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Enhancing Hydrogen Production from Bioenergy Crops via Photoreforming

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Enhancing Hydrogen Production from Bioenergy Crops via Photoreforming

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Abstract

Photoreforming of perennial bioenergy crops (willow, miscanthus, and poplar) has the potential to generate H₂ with reduced environmental impacts. To understand the compositional effects of the biomass on the average rate of H₂ production over the first 30 min of reaction (*r*H₂), the *r*H₂ of model biomass component (i.e., cellulose, hemicellulose, and lignin) mixtures were compared with those from the raw biomass. The higher cellulose or hemicellulose content in

multi-component mixtures resulted in higher rH_2 , whereas lignin reduced hydrogen production rate. However, with raw biomass, the ratio of biomass components alone did not determine the rH_2 via photoreforming with rates of hydrogen production for different varieties of willow ranging between $1.9 \mu\text{mol h}^{-1}$ and $12.3 \mu\text{mol h}^{-1}$, $11.8 \mu\text{mol h}^{-1}$ for a poplar, and $6.8 \mu\text{mol h}^{-1}$ for a miscanthus biomass. In addition, comparable rH_2 of raw poplar and its extracted cellulose via an IonoSolv treatment indicated the possibility of using raw biomass materials without delignification for generating H_2 via photoreforming. Importantly, the rH_2 was positively correlated with the interaction between water and the biomass, as assessed by NMR relaxometry via an examination of the T_1/T_2 ratio. A stronger water-biomass interaction resulted in a higher rH_2 . Genetic modification of biomass has been suggested as a putative way to improve the rH_2 of biomass with an enhanced interaction with water. This research enhances the understanding of factors influencing H_2 production from lignocellulosic biomass by photoreforming and supports the breeding and management of perennial biomass crops to maximise H_2 yields while minimising land area requirements.

Keywords: Hydrogen production, bioenergy crops, photoreforming, ionic liquid pretreatment, NMR relaxometry

Introduction

Lignocellulosic biomass is an abundant renewable resource. Its utilisation is expected to contribute toward minimizing societal dependence on fossil resource-derived energy and materials. Harnessing the energy stored in the chemical bonds of biomass can complement intermittent renewable energy production, while biomass also provides renewable hydrogen and carbon. There is therefore significant interest in the development of biomass conversion technologies to produce energy, biofuels, chemicals, and materials. Hydrogen has an increasing role in sustainable manufacturing as a fuel, an energy storage vector, and as a reagent in many chemical transformations. This has sparked increasing interest in more sustainable means of producing H₂. Photocatalytic reforming of lignocellulosic biomass is an approach of growing interest for the sustainable production of H₂ in addition to the production of value-added chemicals such as sugars, hydroxymethylfurfural (HMF), and formic acid. It is a light-driven chemical transformation employing a catalyst that generates electron-hole pairs for oxidation and reduction reactions in aqueous solution.^[1] The photon energy needed could be sourced from natural sunlight or sustainable artificial light.

The development of catalysts to enhance photocatalytic efficiency has been an area of intense research in photoreforming systems that typically use organic molecules such as alcohols, aldehydes, carboxylic acid, and carbohydrates as the substrate.^[2] Raw lignocellulosic biomass is an interesting substrate as it requires minimal pre-conditioning, leading to lower processing costs. However, raw lignocellulosic biomass and its primary polymeric components, cellulose, hemicellulose, and lignin, are more challenging substrates for photoreforming due to their insolubility in water, which limits interaction with catalysts and, due to absorbing/scattering the light, reduces the light available for the photocatalysis. The mechanism and rate of hydrogen production from photoreforming of cellulose and lignin (and related small model compounds such as glucose and aromatics) have been investigated previously.^[3] The reforming of isolated lignin substrates has been reported to be slow due to significant absorption of light by the substrate.^[4] Higher rates of H₂ production have been reported using cellulose.^[5] These three biomass components can act as sacrificial agents in photocatalytic hydrogen production^[1]. In biomass photocatalysis, photo-excited holes (h⁺) and electrons (e⁻) pairs are generated when photocatalysts absorb the photon energy equal to or greater than its band gap energy (E_{bg}). Hydrogen can be formed during the reduction of H⁺ by the e⁻. Meanwhile, the reactive oxygen species (ROS) such as hydroxyl radicals (·OH) are formed from the reaction between water and h⁺. The scavenging of h⁺ can improve the separation of e⁻-h⁺ pairs to increase the

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3 efficiency of H₂ production. Biomass components undergo oxidation via direct (by h⁺) and
4 indirect (by ·OH) mechanisms to form reaction intermediates (e.g., glucose and formic acid
5 from cellulose) for further h⁺ or ·OH scavenging. Additionally, H₂ can be produced directly
6 from the protons in biomass via photocatalytic reforming [3a].
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10 H₂ production by photoreforming of raw biomass was first demonstrated in 1980 by Kawai et
11 al.[6] and studies using raw biomass to date have predominantly focussed on catalyst
12 development and characterisation and reaction and/or biomass pretreatment conditions (pH,
13 temperature).[7] The various photocatalytic systems (reactor, catalyst, and light sources) were
14 employed but with controversial conclusions on the comparison of H₂ production yields and
15 efficiencies from raw biomass substrates to the extracted biopolymers, cellulose or
16 hemicellulose. For example, poplar wood chips have been photoreformed over a 1.0 wt.%
17 Pt/TiO₂ catalyst achieving a significantly lower H₂ production rate (26 μmol h⁻¹ g_{cat}⁻¹)
18 compared to α-cellulose (275 μmol h⁻¹ g_{cat}⁻¹) whereas comparable H₂ production rates were
19 reported from cellulose and aspen wood over a Cu/In-doped ZnS catalyst fabricated from the
20 ZIF-8 precursor (74 μmol h⁻¹ g_{cat}⁻¹)[7c] and from cellobiose and poplar powder over a 1%Pt/C-
21 ₃N₄ (73 and 83 μmol h⁻¹ g_{cat}⁻¹ respectively).[7d] The current understanding of biomass
22 photoreforming does not allow assessment of the most efficient raw biomass feedstock to
23 produce H₂ or whether raw biomass is indeed a viable feedstock compared to the extracted
24 biopolymers, cellulose or hemicellulose.
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37 In this study, willow, poplar, and miscanthus were selected and studied as representative
38 biomass resources for their ability of producing hydrogen via photoreforming. Short-rotation
39 coppice (SRC) willow is a perennial UK biomass crop with rapid growth and short harvest
40 cycles, providing high yield per unit area of land with minimal fertiliser input,[8] characteristics
41 also shared by the biomass crops poplar and miscanthus.[8] These crops are currently
42 predominantly used for the generation of heat and electricity,[9] however, screening crops for
43 their activity in biomass conversion technologies could inform varietal crop choices for
44 landowners/growers by linking crop choice to the yield of the product (such as H₂) from the
45 conversion process alongside land-use considerations.
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53 Herein, an initial step in assessing the variability in rH₂ by photoreforming of bioenergy crops
54 willow, poplar, and miscanthus has been undertaken. In particular, the photoreforming of
55 different varieties and stem age of SRC willows was investigated and this is also the first study
56 to report using a miscanthus feedstock to produce H₂ through photoreforming. For poplar, the
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effect of genetically engineering one aspect of the lignin structure on the activity of photoreforming was also considered. The rH_2 for the biomass was compared to the rH_2 for individual polymeric components (cellulose, hemicellulose, and lignin), model mixtures of the polymeric components, and biomass fractionated with the emerging IonoSolv approach that uses low-cost ionic liquid-water mixtures to generate a cellulose pulp and a lignin.^[10] NMR relaxometry was used to measure the interaction strength between the water molecules and the biomass solids. A correlation between the rH_2 and the interaction strength between water and biomass was established based on the NMR relaxometry study.

Results and Discussion

Comparison of hydrogen production rates of raw willow vs pure biomass components

Photoreforming reactions in this study were performed over a solid 0.2 wt.% Pt/TiO₂ catalyst (preparation and characterisation are presented in the **Supporting Information, SI**) that has previously been shown to be effective for a wide range of substrates.^[4,5] The average rate of H₂ production over the first 30 min of reaction (rH_2 , recorded during the first 30 min of irradiation) was used as an indicator for activity; time courses for H₂ and CO₂ production are shown in **Figure S1**. Reactions were performed in water (pH = 7.6) at 35±2 °C. It should be noted that the temperature in the reactor under prolonged UV-LED irradiation increased from an initial temperature of 25-30°C. These mild conditions did not induce degradation/depolymerisation of the biomass allowing comparison of the reactivity of the solid biomass particles with the component biopolymers, cellulose, hemicellulose, and lignin.

Initially, the rH_2 for commercially obtained isolated lignocellulosic components hemicellulose, (HC, xylan from beech wood), microcrystalline cellulose (C, from cotton linters), and organosolv lignin (L, extracted from *Platycodon grandiflorum*) were compared. The rH_2 for hemicellulose was higher than cellulose at 37.0 and 28.8 μmol h⁻¹ (**Figure 1a**), respectively. Although both components are carbohydrate polymers, hemicelluloses possess shorter chain lengths (50-200 sub-units),^[11] have lower molecular weights, are often branched, and are amorphous, whereas cellulose is highly crystalline and fibrillar (5,000-10,000 subunits for cellulose in natural biomass),^[11] which likely accelerates the photoreforming reaction of hemicellulose compared to cellulose.^[12] In contrast, a very low rH_2 of 0.7 μmol h⁻¹ was observed for the photoreforming of organosolv lignin in agreement with previous studies.^[5b] Lignin is a phenylpropanoid polymer and is fundamentally different from cellulose and

hemicellulose. The same order was observed for the CO₂ production rate (r_{CO_2}): hemicellulose (13.6 $\mu\text{mol h}^{-1}$) > cellulose (11.2 $\mu\text{mol h}^{-1}$) > organosolv lignin (1.1 $\mu\text{mol h}^{-1}$) with similar H₂:CO₂ ratios observed for hemicellulose (2.7) and cellulose (2.6).

The impact of biomass variability on r_{H_2} was investigated using *Salix* (willow), a diverse and adaptable genus utilised in the UK. Willow cultivars with different stem ages (1-5 years) grown under a variety of conditions (North and South England) (details provided in **Table 1** and **SI**) were selected as representative biomass samples and their biopolymer component composition was determined using a standard compositional analysis.

Table 1: Details of willow biomass used in this study

Willow variety	Sample code	Stem age at harvest (years)	Harvesting method	Compositional analysis ^a		
				%HC	%C	%L
Roth Cheviot	W1	1	chipped*	15.8	39.6	27.3
Tordis	W2	1	cut stems	16.6	38.6	36.6
Tordis	W3	3	cut stems	19.1	51.6	28.9
Tordis/Tora	W4	5	cut stems	19.5	49.7	26.0
Mixed variety	W5	>3	chipped*	18.9	45.5	30.7

^a Compositional analysis performed by a standard method published by the National Renewable Energy Laboratory (NREL) Version 54 (NREL/TP-510-42620).^[13] Details of compositional analysis procedure can be found in the SI and in the literature.^[14] Detailed data for compositional analyses are shown in Table S2. %Hemicellulose (%HC): sum of xylan, galactan, arabinan, and mannan content; %Cellulose (%C): sum of glucan content (glucan was equated to cellulose content); and %Lignin (%L): sum of acid-soluble and acid-insoluble lignin content. *Note, the storage time of chipped willow samples was not recorded, but cell wall materials are generally considered to be quite stable.

The r_{H_2} varied across the willow samples (**Figure 1b**), with the lowest r_{H_2} observed for W1 and the highest r_{H_2} for W5 at 1.9 $\mu\text{mol h}^{-1}$ and 12.3 $\mu\text{mol h}^{-1}$, respectively. The r_{H_2} for the willows was lower than achieved for the polysaccharide components C and HC (**Figure 1a** and **1b**), even for the most reactive willow sample, W5; however, all willows had higher r_{H_2} than the organosolv lignin (0.7 $\mu\text{mol h}^{-1}$) (**Figure 1a** and **1b**).

The difference in r_{H_2} of these willow samples was not related to the biomass preparation procedure (harvesting method, drying, and grinding). For example, the willows with the smallest and highest r_{H_2} , W1 and W5, were chipped at harvest, whereas the other willow samples were cut and stored as stems; however, it should be noted that all willows were also ground and sieved to size <180 μm (as shown in **Table S1**) prior to the reactions. There was

also no effect on r_{H_2} because of the moisture content of the biomass when comparing air-dried (moisture content around 9% for all willows) or oven-dried biomass (at 80 °C for 48 h, **Table S1**). The effect of biomass particle size range on photoreforming activity was also studied for the most active willow, W5 (**Table S1**). No significant effect on the H_2 production with the size of biomass particles was found when varying the size from 180 μm to 1.8 mm, suggesting that grinding to very small particle size is not needed.

The biopolymer composition of the willow also did not correlate with the photoreforming activity (**Figure S2a** and **S2b**). The hemicellulose content of all the willow samples was roughly similar at 15.8 – 19.5% (**Table 1**), whereas the cellulose (39-52%) and lignin content (27-37%) showed more variation across the willow samples. For example, the cellulose content of W4 was higher than the lignin content (**Table 1**), but the r_{H_2} was like the one observed for W2 that had comparable lignin and cellulose contents. The lack of expected correlation between carbohydrate content and photoreforming suggests that additional factors such as the distribution of biopolymers within the cell wall could be related to the observed differences in r_{H_2} for the willows.

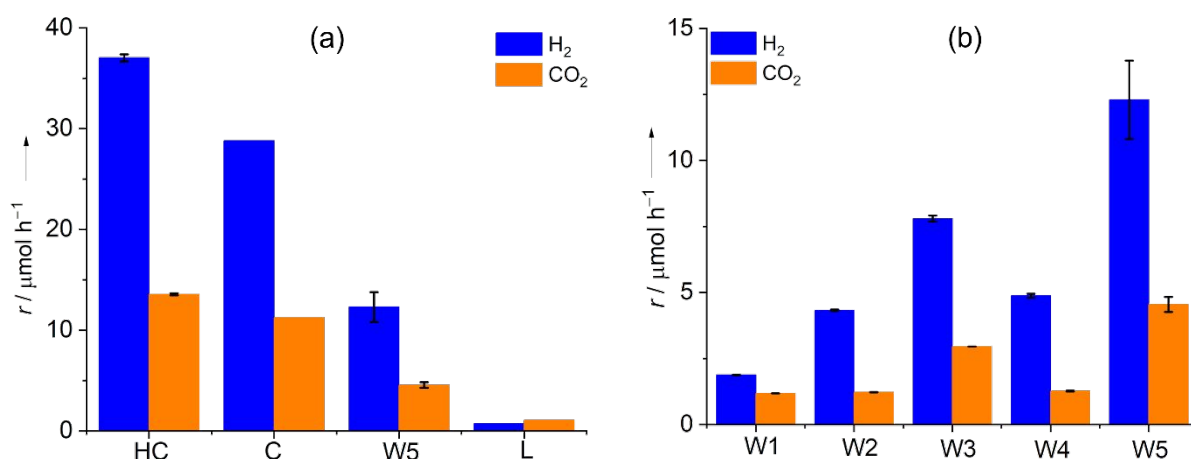


Figure 1. The average rates of gas production over first 30 min reaction (r) obtained from photoreforming of (a) willow of different varieties: W1, 1-year-old Roth Cheviot willow; W2, 1-year-old Tordis willow; W3, 3-year-old Tordis willow; W4, Tordis/Tora 5-year-old and W5, mixed variety willow chips harvested at >3 years old. and (b) pure substrates (hemicellulose, HC; cellulose, C; organosolv lignin, L). Reaction conditions: 1 g L⁻¹ 0.2 wt.% Pt/TiO₂ catalyst and 1 g L⁻¹ substrate in 30 mL water under UV-LED irradiation ($I = \square 43 \text{ mW cm}^{-2}$) at room temperature. The range for data point obtained with duplicate experiments is shown as the error bars. The error bars for cellulose and lignin samples were similar as that for hemicellulose.

Photoreforming of multi-component model mixtures

Multi-component model mixtures were prepared by mixing hemicellulose, cellulose, and lignin in different ratios (**Table 2**) to assess the competitive reactivity of biomass components when present together in aqueous suspension. The rH_2 for component mixtures with different content of hemicellulose, cellulose, and lignin was also examined (**Table 2**). The rH_2 for samples with a cellulose content fixed at 25 wt.%, but varying hemicellulose and lignin contents showed a significant reduction in rH_2 when the amount of lignin was higher. The rH_2 was $21.9 \mu\text{mol h}^{-1}$ for M1 (25 wt.% C + 55 wt.% HC + 20 wt.% L) and $8.1 \mu\text{mol h}^{-1}$ for M3 (25 wt.% C + 20 wt.% HC + 55 wt.% L). When the amount of lignin in the reactor was fixed at 35 wt.% and the cellulose to hemicellulose ratio was varied (i.e., M2: with 35 wt.% L + 45 wt.% C + 20 wt.% HC or in M4: 20 wt.% C and 45 wt.% HC), there was only a small difference in the rH_2 at $13.7 \mu\text{mol h}^{-1}$ and $17.3 \mu\text{mol h}^{-1}$, respectively. Although both hemicellulose and cellulose have shown activity for H_2 production under photoreforming conditions, no correlation was observed between the rH_2 and the amount of hemicellulose or cellulose separately (**Figure S3**). However, when considered together, a correlation between the amount of lignin in the reactor and rH_2 was observed with increasing lignin content reducing the amount of H_2 produced (**Figure S4a**). A similar trend was observed for CO_2 production, as shown in **Figure S4b**. The chromophoric functionalities in lignin can absorb light of wavelength above 300 nm, leading to a reduction in light absorption by the photocatalyst and therefore reducing the activity of H_2 production [3b]. Additionally, during the lignin photoreforming process, the intermediates such as benzoquinone and catechol formed via the aromatic oxidation pathway can poison the photocatalyst by strong adsorption and electron transfer reactions which reduce the H_2 formation on the catalyst [3b].

Table 2: The content of cellulose, hemicellulose, and lignin in the multi component mixtures and their average H_2 production rate during the first 30 min by the irradiation of UV-LED (rH_2 , $\mu\text{mol h}^{-1}$) and production yield during irradiation with UV-LED for 2 h. Reaction conditions: 1 g L^{-1} catalyst and 1 g L^{-1} substrates in 30 mL water with irradiation of UV-LED ($I = 43 \text{ mW cm}^{-2}$) at room temperature. The range for data point obtained with duplicate experiments is shown as the error bars in the table.

Mixture	HC (%)	C (%)	L (%)	Average rate of H_2 production (rH_2 , $\mu\text{mol h}^{-1}$)	H_2 production yield (μmol)
M1	20	25	55	8.1 ± 0.3	19.9
M2	20	45	35	13.7 ± 0.3	32.0
M3	55	25	20	21.9 ± 0.3	44.9
M4	45	20	35	17.3 ± 0.3	34.5

M5	21	36	43	13.4 ± 0.3	27.0
M6	20	42	38	17.1 ± 0.3	37.4

The content of sugars and short chain acids in the liquid phase after the photoreforming reaction of M1 and M2 was also determined (**Table S3**) and compared with that from the pure components. For pure cellulose and hemicellulose, sugars and short chain carboxylic acids (formic and acetic acid) were observed, whereas aromatic compounds (eluting at longer retention times) were the only liquid-phase products observed after photoreforming of lignin, as might be expected. In the multicomponent mixtures, the marker compounds (the compound which is observed uniquely in the liquid products of the photoreforming of each biopolymer, i.e., acetic acid for C, formic acid for HC, and aromatic species for L) were observed, indicating conversion of each biopolymer. Conversely, lignin marker compounds were not observed in the liquid phase when raw biomass (W5 willow) was used, indicating the importance of the biomass structure (biopolymer arrangements and accessibility) in its photoreforming activity. This observation coupled with the fact that the mixed willow (W5) gave the highest rH_2 suggests preferential photoreforming of the cellulose and hemicellulose within the raw biomass. This implies that the accessibility of the cellulose and hemicellulose to the OH radicals generated via the photocatalysis is an important factor in biomass photoreforming and that this varies among raw willow samples.

Photoreforming of miscanthus and poplar bioenergy crops compared to willow

The rH_2 from the willows (milled and pre-dried) indicate that lignocellulosic biomass without chemical pretreatment, for example, may be a viable feedstock for photoreforming. To explore a wider range of bioenergy crops as substrate for photoreforming, the rH_2 for the photoreforming of a miscanthus and a poplar were studied. The sample details of the miscanthus and poplar studied are summarised in the **SI** (Materials and Characterisations).

The measured rH_2 for miscanthus was 6.8 $\mu\text{mol h}^{-1}$ and 11.8 $\mu\text{mol h}^{-1}$ from the poplar (**Figure 2**). The poplar sample generated a rH_2 comparable to the rH_2 observed for W5, the most active willow for photoreforming, whereas the miscanthus sample exhibited 50% of the photoreforming activity of W5. However, the rH_2 for miscanthus was comparable to the average rH_2 of the five willow samples (6.3 $\mu\text{mol h}^{-1}$). Compositional analysis of the biomass samples (**Table S4**) shows no relationship between the cellulose/hemicellulose/lignin content

and rH_2 for miscanthus and poplar, equivalent to the lack of correlation observed for willow (Figure S2).

Photoreforming of IonoSolv fractionated bioenergy crops

Cellulose and lignin present in lignocellulosic biomass can be separated by IonoSolv fractionation (details in Experimental, SI), while hemicellulose is hydrolysed using this approach and removed following solubilisation in the ionic liquid. The IonoSolv cellulose pulps contained native crystalline cellulose (cellulose I structure confirmed by XRD analysis, Figure S5) and hence are like microcrystalline cellulose but provide a more meaningful comparison to the raw biomass being from wood as opposed to the purified, commercial MCC from cotton linters. The rH_2 for the cellulose pulp and lignin obtained using IonoSolv fractionation was compared with the rH_2 obtained for willows W1 and W5, which gave the highest and lowest rH_2 , the raw miscanthus, and the raw poplar (Figure 2). The cellulose pulps demonstrated the highest rate of H_2 production, with higher values for W5 and W1 willow pulps at $18.7 \mu\text{mol h}^{-1}$ and $16.7 \mu\text{mol h}^{-1}$, respectively, and a comparable rate observed for the miscanthus and poplar pulps at $\sim 15 \mu\text{mol h}^{-1}$. The lignins extracted from the different biomass samples gave low activity for H_2 production, with the rH_2 production ranging from 1.3 to $2.1 \mu\text{mol h}^{-1}$, and were comparable to that for organosolv lignin at $0.7 \mu\text{mol h}^{-1}$. The rH_2 for W1, the raw biomass with the lowest photoreforming activity, was comparable to that for the extracted IonoSolv lignin ($1.8 \mu\text{mol h}^{-1}$).

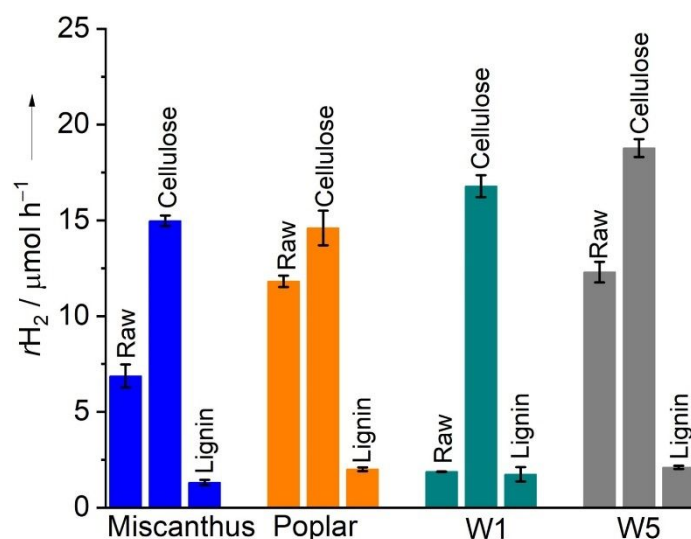


Figure 2. Average H_2 production rate over first 30 min reaction (rH_2) for the photoreforming of various bioenergy crops (a miscanthus, a poplar, W1 and W5 willows) compared to cellulose pulps and lignins generated by IonoSolv fractionation at $170^\circ\text{C}/45$ min for miscanthus and poplar and $150^\circ\text{C}/45$ min for the willow biomass. Reaction conditions: 1 g L^{-1} of $0.2 \text{ wt.}\%$ Pt/TiO₂ catalyst, 1 g L^{-1} raw biomass and

pulps, and lignins in 30 mL water under UV-LED irradiation at 35 °C. UV-LED light intensity: $I = \square 43 \text{ mW cm}^{-2}$. The range for data point obtained with duplicate experiments is shown as the error bars in the figure.

The $r\text{H}_2$ for W1 was comparable to that for the extracted IonoSolv lignin ($1.8 \mu\text{mol h}^{-1}$), whereas the $r\text{H}_2$ for raw W5 and poplar were more comparable to their IonoSolv cellulose pulps and also had a higher $r\text{H}_2$ than their respective lignins (**Figure 2**). The similarity of $r\text{H}_2$ for W5 and the poplar raw biomass and their respective cellulose pulps (**Figure 2**, poplar and W5 willow) suggests that the H_2 production for raw biomass samples could be correlated with the physical properties (morphology, particle size, internal surface area, and porosity) as well as the chemical properties of the biomass (cellulose/hemicellulose/lignin content, localised chemical environment, cellulose crystallinity, hydroxy group content, lignin S/G/H units).^[11a] Indeed, the H_2 production from W1 being comparable to that from its derived lignin (**Figure 2**, W1) would also suggest that the combined chemical and physical properties of the biomass are important for photoreforming activity.

Photoreforming of zip-poplar and IonoSolv fractionated Zip-poplar

A genetically modified “zip-lignin” poplar (labelled Z-Poplar, details in the SI) in which the chemical structure of the lignin had been altered to decrease its recalcitrance to hydrolysis without altering the strength and growth of the tree was also employed. The genetic modification has been shown to alter the cellulose at the microfibrillar level, as it was found to be more disorganised compared to the cellulose in unmodified poplar.^[15] These modifications in the lignin and cellulose of the engineered poplar could prove beneficial for photoreforming. Z-Poplar cellulose pulps and lignin were also generated via IonoSolv fractionation and compared to the unmodified poplar, as shown in **Figure 3**. Photoreforming experiments showed that the genetic modification did not impact the reactivity of the recovered cellulose and lignin, but did alter the reactivity of the raw biomass, with an H_2 yield of $22.3 \mu\text{mol}$ after 5 h of photoreforming for the Z-Poplar compared to $17.2 \mu\text{mol}$ for the unmodified poplar (**Figure 3**). The $r\text{H}_2$ ($14.4 \mu\text{mol h}^{-1}$) and $r\text{CO}_2$ of raw Z-Poplar had a similar $r\text{H}_2$ to that of the recovered cellulose pulp ($r\text{H}_2$, $15.4 \mu\text{mol h}^{-1}$), as shown in **Figures S6**. The genetic modification on biomass could be a way of improving its reactivity of producing H_2 during photoreforming process without extracting out cellulose pulp via IonoSolv fractionation.

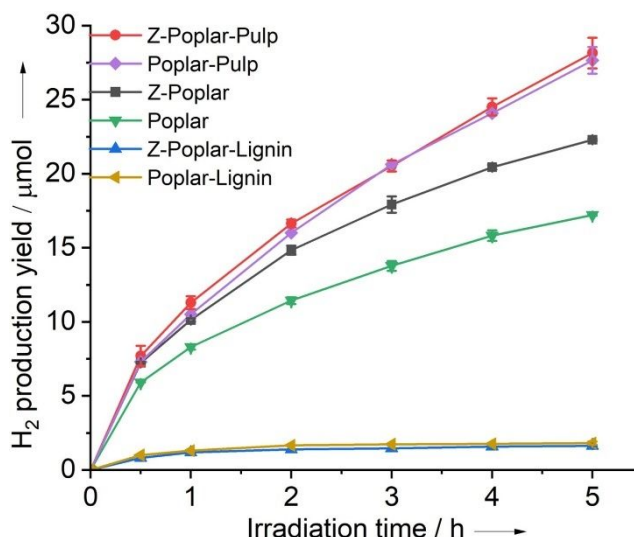


Figure 3. H_2 production as a function of reaction time for photoreforming of wild-type poplar and genetically modified poplar compared to cellulose pulps and lignins isolated from both poplars at $170^\circ\text{C}/45\text{ min}$. Reaction conditions: 1 g L^{-1} catalyst, raw biomass and pulps, and 0.25 g L^{-1} lignin in 30 mL water under UV-LED irradiation at room temperature. UV-LED light intensity: $I = 43\text{ mW cm}^{-2}$. The range for data point obtained with duplicate experiments is shown as the error bars in the figure.

Effect of interaction between water and substrates

Lignocellulosic biomass is a hierarchical, porous, anisotropic composite material that can vary with plant species as well as growing conditions.^[16] Previous work has shown that the nuclear magnetic resonance (NMR) T_1/T_2 relaxation ratio is a robust indicator of surface interactions occurring between a guest molecule and solid surfaces of porous media,^[17] and is largely independent of the internal morphology of the porous medium. A recent study demonstrated the usefulness of the method in the study of a biomass material (walnut shells) used for adsorption applications.^[18] As mentioned above, the H_2 production for raw biomass can be correlated to its physical and chemical properties rather than its bulk composition. The interaction strength of a guest molecule and solid is affected by the physical and chemical properties of the solid surface.^[19]

In general, photogenerated electrons (e^-) and holes (h^+) are formed over the photocatalyst when sufficient photo energy (greater than the bandgap energy of the catalyst) is absorbed by the photocatalyst. In an aqueous system, water is adsorbed on the catalyst and dissociated into H^+ and OH^- . The OH^- is oxidised by the h^+ to form $\cdot\text{OH}$ radicals, while H^+ in the system is reduced by the e^- to form H_2 .^[4] *In situ* (photo)hydrolysis of biomass (action of photogenerated $\text{H}^+/\cdot\text{OH}$) is likely to be promoted in biomass samples in which water has greater mobility/access to the more hydrophilic and reactive biomass components. Water has been identified to play the role

of a proton-conduction medium, able to transport H^+ ,^[20] in the autohydrolysis of biomass, H_3O^+ (a protonated H_2O molecule) was reported to play a role in the penetration of biomass structure aiding hemicellulose hydrolysis.^[21] The mechanism indicates it is the activated water ($\cdot\text{OH}$) that interacts with the solid biomass causing hydrolysis and decomposition to H_2 . Without this interaction the system (i.e., solid biomass and solid catalysts in an aqueous system) does not operate. The interaction between water molecules and biomass solids was therefore measured to provide the information of this interaction strength affecting on the $r\text{H}_2$. Herein, the NMR T_1/T_2 ratio was used to probe the interaction strength of water with biomass samples (details can be found in the SI) to identify the effect of this interaction on the photoreforming of raw biomass.

The NMR T_1/T_2 ratios of water in the lignocellulosic biomass samples are summarised in **Table S5**. As shown in the table, the experimental data fall within two groups of values: a group comprising poplar and W5, showing higher ratios at around 5.7; and the group of miscanthus, W1, W2, W3, and W4 willows showing lower ratios at around 2.5. A clear correlation can be seen (**Figure 4**) between the T_1/T_2 values and their initial production rates of H_2 from photoreforming. The interaction of water with poplar was increased for the Z-Poplar sample and follows the correlation observed between $r\text{H}_2$ and NMR T_1/T_2 ratio. With little structural differences between the lignin of the poplar and Z-Poplar, the enhanced H_2 production may be attributed to changes in the cell wall porosity and/or modification of the cellulose structure, resulting in improved access/interaction of water.

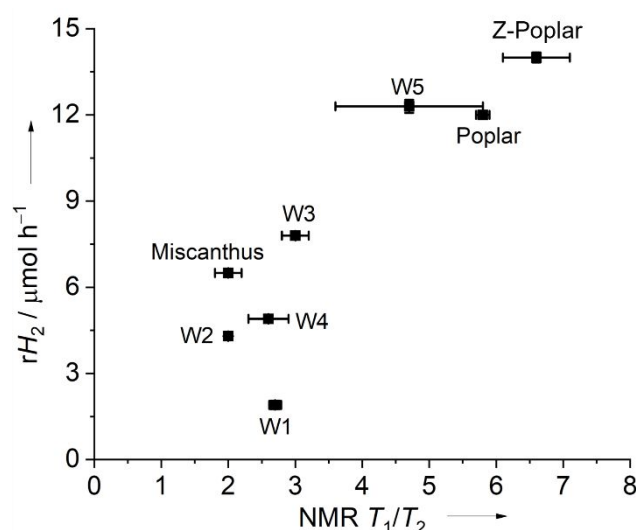


Figure 4. Correlation of NMR T_1/T_2 and the average production rates of H_2 over the first 30 min reaction ($r\text{H}_2$) from the photoreforming of biomass (willow, miscanthus and poplar): W1 – 1-year-old Roth Cheviot willow, W2 – 1-year-old Tordis willow, W3 – 3-year-old Tordis willow, W4 – Tordis/Tora 5-

year-old and W5 – mixed variety willow chips harvested at >3 years old. The standard deviation for data point obtained with repeated experiments (3-4 times) is showed as the error bars in the figure.

The higher NMR T_1/T_2 values indicates a higher interaction strength, on average, between water and the biomass. This suggests that photoreforming activity is related to the strength of interaction between water and biomass components. In this context, the NMR results reported in **Figure 4** suggest that water interaction with the substrate plays a key role in determining the reactivity of the system, and NMR relaxation measurements can be used as a predictive indicator for reaction performance. This correlation could be extended to pure components (C and L, as shown in Figure S14, SI), however, the IonoSolv extracted cellulose and lignin samples did not follow the trend for the raw biomass samples. This is thought to be due to residual ionic liquid being present following the IonoSolv treatment.

Conclusions

Several bioenergy crops, including different varieties of willow and two poplar (wildtype and genetically modified), and one type of miscanthus, were studied as substrates for photoreforming and shown to produce H_2 . Willow generated H_2 at widely varying rates between 1.9 and 12.3 $\mu\text{mol h}^{-1}$, with poplar and miscanthus falling within that range with 11.8 $\mu\text{mol h}^{-1}$ and 6.8 $\mu\text{mol h}^{-1}$, respectively with the Z-Poplar showing highest rH_2 of 14.4 $\mu\text{mol h}^{-1}$. Although the rH_2 was generally lower for raw biomass than for cellulose or hemicellulose, the raw poplar samples (wild type and poplar with a genetic modification of the lignin) exhibited rH_2 approaching those achieved with cellulose pulps obtained with Ionosolv fractionation. The varied rH_2 from the photoreforming of raw bioenergy crops highlights the potential benefits from considering conversion activity in conjunction with parameters such as yield per land area in breeding programmes and varietal crop selections. We additionally demonstrate the potential added value of NMR T_1/T_2 analysis in screening biomass feedstocks for H_2 production as a convenient alternative to calculating the level following a determination of the amount of each of the polymer components in the raw biomass. Assessment of the interaction between water and biomass could be part of a characterisation toolkit of biomass properties, linking to mechanistic insights and photoreforming system optimisation for biomass feedstocks (reactor and catalyst design and light source).

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Author Information Notes

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Associated Content

Experimental section (Materials and Characterisation; Procedure of Ionosolv Treatment and Characterisations; Photocatalytic Reforming Reaction; Nuclear Magnetic Resonance Spectroscopy NMR T_1/T_2 measurements) and supporting tables and figures are included in the Supporting Information (SI)

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TOC Graphic

