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Metal triflates are tunable acidic catalysts for high yielding conversion of cellulosic biomass into ethyl levulinate

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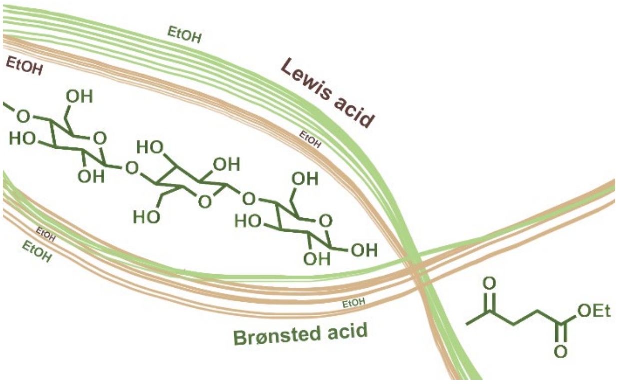
Abstract: Metal triflates and their mixtures with Brønsted acids are excellent catalysts for the selective and high yielding transformation of microcrystalline cellulose into ethyl levulinate, in ethanol, producing synergistic catalyst effects in some instances. The pretreatment of raw and unrefined cellulosic materials with a deep eutectic solvent enables similarly excellent catalysed conversion thereof into ethyl levulinate in superb yield (up to 75%) and selectivity (up to 88%). When using fermentation-derived ethanol, the product possesses 100% renewable content.

Keywords: Biomass, cellulose, acid catalysis, deep eutectic solvents, green chemistry



1. Introduction

Cellulose is the most naturally abundant polysaccharide with the scale and potential to reduce reliance on fossil-derived resources [1,2]. In the presence of acid catalysts, cellulose may be transformed into a large portfolio of organic building block molecules (platform chemicals) creating a potentially inexhaustible source of carbon neutral bulk chemicals [1–4]. The direct conversion of cellulosic materials into desirable products is challenging, involving a complex set of reactions that relies differentially upon Brønsted acid catalysis and Lewis acid catalysis [2,5]. Besides these stringent requirements of the catalyst, complexities arise because of the low selectivity of many processes and the forcing conditions required to promote catalytic reactions [2]. To circumvent the difficulties associated with cellulosic substances, many current practices employ edible low molecular weight saccharides as substrates (e.g., sucrose, glucose, or fructose), or pretreated cellulose, such as microcrystalline cellulose (MCC is obtained by treatment of wood pulp with mineral acids) or ball-milled cellulose [2,6–8]. The use of food sources in chemical processes, along with energy demanding pretreatment of native cellulose, reduce the overall sustainability of biorefinery and may become a source of ethical and social concerns. There is thus an imperative to develop new and efficient catalytic systems to perform the complexity of tasks requisite to transform native cellulose into desirable platform chemicals under mild processing conditions.

Metal trifluoromethanesulfonates (metal triflates) are a class of green homogeneous acidic catalysts, which have been efficiently employed in a number of chemical processes, including valorisation of polysaccharides [5,9–13]. These catalysts are able to selectively promote Lewis acid catalysed reactions, or Brønsted acid catalysed processes through Lewis acid-assisted Brønsted acidity [5,14,15]. Several elegant studies have led to deeper insights into the role of metal triflates in the catalytic valorisation of carbohydrates in methanol [5,8,11]. The processes detailed in these papers demonstrate the transformation of glucose, MCC, or ball-milled cellulose, into methyl levulinate or into α-hydroxy methyl esters. For example, $Sn(OTf)_2$ catalyses the formation of a small range of α-hydroxy methyl esters in good yield, directly from cellulose [8]. Such cellulose-derived low molecular weight esters hold significant promise for industrial applications, including the production of fuels, plastics and other speciality chemicals [8,16,17]. The valorisation of cellulosic biomass into alkyl levulinates other than methyl levulinate, has remained somewhat overlooked. Very few catalysts, such as sulfuric acid or aluminium sulfate, have been reported for the direct transformation of cellulose into ethyl levulinate and other alkyl levulinates, with moderate performance. Other methods rely mostly on the catalytic reaction of low molecular weight saccharides and levulinic acid [17,18]. In the present work, we develop a method to perform the direct and selective conversion of cellulosic biomass into ethyl levulinate (ELev). In particular, we investigate the activity of metal triflates, Brønsted acids, and Lewis acid-assisted Brønsted acids in catalytic reactions of MCC in ethanol. We develop a sustainable method to pretreat unrefined cellulose using a deep eutectic solvent (DES) and ultimately apply the optimised methods to the valorisation of low-value cellulosic materials.

2. Materials and Methods

2.1. Materials

Microcrystalline cellulose, metal triflate catalysts ($Al(OTf)_3$, $Y(OTf)_3$, AgOTf, $In(OTf)_3$, $Sn(OTf)_2$, $La(OTf)_3$, $Yb(OTf)_3$, or $Hf(OTf)_4$, with purity 97.0–99.9%) and choline chloride (> 98%) were used as supplied from Sigma-Aldrich (Australia). *p*-Toluenesulfonic acid monohydrate (> 98%, Sigma-Aldrich, Australia) was dried under reduced pressure (60 °C, 1 mbar, 12 h) to generate anhydrous TsOH [5]. Analytical grade ethanol (water content of < 0.2%), phosphoric acid (H_3PO_4, 85 wt% aqueous solution) and oxalic acid dihydrate (> 99%)

were used as received from Chem-Supply (Australia). Wood pulp (*Pinus*), cellulose extracted from eucalyptus and *Pinus* (unbleached and bleached, BKT, Kinleith, New Zealand) were a generous gift from Dr Simon Hinkley, The Ferrier Research Institute, Victoria University of Wellington (New Zealand). Softwood chips were sourced from local growers (Australia). The content of cellulose in the substrates was established by a standard analytical procedure NREL/TP-510-42618 [19]. The DES based on choline chloride and oxalic acid dihydrate (1:1 molar ratio) was prepared according to reference [20].

2.2. Acid-catalysed conversion of cellulose

Cellulose (50 mg), ethanol (4.00 mL), metal triflate ($Al(OTf)_3$, $Y(OTf)_3$, AgOTf, $In(OTf)_3$, $Sn(OTf)_2$, $La(OTf)_3$, $Yb(OTf)_3$, or $Hf(OTf)_4$, 0.05 mmol) and/or Brønsted acid (H_3PO_4, or TsOH, 0.05 mmol) were introduced to a 10 mL teflon lined stainless steel autoclave equipped with a magnetic follower and the reactor was sealed. The mixture was heated and stirred at the predetermined temperature for a fixed period of time. After completion of the process, the reactor was cooled in an ice bath. The reaction mixture was centrifuged (3,000 × g for 20 min) to recover the ethanol phase and unreacted substrate. The recovered solution was analysed by chromatography, as detailed in the Supporting information, to provide the yield of ELev specified in the main text. The recovered solids were washed with aqueous ethanol (95 vol%, 3 × 10.0 mL), vacuum oven-dried (60 °C, 1 mbar, 6 h) and weighed to calculate the conversion of substrate specified in the main text. Isolated ELev gave satisfactory analytical data (Fig. S1 and S2, Supporting information) [21]. Additional details of analytical procedures and general methods are specified in the Supporting information.

2.3. Pretreatment of cellulose

Cellulosic biomass (eucalyptus cellulose, *Pinus* cellulose, wood pulp, or softwood chips, 500 mg) and choline chloride/oxalic acid dihydrate solvent (1:1 molar ratio, 10.000 g) were introduced to a round-bottom flask equipped with a thermometer and magnetic follower and the mixture was heated and agitated at 80 °C for 2 h, resulting in a turbid suspension. The mixture was diluted with water (30.0 mL) to precipitate cellulose, which was recovered, washed with aqueous ethanol (3 × 30.0 mL, 95 vol%), vacuum oven-dried (60 °C, 1 mbar, 6 h) and weighed to determine the yield (Table S1, Supporting information). The recovery of the DES comprised extraction with ethyl acetate (2 × 30 mL) to remove traces of non-polar by-products (5-(hydroxymethyl)furfural, furyl hydroxymethyl ketone, and furfural, as established by HPLC trace analysis), followed by evaporation of water under reduced pressure (45 °C, 10 mbar).

3. Results and Discussion

The activity of a range of metal triflates ($Al(OTf)_3$, $In(OTf)_3$, $Sn(OTf)_2$, $Hf(OTf)_4$, $Y(OTf)_3$, AgOTf, $La(OTf)_3$, or $Yb(OTf)_3$) was explored for the catalytic conversion of MCC in ethanol media at 160 °C for 4 h (reaction parameters were selected based on exploratory work probing the conversion of cellulose in ethanol under various processing conditions (not shown); the specified reaction temperature and time are optimal for the present catalytic study). Table 1 demonstrates that *hard* Lewis acids (based on Pearson's HSAB principles) [22,23], such as $Al(OTf)_3$, $In(OTf)_3$, $Sn(OTf)_2$, or $Hf(OTf)_4$, catalysed the direct transformation of cellulose into ELev (yield up to 32 mol%, based on anhydroglucose units present in cellulose, Table 1, entries 1, 4, 7, 10), in moderate selectivity towards the product (ELev selectivity up to 46 mol%, Table 1, entries 1, 4, 7, 10); no conversion of cellulose was observed without addition of the acidic catalyst (Table 1, entry 28). The conversion of cellulose into alkyl levulinates proceeds via the cascade of Brønsted acid and Lewis acid catalysed reactions shown in Scheme 1. This involves solvolysis into low molecular weight carbohydrates, aldose-ketose isomerisation, dehydration into furaldehydes (converting into acetals in the presence of ethanol), and rehydration thereof into levulinic acid derivatives [2,5]. This suggests that *hard* Lewis acids ($Al(OTf)_3$, $In(OTf)_3$, $Sn(OTf)_2$, and $Hf(OTf)_4$) possess the Brønsted acidity required to catalyse the various processes towards ELev, as represented in Scheme 1. In previous instances, the required Brønsted acidity was achieved by the addition of sulfonic acids [11] or the hydrolysis of Al salts [18]. pH measurements of aqueous ethanolic solutions of various metal triflates confirmed that *hard* Lewis acids possess strong Brønsted acidity. This acidity is attributed to Lewis acid-assisted Brønsted acidity, derived from the complexation of the metal centre with a protic solvent (Scheme 2) [5,15]. The origin of the acidity with metal triflates is thus distinctive: Metal salts such as sulfates, chlorides, or nitrates hydrolyse into the corresponding Brønsted acids in aqueous methanol [18]. Conversely, and in distinct contrast, metal triflates provide Lewis acid-assisted Brønsted acidity, without hydrolysis [5,10,13,15,24]. Chromatographic-analysis of the reaction mixture (details of are presented in the Supporting information) showed only trace amounts of glucose, 5-(hydroxymethyl)furfural, diethyl acetals of the furan derivatives, and 5-(ethoxymethyl)furfural, respectively. These are putative intermediates towards ELev (Scheme 1), supporting the proposed pathway. However, there was also a mass of dark-brown high molecular weight by-product humins (condensation products of intermediate saccharides with aldehydes [5,25]), which immediately accounts for the mass losses and reduced selectivity to ELev (Table 1). In contrast to *hard* Lewis acids, *soft* Lewis acidic metal triflates, such as $Y(OTf)_3$, AgOTf, $La(OTf)_3$, or $Yb(OTf)_3$, failed altogether to catalyse the conversion of the MCC into ELev or into by-product humins. Instead, they provided only moderate mass losses of cellulose (conversion of MCC up to 23 mol%, Table 1, entries 13, 17, 20, 23), possibly due to the ethanolysis thereof into ethanol-soluble oligosaccharides. The poor performance of soft Lewis acids is likely due to their weak interaction with hard *O*-containing substrate and the ensuing overall lower Brønsted acidity, as is evident from pH measurements (Table 1). Brønsted acid catalysts (TsOH and H_3PO_4, Table 1, entries 26, 27) provided similar outcomes, i.e. low conversion of MCC. In previous work, TsOH enabled conversion of MCC in methanol at the higher temperature of 180 °C, predominantly into 'sugars' (yield 78 %) but also into some methyl levulinate (yield 20 %) [11].

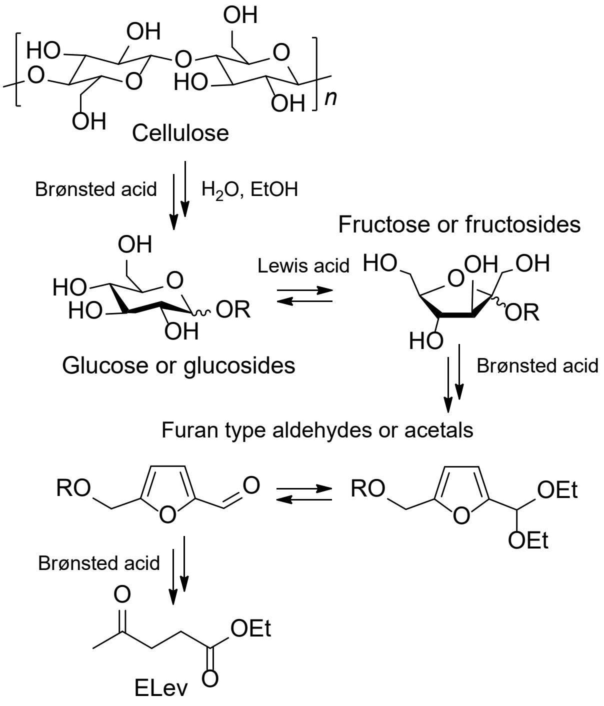
Table 1. Acid-catalysed transformation of microcrystalline cellulose into ELev [a]

Entry	Acid catalyst	Conv (%)	ELev yield (%)	ELev selectivity (%)	pH [b] 0.01 M
1	Al(OTf)$_3$	74	32	43	1.82
2	Al(OTf)$_3$/TsOH	68	59	87	1.81
3	Al(OTf)$_3$/H_3PO_4	60	20	33	1.64
4	In(OTf)$_3$	79	20	25	1.59
5	In(OTf)$_3$/TsOH	63	45	71	1.63
6	In(OTf)$_3$/H_3PO_4	61	37	61	1.52
7	Sn(OTf)$_2$	50	23	46	1.51
8	Sn(OTf)$_2$/TsOH	60	52	87	1.59
9	Sn(OTf)$_2$/H_3PO_4	43	25	58	1.65
10	Hf(OTf)$_4$	73	24	33	1.33
11	Hf(OTf)$_4$/TsOH	82	57	70	1.49
12	Hf(OTf)$_4$/H_3PO_4	78	47	60	1.51
13	Y(OTf)$_3$	15	0	0	3.97
14	Y(OTf)$_3$/TsOH	46	27	59	1.89
15	Y(OTf)$_3$/H_3PO_4	78	68	87	1.54
16 [c]	Y(OTf)$_3$/H_3PO_4	85	75	88	1.54
17	AgOTf	2	0	0	4.63
18	AgOTf/TsOH	22	0	0	1.95
19	AgOTf/H_3PO_4	1	0	0	2.08
20	La(OTf)$_3$	10	0	0	4.23
21	La(OTf)$_3$/TsOH	42	14	33	1.88
22	La(OTf)$_3$/H_3PO_4	68	53	78	1.54
23	Yb(OTf)$_3$	23	0	0	3.62
24	Yb(OTf)$_3$/TsOH	50	24	48	1.91
25	Yb(OTf)$_3$/H_3PO_4	83	53	64	1.59
26	TsOH	35	0	0	1.69
27	H_3PO_4	12	0	0	3.50
28	none	0	0	0	5.60

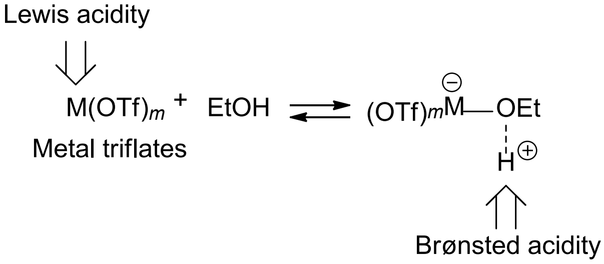
[a] Reaction outcomes are specified in mol% based on anhydroglucose unit present in cellulose. OTf = trifluoromethanesulfonate. TsOH = *p*-toluenesulfonic acid. Reaction conditions: MCC (50 mg), ethanol (4.00 mL), catalyst (0.05 mmol; 0.05 mmol each acid for combined catalysts), 160 °C, 4 h.

[b] pH readings were performed in triplicate in aqueous ethanol (95 vol% of alcohol) at room temperature.

[c] Reaction temperature = 180 °C, time = 2 h.

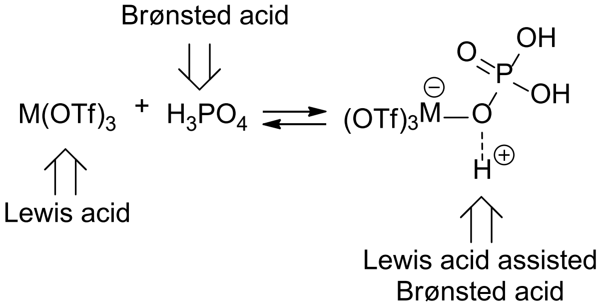


Scheme 1. Acid-catalysed transformation of cellulose into ELev. n = integer, R = H or Et.



Scheme 2. Origin of Brønsted acidity by the interaction of Lewis acidic metal triflates and ethanol. m = 1–4, M = metal.

We have previously reported significant improvements to catalysed processes when employing specific targeted mixed Lewis-Brønsted acid systems with demonstrated synergistic effects [5,13,24]. Mixed acid systems have been specifically employed in the catalytic transformation of (poly)carbohydrates into platform chemicals in aqueous or methanol media [5,11], and we considered that this approach may benefit the present research. In particular, our previous work has highlighted that the combination of low activity metal triflates such as La, Gd, and Yb in combination with phosphoric acid, not sulfonic acids, produces synergistic effects [24]. That study also showed that a 1:1 ratio of metal triflate/H_3PO_4 was optimum. We therefore investigated the conversion of MCC in ethanol applying mixtures of Lewis acidic metal triflates and TsOH or H_3PO_4. As is evident from Table 1, combined acids provided higher yield and selectivity to ELev, with the exception of AgOTf (Table 1, entries 17–19), which gave no transformation of cellulose into ELev under the prevailing reaction conditions. Specifically, *hard* Lewis acids in combinations with TsOH improved the yield of ELev (yield up to 59 mol% with $Al(OTf)_3$/TsOH, Table 1, entry 2), most likely due to the selective solvolysis of cellulose into intermediate low molecular weight saccharides catalysed by the Brønsted acidic counterpart (Scheme 1) [2,11]. This is consistent with previous studies [11]. In the previous work [11], similar effects were achievable with mixed $In(OTf)_3$ and various sulfonic acids in the transformation of cellulose into methyl levulinate. The authors [11] note that TsOH (Brønsted acid) mostly improved the rate of the solvolysis into soluble sugars, while $In(OTf)_3$ (Lewis acid) effectively promoted the subsequent conversion of monosaccharides into methyl levulinate, likely via Lewis acid-catalysed aldose-ketose isomerisation (Scheme 1). Therefore, the two acids (Brønsted sulfonic acid and *hard* Lewis) separately and independently improved different catalytic reactions of cellulose towards methyl levulinate by additive effects [11]. H_3PO_4 had an inhibitory effect on *hard* Lewis acids. In contrast, we have shown that *soft* Lewis acid-Brønsted acid combinations produce *synergistic* effects [5,13,24] leading to dramatic increases of the catalytic activity through a Lewis acid-assisted Brønsted acidity mechanism [14,15], especially highlighted by combinations of group 3 metal triflates with H_3PO_4 (Table 1, entries 15, 16, 22, 25). Noticeably, individual *soft* Lewis acids, or Brønsted acids, did not promote the conversion of cellulose into ELev (Table 1, entries 13, 20, 23, 26, 27), affording only low conversions of cellulose. In combination, however, rather active catalysts are formed via an assisted acidity mechanism (Scheme 3), which is capable of promoting all stages of catalytic process (Scheme 1) [14,15].



Scheme 3. Origination of Lewis acid assisted Brønsted acid complex by the interaction of metal triflates and phosphoric acid. M = Y, La or Yb.

The manifestation of the Lewis acid-assisted Brønsted acidity is immediately apparent from pH readings of aqueous ethanolic solutions of mixed Lewis acids and H_3PO_4 or TsOH. It is notable that triflates of Al, In, Sn, and Hf produced more or less consistent pH reading in the presence or absence of added Brønsted acids. Evidently, the *hard* Lewis acids already produce high Brønsted acidity from the metal-solvent interactions, which is scarcely strengthened by the presence of the Brønsted acids. Also notable is that mixtures of soft Lewis acids with TsOH gave mixtures with higher pH (i.e. less acidic) than neat TsOH. The standout is the mixtures of soft Lewis acids with phosphoric acid (Table 1, entries 15, 19, 22, 25), where highly acidic media are generated, which are significantly more acidic than either reacting partner. Soft metal triflates have been demonstrated by NMR spectroscopy to strongly coordinate to phosphoric acid [24], thereby enhancing its acidity. The experimental results shown in Table 1, entries 15, 19, 22, 25, perfectly reflect the improved catalysts; in particular, $Y(OTf)_3/H_3PO_4$ offered superb selectivity towards desirable products without significant formation of by-product humins (ELev yield 68 mol%, selectivity 87 mol%, Table 1, entry 15). Even higher yields and selectivity to ELev can be reached with combined acid catalyst $Y(OTf)_3/H_3PO_4$ at slightly elevated temperatures (75 mol% yield and 88 mol% selectivity, 180 °C, 2 h, Table 1, entry 16).

We sought to better understand the origins of the catalyst activity and conducted a spectroscopic study of metal triflates in ethanol media. Interrogation of the IR spectra confirmed that individual Lewis acids coordinate to solvent molecules, possibly as represented in Scheme 2. This is shown by changes to the O–H stretching mode of ethanol (Fig. 1) [26]. Deconvolution of the hydroxyl region confirmed the occurrence of two peaks (Fig. 1), which we assign to free solvent and secondly to ethanol present in the coordination sphere of the metal centre (Scheme 2). The complexation of ethanol with metal triflates is also evidenced by the appearance of a C–O stretching vibration near 1175 cm^{-1} (Fig. 2c and Fig. S3, Supporting information) [26]. The free solvent has corresponding vibrations at 1087 and 1044 cm^{-1} (Fig. S3, Supporting information). This solvent-solute interaction accounts for the formation of Lewis acid-assisted Brønsted acid complexes (in the form of $[M(OTf)_n]$—OEt···H, where M = metal), explaining the amplified Brønsted acidity of metal triflates (Table 1 and Scheme 2) [5,10,15]. IR studies of mixed Lewis-Brønsted acids revealed that characteristic vibrations for TsOH were only slightly perturbed in the presence of metal triflates, suggesting weak or no interactions between the two entities (Fig. 2a, d and Fig. S4, Supporting information). In sharp contrast, the P–OH stretching mode at 995 cm^{-1} and $O{=}PO_3$ deformation mode at 490 cm^{-1} associated with free H_3PO_4 reduced dramatically in combination with *soft* Lewis acids (Fig. 2b, e and Fig. S4, Supporting information) [27,28]. It remains evident with $Al(OTf)_3$ and to a lesser extent with $In(OTf)_3$, indicative of poorer binding. This observation points to the favourable complexation between Lewis acids and phosphoric acid, which, in the cases of soft Lewis acids, leads to high Lewis acid-assisted Brønsted acidity (Scheme 3). These data perfectly correlate with the synthesis outcomes and help to rationalise the experimental observations in the catalytic reactions of cellulose (Table 1). Importantly, the results show definite *synergistic* effects in the present work, which are clearly distinct from the previously noted *additive* effects [11], or catalysts generated by hydrolysis of metal salts [18].

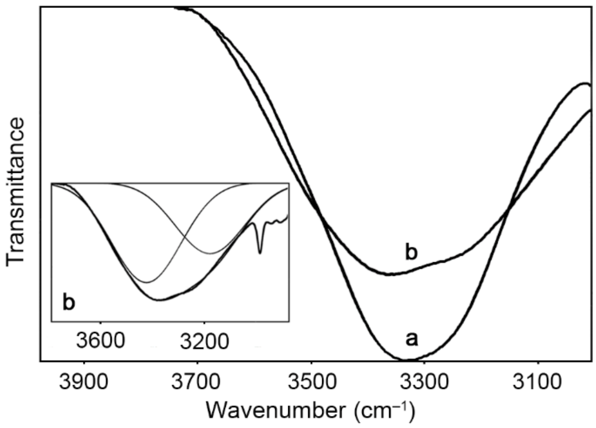


Fig. 1. IR spectra of a) ethanol and b) ethanol 0.1 M solution of $Y(OTf)_3$ in ethanol. The inset shows the deconvoluted spectra of b.

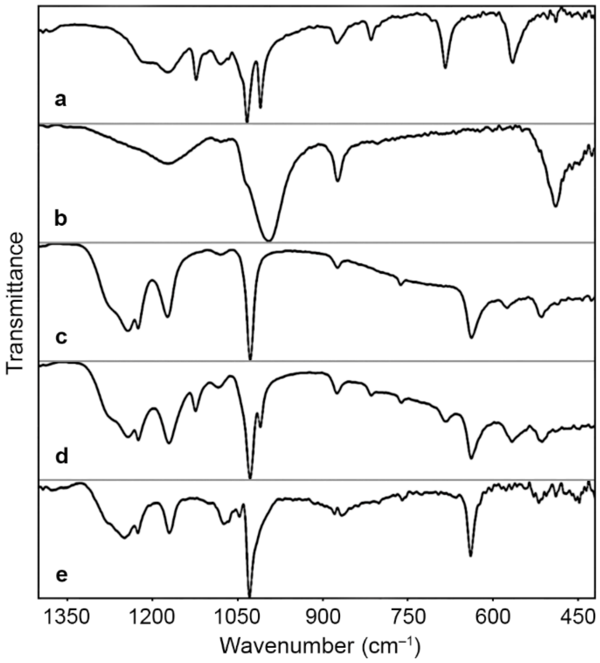


Fig. 2. IR spectra of 0.1 M ethanol solutions of a) TsOH, b) H_3PO_4, c) $Y(OTf)_3$, d) $Y(OTf)_3$/TsOH and e) $Y(OTf)_3/H_3PO_4$. Ethanol peaks were subtracted from spectra. Characteristic vibrations of triflates (1244, 1226, 1030, 763, 640, 577 and 517 cm^{-1}) correspond with data reported in the literature [29].

With the view to converting other cellulosic sources into ELev, we conducted the direct processing of cellulose obtained from eucalyptus and *Pinus* (bleached and unbleached cellulose), wood pulp and softwood chips, in ethanol, employing our catalytic system $Y(OTf)_3/H_3PO_4$ at 180 °C for 2 h (Table 2). As mentioned, MCC is a material obtained by the treatment of native cellulose and is relatively widely used as a medium value commercial product [7]. However, the use of low value or waste cellulosic streams is more desirable and is investigated in the present study. Reactions of native cellulose were less efficient than MCC (Table 2, entry 1, 2, 4, 6, 8, 11). Apparently, the rigid molecular structure of bulk cellulose affected the mass transfer processes restricting the accessibility of the catalyst and the solvent-reagent to the substrate [1,2,6]; this is mostly because of the larger particle size of the bulk cellulose and higher molecular weight of the native polysaccharides, which factors altogether reduced the rate of catalytic reactions [2,8]. In addition, the transformation of native cellulose was accompanied by the formation of humins, reducing selectivity of the valuable product. This may become a serious obstacle for large volume processes. While this potential hurdle is commonly overcome at a bench scale by ball-milling of cellulosic substrates [2,8], or other drastic methods [30], the problem of energy efficient pretreatment remains essentially unsolved.

Table 2. Acid-catalysed transformation of cellulosic biomass into ELev [a]

Entry	Substrate	Conv (%)	ELev yield (%)	ELev selectivity (%)
1	MCC	85	75	88
2	Eucalyptus cellulose	78	59	76
3 [b]		81	72	89
4	*Pinus* cellulose	81	68	84
5 [b]		83	73	88
6	*Pinus* cellulose (unbleached)	80	65	81
7 [b]		85	75	88
8	Wood pulp (*Pinus*)	64	53	–
9 [b]		80	62	–
10 [b,c]		81	62	–
11	Softwood chips	77	52	–
12 [d] [36]	Wood pulp (*Pinus*)	–	26	–
13 [d] [36]	Wood chips (*Pinus*)	–	17	–
14 [e] [37]	Cellulosic fibre	–	45	–
15 [f] [11]	MCC	–	75 (MLev)	–
16 [g] [18]	MCC	100	71 (MLev)	71 (MLev)

[a] Reaction outcomes are specified in mol% based on anhydroglucose unit present in cellulose. Conversion and yield are specified in wt% based on the total carbohydrate content in substrate for wood pulp and softwood chips because both cellulose and hemicellulose (another polysaccharide present in lignocellulose) are convertible into ELev. MLev = methyl levulinate. Reaction conditions: substrate (50 mg), ethanol (4.00 mL), $Y(OTf)_3$ (0.05 mmol), H_3PO_4 (0.05 mmol), 180 °C, 2 h.

[b] Pretreated substrate is employed. Pretreatment conditions: substrate (0.500 g), choline chloride/oxalic acid dihydrate (1:1 molar ratio, 10.000 g), 80 °C, 2 h.

[c] Reaction conditions: substrate (300 mg), ethanol (24.00 mL), $Y(OTf)_3$ (0.3 mmol), H_3PO_4 (0.3 mmol), 180 °C, 2 h.

[d] Reaction conditions: substrate (60 g), aqueous sulfuric acid (0.4 N, 300 g), 190 °C, 2 h, then solvent exchange with ethanol (150 g), 145 °C, 2 h [36].

[e] Reaction conditions: substrate (20 g), ethanol solution of sulfuric acid, 200 °C [37].

[f] Reaction conditions: substrate (2.5 mmol as glucose unit), methanol (20 mL), $In(OTf)_3$ (0.02 mmol), 2-naphthalenesulfonic acid (0.1 mmol), 180 °C, 5 h [11].

[g] Reaction conditions: substrate (3 mmol), methanol (14 mL), H_2O (0.6 mL), $Al_2(SO_4)_3$ (1.2 mmol), 800 W, 180 °C, 40 min [18].

DESs are a class of green, and sometimes fully renewable, ionic liquids, in which there is significant interest for the valorisation of cellulosic biomass [31]. In particular, the deep eutectic mixture of choline chloride and oxalic acid has been efficiently applied to the fractionation of lignocellulosic biomass, production of cellulose nanocrystals and nanofibres by treatment of cellulose in this DES and subsequent microfluidic homogenisation or ball-milling, respectively [32–34]. In the present study, we established that native cellulose is amenable to deconstruction in a DES based on choline chloride and oxalic acid dihydrate (1:1 molar ratio) into fine particulate cellulosic material (details of the structure of the recovered materials are provided in the Supporting information, Table S1 and Fig. S5). This was accomplished by treatment of native cellulose in the DES at 80 °C for 2 h. Dilution of the DES with water, followed by washing and drying, afforded a fine cellulosic powder in 67–98 wt% yield (based on substrate loading) with particle size and structure consistent with MCC (Table S1, Fig. S5, Supporting information). This approach was effectively applied to reactions of cellulose from eucalyptus and *Pinus* (bleached and unbleached), and to wood pulp, providing fine cellulosic powders in each instance (average particle size 54–86 μm, Table S1, Supporting information). The yield of cellulose was diminished only for wood pulp (67 wt%, Table S1, Supporting information), likely associated with losses of other macromolecules such as hemicellulose and lignin, which are known to be soluble in DESs [31]. It is noteworthy that the DES may be recovered by extraction of nonpolar furanoids with ethyl acetate (trace amounts of furanoids were identified, which causes the formation of humins during recycling) and evaporation of water (the antisolvent used to precipitate cellulose powder from the DES) from the ionic solvent. The recovered media can be reused without any changes to the recovered cellulose (Table S1, Supporting information). One persistent drawback in this set of reactions is that softwood resisted the pretreatment under the conditions applied (80 °C, 2 h), likely due to the more intractable molecular structure of raw biomass [2,35]. Longer processing of wood chips and higher temperatures caused the formation of humins, and thus we found this method inappropriate for raw lignocellulose. Nevertheless, the subsequent conversion of DES-pretreated cellulosic materials (eucalyptus and *Pinus* cellulose, wood pulp) in ethanol and applying the combined acid catalyst $Y(OTf)_3/H_3PO_4$ enabled notable increases in the yield and selectivity of ELev (Table 2, entries 3, 5, 7, 9). Similarly excellent yields of ELev were obtained for the conversion of pretreated wood pulp performed at larger scale (Table 2, entry 10). The results compare very favourably with benchmarks in the literature (Table 2, entries 12–16) [11,17,18,36,37]. Moreover, our method does not require solvent exchange during the processing, prolonged reaction times, use of corrosive mineral acids or energy demanding microwave irradiation, as was previously employed in other studies (Table 2). These outcomes improve on the state-of-the-art methods, and offer a new technique to produce valuable ELev in high yield and selectivity, from low value cellulosic substrates, employing green solvents and catalysts.

Conclusions

This work demonstrates the acid-catalysed high yielding and selective transformation of cellulosic materials in ethanol into value added ELev. The use of metal triflates and their analogous Brønsted acid-assisted systems as catalysts, delivered superb yields (up to 75 mol%) and selectivity (up to 89 mol%) of the target platform molecule. To deliver such outcomes, the use of hard Lewis acids or the combined acid catalyst $Y(OTf)_3/H_3PO_4$ are preferred. Such systems deliver the necessary Lewis acidity and Brønsted acidity to expedite the cascade of reactions required for this transformation. The pretreatment of cellulosic biomass using the renewable deep eutectic system choline chloride/oxalic acid, with subsequent acid-catalysed processing in ethanol, enabled the high-yielding and highly selective direct conversion of the cellulosic raw materials that are available via large volume cellulose refining technologies.

These new methods offer a springboard for biorefinery activities, involving green solvents and catalysts in the valorisation of biomass, even though not all of the problems have been solved. Native lignocellulose, such as wood biomass, is less efficiently converted under our conditions. The technology itself still requires efficient methods to recover the product and the catalyst before the method could be scaled up.

Acknowledgment

We thank the University of Technology Sydney for financial support, and Dr Simon Hinkley, The Ferrier Research Institute, Victoria University of Wellington (New Zealand) for the gifted eucalyptus and *Pinus* cellulosic materials.

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