Reactive Eutectic Media for Lignocellulosic Biomass Fractionation

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This study introduces an alternative approach towards lignocellulosic biomass fractionation. For this purpose, reactive eutectic media (REM) based on ammonium formate and different organic acids are investigated, possible products are identified, and the REM are employed for lignin extraction and terminal isolation of cellulose pulp from beech wood. The method promises a considerable process intensification by simultaneous separation of high purity cellulose pulp, lignin isolation as a cationically modified species, and production of value-added chemicals from reaction products of the REM. This study puts a further focus on the generated cellulose pulp and investigates it with respect to surface charge and fiber length.

Introduction

Deep eutectic solvents, low-melting point mixtures or natural eutectic solvents,[1] paved their way as alternative media for various applications.[2–4] One such application is the use in biomass treatments,[5–9] where such solvents profit from their abundancy of hydrogen bonding as well as the possibility to tune their properties by choice and ratio of components. In addition, if one of the components is reactive, the media can serve as the reaction medium as well as the reactant and thereby enable innovative approaches that aspire towards the Green Chemistry principles. Reactive eutectic media (REM) arisen on that ground are showed beneficial for processing of biomaterials.[10,11] More specifically, REM based on ammonium formate and organic acids have been explored by our group for the treatment of cellulose to isolate positively charged nanocrystals.[12–14] In the present study, we will advance their scope and show that they can also be used for the separation of raw lignocellulosic biomass. This approach combines isolation of cellulose pulp and nitrogen-modified lignin products with the synthesis of value-added organic platform chemicals from the reactions of the REM components allowing to valorize naturally occurring organic acids. This implies a substantial process intensification and presents a novel approach for the implementation of the biorefinery concept.

The biorefinery presents an alternative to today's petroleum refinery and is a cornerstone of a future chemical industry that should serve the circular economy and strives to operate sustainably. In the case of lignocellulosic biomass as a starting material, this means that the three main components (cellulose, hemicellulose and lignin) are all used and exploited to produce value-added chemicals, materials and fuels, with minimal solvent and energy use as well as wastes. Established processes are mostly geared towards cellulose valorization, while the other components are still mostly burned. Due to the harsh reaction conditions of a classical paper mill, the native lignin is prone to undergo fragmentation and repolymerization reactions and ultimately forms a structure that is found less suitable for further downstream processing or other applications.

New fractionation treatments for biomass have been investigated in order to change this. One approach is the use of alternative solvent systems, which manage to yield reactive and less condensed types of lignin. Methods which rely on this approach include ammonia-based fractionation,[15,16] ionic liquid (IL)-assisted fractionation,[17,18] treatment with deep eutectic solvents,[19] γ-valerolactone-assisted hydrolysis[20] and ethylenediamine pretreatment.[21,22] While these methods give promising results, they also come with a drawback of much higher solvent costs, which can be considered as a serious process drawback.

Here, we endeavor to apply an alternative solvent system for the fractionation of biomass by application of REM based on ammonium formate and different organic acids. In the treatment of biomass, we hypothesize that the organic acid catalyzes the lignin depolymerization while ammonium formate acts as a weak, reductive amination agent to introduce nitrogen-containing functional groups into the lignin structure. Additionally, the REM components reacts to form a solvent for improved lignin dissolution, which results in a promisingly high lignin removal from the cellulose pulp. The whole approach enables better utilization of the process energy for a wider product range because it yields three value added products at processing conditions that are quite common for lignocelullosic biomass treatment.

This study will introduce the overall concept of REM for biomass fractionation and will put a focus on the obtained cellulose pulp.

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Experimental

REM Reaction

The REM were prepared by simply mixing the components, as listed in Table 1. All REM employed in this work consist of ammonium formate and an organic acid. The different organic acids used are levulinic acid (LvAc), lactic acid (LacAc) and acetic acid (AcAc), which were selected to be low cost and bio-based. Furthermore, some REM contain the additional components propylene glycol (PG) and ethylene glycol (EG) as part of the REM. In the following, the respective REM will be referred to by the employed organic acid (LvAc, LacAc or AcAc) as well as by the use of additional solvent (n, PG or EG).

The cellulose isolated in LvAc-n and LacAc-PG eutectics was subjected to repeated treatment under the same conditions in the corresponding eutectics. The samples of cellulose obtained after the double treatment in eutectic are connotated 2×LvAc-n and 2×LacAc-PG. All samples independent from the number of treatments were run 15–20 times (5–7 times for repeated treatment cellulose) through laboratory homogenizer S-PCH-10 (Homogenizing Systems LTD, UK) at ca. 1000 bar pressure.

For the REM reaction, the components were transferred to a 35 ml quartz vial, facilitated with a magnetic stirrer and sealed with a Teflon lined cap. The vial was heated in a microwave oven (Discover SP) with a power of 100 Watt under vigorous stirring and kept at 160 °C for 30 minutes to 2 hours. The microwave power output was adjusted to mimic conventional heating and no meaningful difference with the reactions performed in autoclave was observed, but allowed for more convenient reaction performance.[23]

After synthesis, the REM was qualitatively analyzed, using gas chromatography – mass spectrometry (GC-MS) and nuclear-magnetic resonance (NMR). Quantitative ^{1}H NMR was applied to calculate the substrate conversion and yields of products using dimethyl sulfoxide (DMSO) as an internal standard and D_2O solvent. The detailed procedures can be found in the SI.
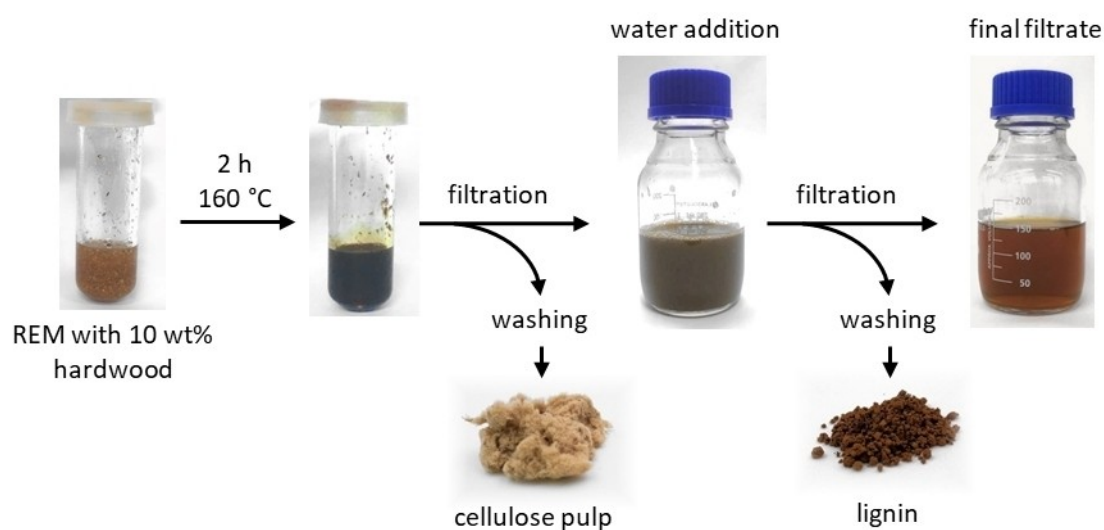
REM Treatment of Biomass

As shown in Figure 1, 10 wt% of dried beech wood sawdust was mixed with the respective REM. After treatment at 160 °C for 2 h in the microwave oven, the cellulose fraction was separated by vacuum filtration. The filter cake was mechanically pressed to remove as much of the filtrate as possible and consecutively washed with ethanol and acetone. The product was then washed with water and dried in the vacuum oven at 45 °C overnight, yielding dried cellulose pulp.

The filtrate was collected and concentrated by rotary evaporation at 45 °C. Water was added, five times the volume of the filtrate, and

Table 1. Composition of employed REM: ammonium formate was combined with one of the organic acids or their mixture without additional components; PG or EG was added to the mixture with the same molar ratio. The molar ratio of ammonium formate was 3 for all eutectics.

Sample connotations			REM components		
			Ammonium formate (molar ratio 3)	Organic acid (molar ratio 1)	Additional components (molar ratio 4)
LvAc-n LacAc-n AcAc-n	LvAc LacAc AcAc	| n	Ammonium formate	Levulinic acid (LvAc) Lactic acid (LacAc) Acetic acid (AcAc)	None (n)
LvAc-PG LacAc-PG AcAc-PG Mix-PG	LvAc LacAc AcAc Mix	| PG	Ammonium formate	Levulinic acid (LvAc) Lactic acid (LacAc) Acetic acid (AcAc) Mix of LvAc, LacAc, AcAc	Propylene glycol (PG)
LacAc-EG AcAc-EG	LacAc AcAc	| EG	Ammonium formate	Lactic acid (LacAc) Acetic acid (AcAc)	Ethylene glycol (EG)

Figure 1. Process scheme of lignocellulosic biomass treatment with REM.

the solution was stored in the fridge at 5 °C overnight. The following day, the diluted filtrate was centrifuged to yield the precipitated lignin, while the supernatant was collected and stored. Lignin was washed with water several times and freeze-dried overnight.

The cellulose fraction was analyzed on the residual lignin content using Klason lignin quantification according to the NREL analytical procedure. Furthermore, fiber length was investigated with transmission electron microscopy (TEM) after treatment with a high-pressure homogenizer. The molecular weight of cellulose was determined with gel permeation chromatography (GPC) in N-Methyl-2-pyrrolidon (NMP) after carbanilation. ATR-IR analysis was performed to characterize functionality of isolated cellulose. Finally, the samples were characterized in terms of their Zeta-potential and their crystallinity index (CI) was defined from powder X-ray diffraction (PXRD) measurements. The dried lignin and cellulose samples, were studied with elemental analysis. The detailed procedures can be found in the SI.

Results and Discussions

Investigating the REM Reaction

In previous work, ammonium formate featured a high reactivity as a Leuckart-Wallach or Maillard reagent when applied as a component in eutectic mixtures.[12,23] This work therefore starts with the investigation of the neat reactions of the REM, which will later be applied for biomass treatment. Our investigation revealed that the employed organic acids, namely levulinic (LvAc), lactic (LacAc) and acetic (AcAc), undergo different reactions with ammonium formate. The products were identified by ^{1}H NMR and GC-MS (see Figure S1–S3 in the SI) and are summarized below in Table 2 for the reaction conditions that are also employed during biomass treatment.

Table 2. Reaction of different organic acids with ammonium formate at 160 °C for 2 h. Yields and conversions were measured with quantitative NMR.

| Organic acid	Main product	Yield (%)	Conversion (%)
Levulinic acid (LvAc)	5-methyl-2-pyrrolidone (5MP)	70	100
Lactic acid (LacAc)	Lactamide	47	47
Acetic Acid (AcAc)	Acetamide	56	56

Reactions of LacAc or AcAc with ammonium formate lead to formation of the respective amides. Primary amides are extensively used in organic synthesis as they can be found in pharmaceuticals, natural products and biologically-active molecules.[24] The most common synthetic methods currently used for the direct amidation of carboxylic acids require harsh reaction conditions and long reaction times.[25] The fact that this approach generates them simultaneously throughout biomass treatment can also be seen as an upgrading of the biomass solvent.

The reaction of LvAc with ammonium formate proceeds to a different product due to the carbonyl group of LvAc and underwent a Leuckart-Wallach reaction with ammonium formate.[26] The main product here is 5-methyl-2-pyrrolidone (5MP). This reaction has been relatively well-studied in recent years[26–31] since 5MP and its N-substituted derivatives are a highly promising class of solvents and educts. 5MP for instance can substitute NMP and is a precursor for surfactants or pharmaceuticals.[32,33] Levulinic acid for the reaction is synthesized by acidic dehydration and is an already known biorefinery platform chemical.

In case of applying the REM for biomass processing, those reaction will take place in parallel to the biomass treatment, and the generated substances will affect solubility and processing. In order to reveal those influences, we only applied the conditions suitable for biomass processing based on primary results without the optimization of the reactions conditions towards the highest yields of the solvent products. We revealed that under those conditions around half of the LacAc and AcAc was converted to the corresponding amides (Table 2). The LvAc underwent complete conversion resulting in 70 % yield of 5 MP. The synthesis of 5 MP in an independent, optimized analogous process can reach yields more than 90 %, as shown by Wu et al..[26,31] However, this work aimed towards a proof of concept for synthesis of 5 MP as a side product while optimizing conditions for the separation of lignocellulosic biomass.

Biomass Treatment in REM

When treating full lignocellulosic biomass, the question arises how well the REM serves as a lignin solvent, which again will strongly depend on the chemical composition of the mixtures. We first tested two-component eutectics composed of ammonium formate and the corresponding acids. Figure 2
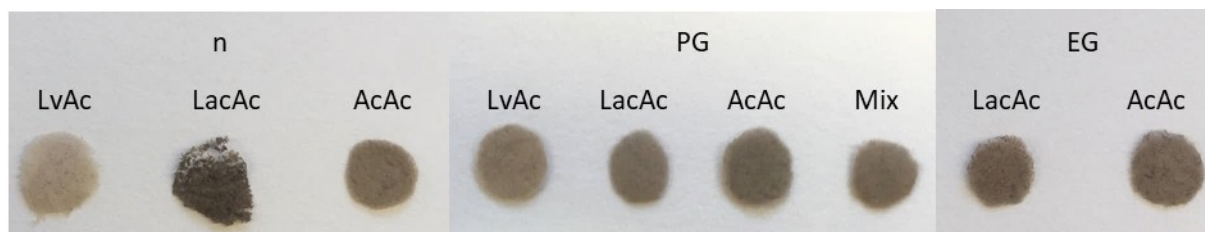
Figure 2. Physical appearance of cellulose fractions isolated by treatment in different REM; discoloration of the resulted pulps is in agreement with the residual lignin content.

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depicts the visual appearance of the cellulose fractions separated in different REM. The isolated pulps were colored from Hazel Wood yellow from LvAc eutectic to Coffee brown color of the pulp isolated with the LacAc, in good accordance with the amount of lignin remaining in them, as quantified as the Klason lignin content (Figure 3). The two-component REM showed the widest variation of their capacity for extracting lignin caused by the nature of the acid and the product of its transformation during the pulping. The REM composed of LacAc-n and AcAc-n are only moderate lignin extraction solvents (which is why they will not be considered any further). LvAc-n on the other hand resulted in an excellent delignification and removed even in our simplified, one stage extraction setup 92% of lignin. This drastic difference in the delignification efficiency is related to the high content of 5 MP, as explained above. This matches the result of previous studies that showed excellent lignin dissolving properties of the similar, but reproduction toxic, NMP. Similarity of the dissolution properties of 5MP to NMP can be expected and thus can explain the performance of LvAc-n eutectic for delignification.[34]

Because not all two-component REM appeared to have good lignin solvents properties by themselves, we investigated the potential addition of propylene glycol (PG) and ethylene glycol (EG) to the REM to facilitate lignin dissolution. Addition of a third low molecular weight component to eutectic solvents is a common practice to tune the physico-chemical properties of those designer solvents. The desired effect is often a decreased viscosity,[23,35] but physical and chemical benefits of the presence of third component are also often found.[7,36,37] Both PG and EG have shown to be good lignin solvents in previous studies,[38,39] can be bio-derived[40,41] and offer low vapor pressures.
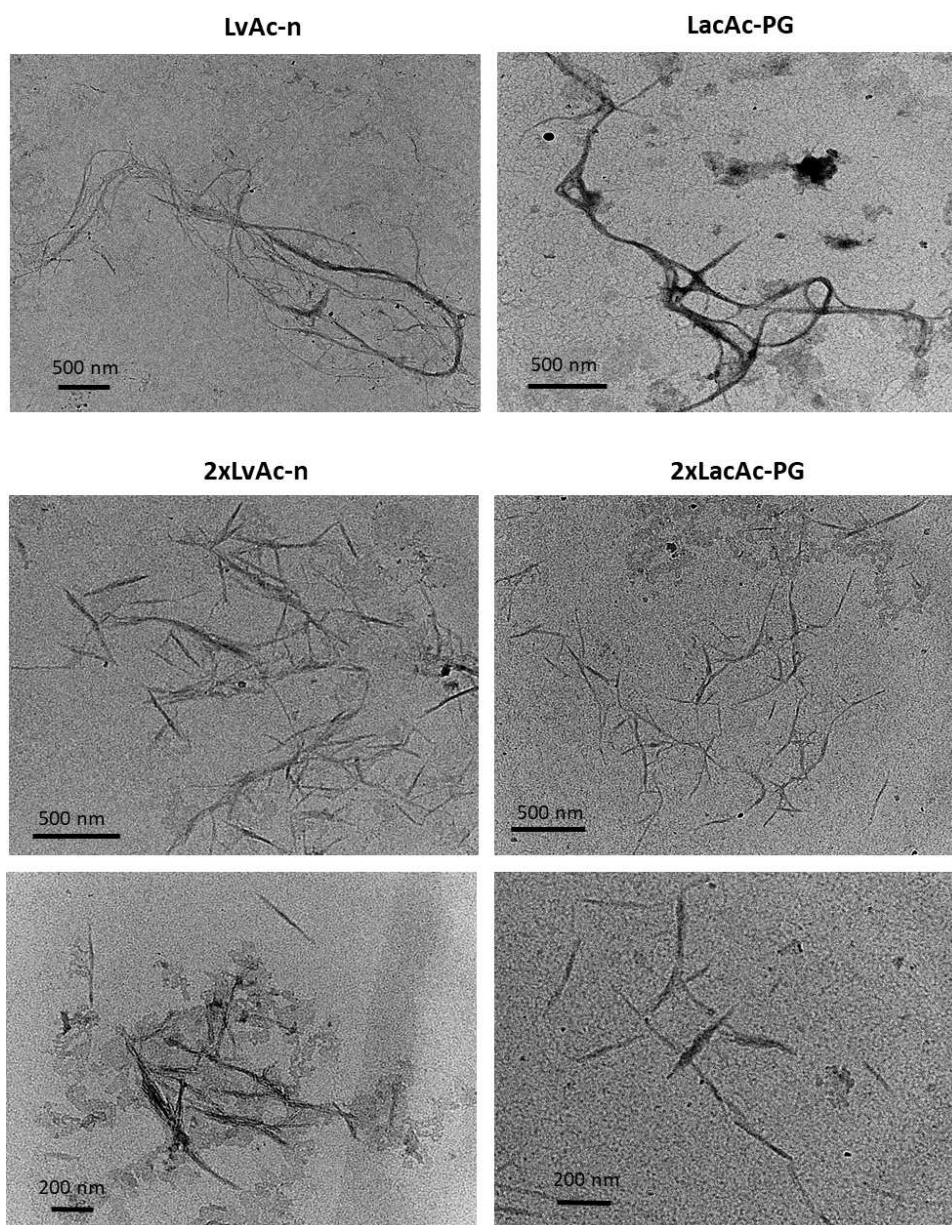
The addition of glycol solvents to the REM in our experiments appears to eliminate the dependence of lignin solubility on the specific organic acid and lignin removal became dependent on the glycol used (Figure 3). Namely addition of PG

appears to work better than EG and extracts on average 86% of lignin compared to 74% for REM with the EG practically independent on the nature of organic acid.

Jaekel et al. used REM based on ammonium formate and different organic acids to treat lignin-free cellulose to isolate cationic cellulose nanocrystals with an aspect ratio of ca. 20–30.[12] When treating lignocellulosic biomass in the similar REM, we could have expect to obtain nanostructured cellulose crystals presumably with some lignin (lignin-containing nanocellulose). However, after applying the REM to the lignocellulosic biomass and subjecting the products to high pressure homogenization, the TEM revealed in the samples fibers with a width of tens of nanometers and lengths of above several micrometers (Figure 4). The observed difference of cellulose properties could be related to the starting material. While the previous study relied on pure cellulose, employing raw lignocellulosic biomass entails combination of several chemical reaction in the reaction mixture. The reactions between the REM components are fast reactions taking place at the beginning of the treatment. In case of the LvAc it gives benefits of generating a good solvent for lignin and supports the delignification as mentioned above. As a Leuckart reagent, ammonium formate will target carbonyl groups of lignin as they are conjugated with the extended aromatic system of lignin and thus activated to nucleophilic attack of ammonia cation.[42,43] Based on this, we can assume that lignin will react first, and only close to the end of reaction ammonium formate can reach and react with the single cellulose fibers. Lignin with a nitrogen content of ca. 5 wt% (Table 4) is isolated after the treatment while the cellulose fraction has a ten times lower nitrogen content. Due to this chemical protection, the isolated cellulose fibers remain much longer and preserve a negative charge, typical for cellulose (Figure 6). However, as expected after the treatment in eutectic solvents, the isolation of nanofibers by high pressure homogenization requires only a few cycles.
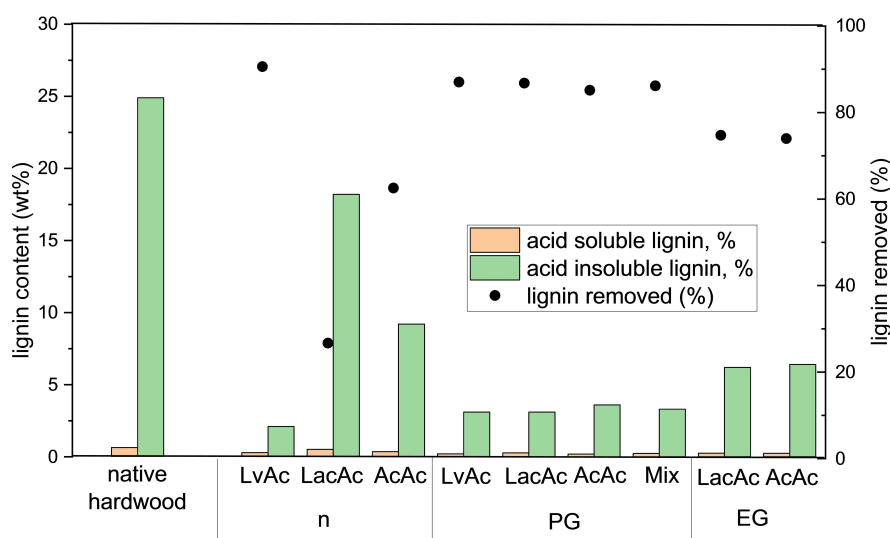
Figure 3. Lignin content and lignin removal for cellulose samples, obtained after beech wood treatment with different REM. Sample Mix-PG are obtained from treatment with a REM based on a 50/50 mix of LacAc and AcAc.

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Figure 4. TEM images of cellulose pulp isolated in LvAc-n and LacAc-PG eutectics; the top row TEM images depict cellulose fibers after the one time treatment in eutectic, the bottom rows TEM images depict cellulose crystals obtained after the repeated treatment of cellulose pulp in the same eutectic; all samples are after 15–20 rounds (5–7 rounds for the repeated treatment) of homogenization.

For testing this hypothesis, we subjected two of the obtained cellulose fractions one more time to the treatment in the respective REM (2×Lv-n and 2×Lc-PG) without the lignin, and indeed, cellulose nanocrystals of shorter length (ca. 250–500 nm) were obtained (TEM in Figure 4).

This observation was supported by GPC measurements of the cellulose fraction after single and double treatments. For the GPC measurement, the cellulose was carbanilated with phenyl isocyanate that introduces three aromatic groups to each glucose molecule in the cellulose chain and which allows its solubility in the GPC solvent NMP/LiBr. As shown in Figure 5, the molecular weight decreased after the repeated treatment

with REM and this revealed that the fiber length becomes much shorter.

Another observable difference between REM treatment of pure cellulose vs. lignocellulosic biomass is the surface charge. As shown in Figure 6, Zeta-potential measurements revealed a negative charge of the cellulose fibers after the first treatment in REM, while repeating the treatment yielded positively charged cellulose nanocrystals. This indicates the formation of cationic nanocellulose, with nitrogen-containing functional groups. Use of the same REM for the delignification and generation of cationic cellulose nanocrystals drastically simplifies the intermediate washing steps and allows to use cellulose pulp right after filtration.
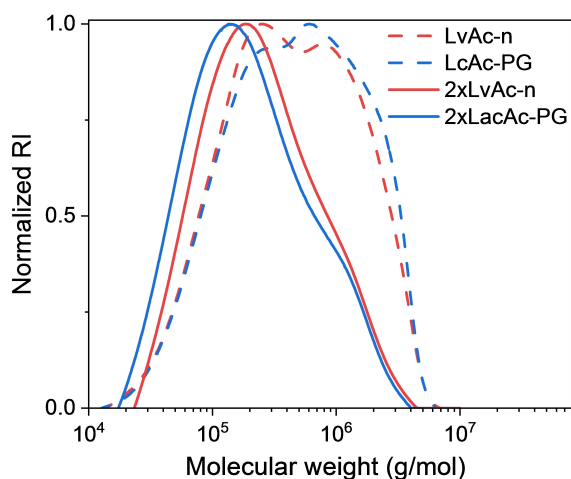
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Figure 5. GPC of cellulose samples after carbanilation and using a pullulan standard.
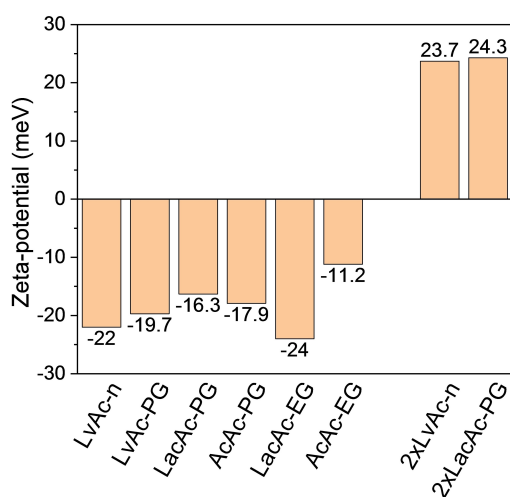

Figure 6. Zeta-potential of cellulose samples in water.

The crystallinity index (CI) of the cellulose samples was calculated by peak height analysis from PXRD plots. The results in Table 3 revealed that all samples featured a relatively high crystallinity, with a CI between 72% and 76%. The CI increased for the samples which were treated twice in the REM to around 78% supporting the observation of etching towards cellulose nanocrystals.

Elemental analysis of the cellulose samples indicated the presence of nitrogen (Table 4). Amine groups may likely to be introduced to the cellulose structure via a Leuckart-Wallach reaction of ammonium formate with the reducing end of the cellulose chain. This explanation suggests itself as it has also been observed by our group for the treatment of pure cellulose with the same kind of REM.[12] Just like for pure cellulose, the cellulose samples in this work feature an emerging peak in FTIR at 1650 cm^{-1}, which can be assigned to primary amines (Figure S4).

The elemental analysis of the recovered lignin indicated the presence of nitrogen of as shown in Table 4. The structural composition of the regenerated lignin will be the subject of the future work.

Conclusion and Outlook

In this work, we propose the treatment of lignocellulosic biomass in a REM based on ammonium formate and organic acids as a part of the biorefinery scheme. The method allows separated isolation of cellulose and lignin, while generating value added chemicals from the REM itself. Thus, it demonstrates an opportunity for process intensification.

The different analyzed REM varied in their ability for lignin extraction. While REM with LvAc showed excellent performance, REM with other organic acids are weaker, but could be boosted by adding secondary solvents, such as propylene glycol or ethylene glycol. The generated cellulose fractions showed low lignin contents and (relatively) long fibers. By repeated treatment of the cellulose pulp, cationic nanocellulose could be obtained, which is in accordance with previous studies of pure

Table 3. Crystallinity index (CI) of cellulose samples calculated using the peak height analysis of PXRD data.

Sample	LvAc-n	LvAc-PG	LacAc-PG	AcAc-PG	LacAc-EG	AcAc-EG	2×LvAc-n	2×LacAc-PG
CI (%)	75.8	72.3	75.0	71.8	72.5	73.0	78.1	78.4

Table 4. Elemental analysis of lignin and cellulose samples from treatment with different REM.

REM treatment	lignin				cellulose			
	N (%)	C (%)	H (%)	O (%)	N (%)	C (%)	H (%)	O (%)
LvAc-n	5.1	61.0	6.2	27.7	0.24	42.3	6.1	51.0
LvAc-PG	5.3	61.6	6.3	26.8	0.15	41.6	6.1	51.9
LacAc-PG	5.2	61.9	5.9	27.0	0.17	42.1	6.2	51.3
AcAc-PG	4.8	61.6	5.8	27.7	0.20	42.8	6.2	50.5
LacAc-EG	4.4	60.5	5.9	29.3	0.27	44.0	6.3	49.2
AcAc-EG	4.3	61.5	6.0	28.2	0.26	43.2	6.2	50.2

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cellulose. The chemical composition and properties of the isolated lignin will be the subject of future work. The hemicellulose is expected to hydrolyze under the reaction conditions and duration and the resulted sugars aminated into melanoidins.

The study also underlines the excellent solvent properties of pyrrolidones for lignin extraction. In this work 5MP from LvAc was investigated but a previous study attested similar properties to NMP. Considering, that LvAc can be used to produce a wide range of N-substituted-5MP there is certainly an opportunity for further investigations in this direction with respect to biomass separation.

Acknowledgements

Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

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