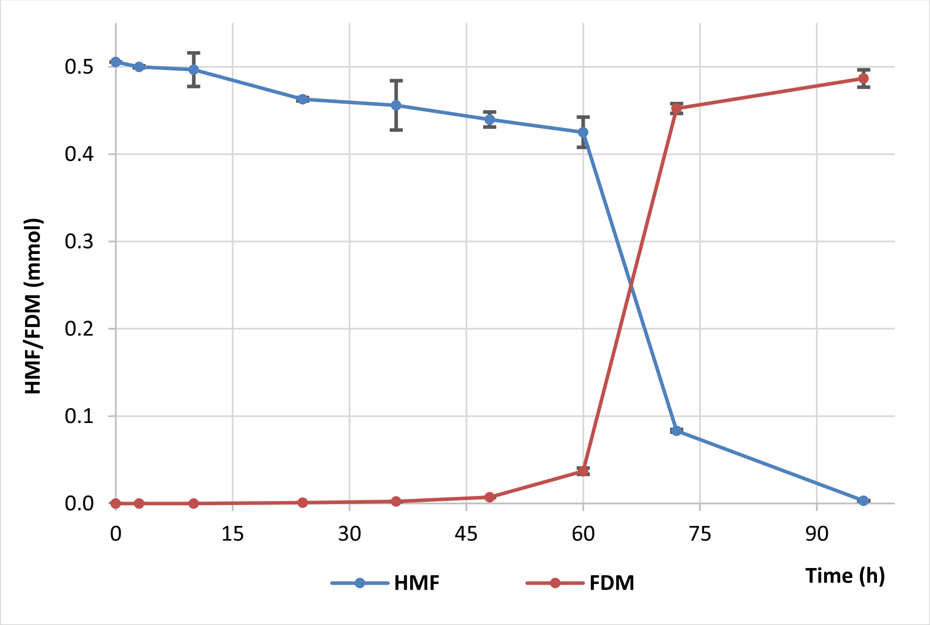

Fig. 3. Changes in the amounts of 5-hydroxymethylfurfural (HMF) and 2,5-furandimethanol (FDM) during the biocatalytic reduction of 5-hydroxymethylfurfural (HMF) using coconut (*Cocos nucifera* L.) water.

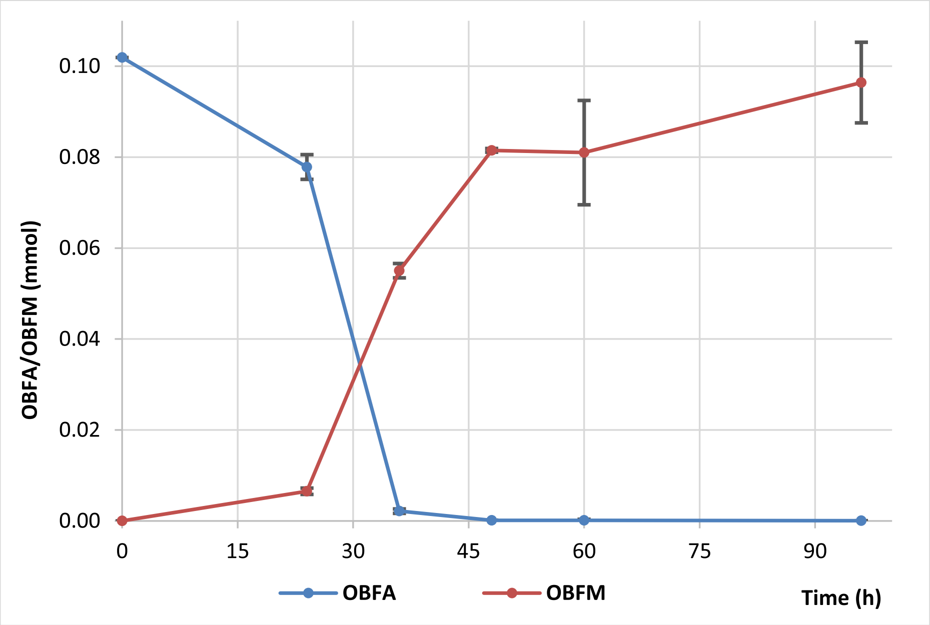

Fig. 4. Changes in the amounts of 5, 5'-[oxybis(methylene)]bis[2-furaldehyde] (OBFA) and 5,5'-[oxybis(methylene)]bis-[2-furanmethanol] (OBFM) during the biocatalytic reduction of 5, 5'-[oxybis(methylene)]bis[2-furaldehyde] (OBFA) using coconut (*Cocos nucifera* L.) water.

solid, m.pt. 92–93 °C, Lit. 92–93 °C (Timko et al., 1977). ^{1}H NMR ($CDCl_3$) δ 4.38 (4H, s), 4.47 (4H, s), 5.50 (2H, bs), 6.15 (2H, s), 6.19 (2H, s).

2.4. Reusability of coconut (Cocos nucifera L.) water in the biocatalytic reduction of 5-hydroxymethylfurfural (HMF) to 2,5-furandimethanol (FDM)

5-Hydroxymethylfurfural (32 mg, 0.25 mmol) was suspended in 50.0 mL of coconut water in a 250 mL Erlenmeyer flask and the closed mixture was stirred at 300 rpm at 23 °C, using a 12 mm Teflon coated siring bar and a IKA C-Mag HS Digital stirring hot plate (Model no: 3581201) for 96 h. A 1.00 mL aliquot was withdrawn from the reaction mixture, diluted with 1.0 mL of methanol and analyzed as described in the earlier procedure. Then a second portion of HMF (32 mg, 0.25 mmol) was added to the same reaction mixture, stirred at 300 rpm at room temperature for 96 h and analyzed as in the first sample. The HMF additions were repeated with two more portions. The experiments were carried out in duplicate and the changes in the amounts of HMF and FDM with time are shown in Fig. 5.

3. Results and discussion

We have found that coconut water can be used as an effective

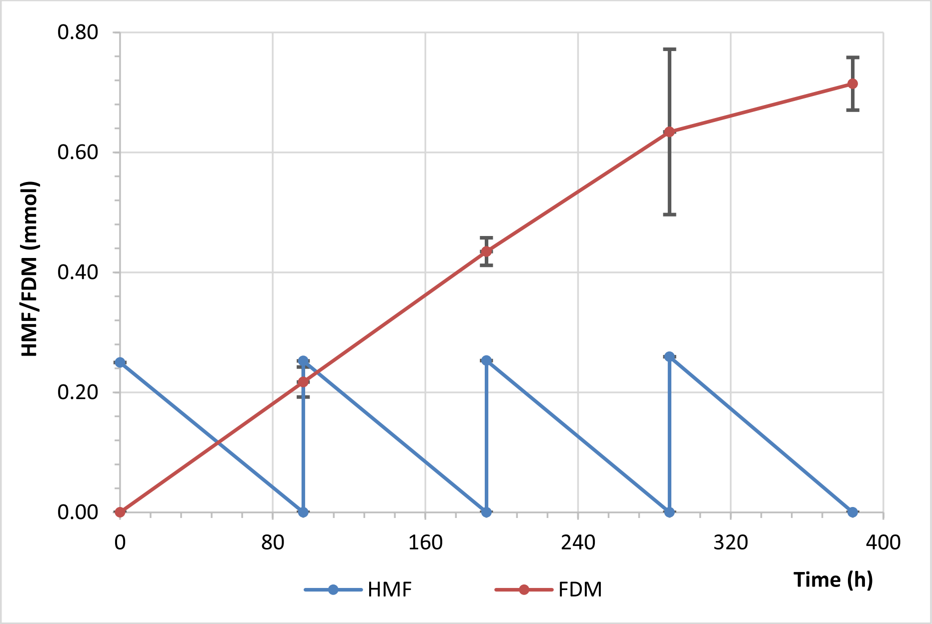

Fig. 5. Changes in the amounts of 5-hydroxymethylfurfural (HMF) and 2,5-furandimethanol (FDM) in the reuse of coconut (*Cocos nucifera* L.) water during the biocatalytic reduction of 5-hydroxymethylfurfural (HMF). Four consecutive additions of 0.25 mmol portions of HMF.

biocatalyst for the reduction of 5-hydroxymethylfurfural (HMF, **1**) to 2,5-furandimethanol (FDM, **2**) at room temperature without the addition of any additional reagents as shown in Fig. 1. The previously reported *E. coli* CCZU-K14 whole cells and yeast strain *Meyerozyma guilliermondii* SC1103 based methods required the addition of glucose as a co-substrate for the reduction of HMF to FDM, whereas the use of inexpensive agricultural by product coconut water eliminate the requirement of using a co-substrate. The experiment was carried out by suspending 0.51 mmol of HMF in 50 mL of coconut water and stirring at room temperature. The reaction was monitored by quantitative LC-MS analysis of a series of 1.0 mL aliquots withdrawn during the reaction. The product formed was confirmed as 2,5-furandimethanol (FDM, **2**) by melting point of the isolated product as well as by 1H NMR spectroscopy; after extraction of the reaction product to ethyl acetate, evaporation of the solvent under reduced pressure and recording the 1H NMR in CDCl3. The 1H NMR was identical to the data reported by Goswami et al. (2008) confirming the identity of the product. The changes in the amounts of 5-hydroxymethylfurfural and 2,5-furandimethanol during the HMF reduction is shown in Fig. 3. The plots of amounts of starting compound and product (mmol) are shown here, instead of the product yield to illustrate the decrease in starting compounds and the rise in product concentrations. The HMF concentration in the reaction medium rapidly decreases after about 50 h and the efficient conversion to FDM is clearly evident from the plot. The practically complete conversion of 0.51 mmol of HMF to 0.49 mmol of FDM was achieved after 96 h of reaction at room temperature. This corresponds to a 96% yield. In a reference experiment to check if any HMF or FDM is formed from natural sugars in coconut water, similar analysis of a coconut water sample without added HMF showed no HMF or FDM in detectable levels after 96 h. Another control experiment using similar concentration of HMF in deionized water and stirring under identical conditions produced no change in HMF after 96 h. Coconut water in mature coconuts is known to contain about 10 mg/mL of sucrose as the major sugar; in addition, glucose and fructose are also present in about 2 mg/mL each (Yong et al., 2009). Sorbitol (15 mg/mL) is the dominant sugar alcohol in coconut water; in addition, mannitol and inositol are also known in minor amounts (Yong et al., 2009). Coconut water is known as a rich source of enzymes: reductase, acid phosphotase, catalase, dehydrogenase, diastase, peroxidase and RNA polymerase, however the quantitative information about these enzymes are rare (Yong et al., 2009), (Prades et al., 2012). As our control experiment without the addition of HMF failed to produce any HMF or FDM after 96 h, we can conclude that the natural sugars in coconut water are not converted to HMF during the process, however these sugars may help as a co-substrate in the reduction of HMF to FDM. The coconut water is reported to contain reductase enzymes with alcohol dehydrogenase systems (Yong et al., 2009), (Prades et al., 2012). Therefore, the reduction of HMF to FDM is most likely due to this reductase activity following the reported reduction mechanism (Yong et al., 2009), (Prades et al., 2012).

In order to prove the wider applicability of the biocatalysis method we have tested the reduction of the HMF dimer 5,5'-[oxybis(methylene)]bis[2-furaldehyde] (OBFA) to the corresponding diol 5,5'-[oxybis(methylene)]bis-[2-furanmethanol] (OBFM) as well. We have recently reported the preparation of this symmetrical dialdehyde-ether from D-fructose in good yields and efficient biocatalytic conversion of this renewable feedstock to the related diol OBFM may provide a useful route to a renewable diol monomer suitable for polyester synthesis (Amarasekara et al., 2017). The changes in the amounts of OBFA and OBFM during the biocatalytic reduction is shown in Fig. 4. In this instance the rapid conversion of the dialdehyde occurs around 25–50 h, and complete disappearance of OBFA was observed after 60 h, and 95% yield was achieved after 96 h. The product formed in the biocatalytic reduction of OBFA was confirmed as OBFM by using 1H NMR spectroscopy as described in the procedure 2.3. The 1H NMR data of the product was identical to the data reported for 5,5'-[oxybis(methylene)]bis-[2-furanmethanol] by Timiko et al. confirming the product (Timko et al., 1977). In addition the melting point of the isolated product was also identical to the reported value (Timko et al., 1977).

Additionally, we have studied the reusability of coconut water as a biocatalytic system for the reduction of HMF by using the same coconut water medium for the conversion of HMF to FDM by consecutive addition of HMF in four catalytic cycles. The results of this experiment are shown in Fig. 5. The coconut water remains active for the reduction of HMF to FDM for four catalytic cycles and the FDM concentration in the medium shows a steady increase during the successive additions of HMF, appears to get completely converted to the reduced product FDM; further the diol formed appears to be stable in the coconut water medium after 384 h.

4. Conclusion

We have shown that coconut water can be used as a biocatalyst without additional co-substrate for the reduction of renewable feedstock 5-hydroxymethylfurfural to 2,5-furandimethanol at room temperature in 96% yield. Similarly the HMF dimer 5,5'-[oxybis(methylene)]bis[2-furaldehyde] can be reduced to the corresponding diol 5,5'-[oxybis(methylene)]bis-[2-furanmethanol] in 95% yield under similar conditions. In addition, we have demonstrated that coconut water can be reused in this biocatalytic transformation. The toxicity effects of sugar dehydration byproducts such as HMF towards yeast are well known and overcoming these inhibitory effects of lignocellulose hydrolyzate poses a significant technical challenge for lower-cost cellulosic ethanol production (Liu, 2011), (Azhar et al., 2017). The use of agricultural by-product coconut water as a biocatalyst provides a simple, inexpensive and efficient method for detoxification of cellulose hydrolyzate before fermentation in cellulosic ethanol industry, as well as in upgrading the biomass derived furan aldehydes to corresponding alcohols useful as renewable feedstocks for the polymer industry.

CRediT authorship contribution statement

Ananda S. Amarasekara: Conceptualization, Writing - original draft, Writing - review & editing. **Cristian D. Gutierrez Reyes:** Data curation, Formal analysis. **Rocio Garcia Obregon:** Methodology.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.bcab.2020.101551.

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