Current strategies for industrial plastic production from non-edible biomass

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Abstract

Realistically replacing petroleum-based plastics will require efficient routes to performance polymers using scalable processes from abundantly available lignocellulosic biomass. We surveyed academic and patent literature for processes in the latest stages of commercial development to draw out design strategies that have enabled their success. We found that these processes consist of chemocatalytic transformations of non-edible biomass to rigid plastic precursors with high drop-in readiness via a stable, hydrophobic, and distillable platform molecule. However, due to the deoxygenated nature of these precursors, the processes suffer from low biomass utilization efficiency and high process complexity—thereby limiting their sustainability. We discuss our group's preliminary efforts to design novel monomers with lower drop-in readiness, but with increased process efficiency and simplicity from biomass.

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Introduction

There has been enormous development into renewable and sustainable plastics but they currently only represent ∼1% of the global plastics market [1]. Although a large array of sustainable monomers have been developed from plant-based carbohydrates, the bottleneck lies in the production cost from highly abundant, sustainable feedstocks [2]. Currently, the most affordable and accessible feedstocks for these carbohydrates—and hence the ones used at present in industrial bioplastic production—are edible crops with high sugar loadings such as corn, sugarcane, and sugar beets. A transition to non-edible biomass, or lignocellulose, is required to increase scale without heavily competing with food [3], improve sustainability [4], and ultimately, drive down cost [5,6]. Ideally, non-edible biomass would be converted into low-cost streams of sugars that could be dropped into existing plastic precursor production processes that were developed around purified sugars (*e.g.* fermentation). Unfortunately, producing low-cost streams of clean upgradeable sugars from lignocellulosic biomass is inherently challenging for two main reasons. First, lignocellulose is a highly heterogeneous, stable, and recalcitrant feedstock made up of unstable, reactive, and non-volatile oxygenates which leads to degradation reactions and complex mixtures. Secondly, carbohydrates are extremely difficult to separate from such mixtures as they are not extractable from aqueous streams, nor distillable, and are easily degraded. After decades of research in academia [7−12] and interest from industry [13−15], projected prices of purified lignocellulosic sugars are dropping but are still not cost-competitive with food-based sugars [6,16]. Likely as a consequence of these uncompetitive costs, we have not found any industrial processes that convert lignocellulose to plastics via biological means. Strategies to further decrease the costs of refined lignocellulosic sugar streams will be crucial in enabling a sustainable plastics economy, but will not be the focus of this review and has been extensively reviewed elsewhere [17−21].

Here, we identified a limited number of emerging technologies and commercial ventures that are already successfully utilizing lignocellulose to produce plastic

Figure 1
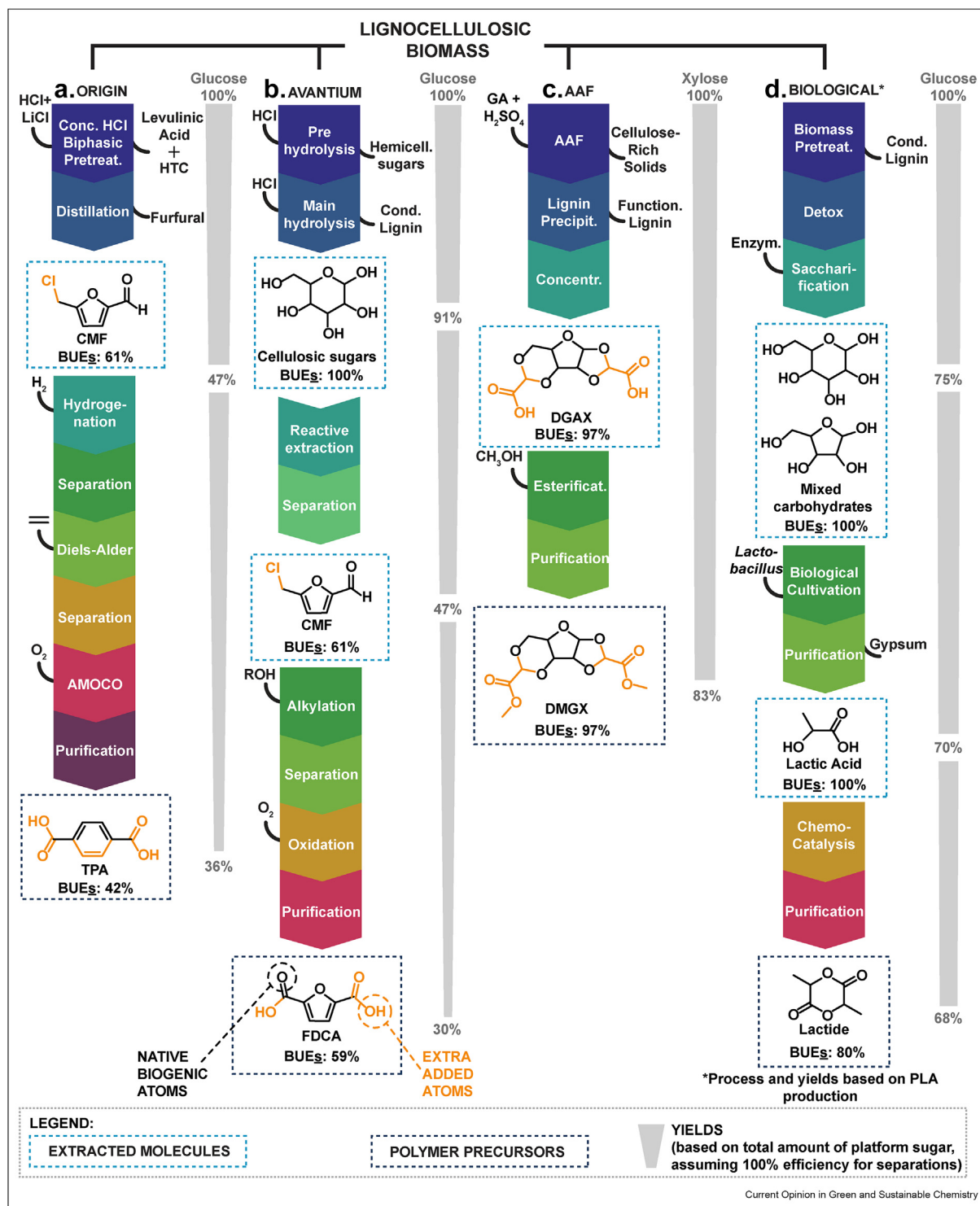
Overview of chemocatalytic and biological pathways from lignocellulosic biomass to carbohydrate-based plastic precursors. Atoms highlighted in orange originate from sources other than the original biomass feedstock. Yields are calculated based on the best performance data available in the public domain and assume separation efficiencies of 100%. Process information and yields for the biological routes are based on a "best case scenario" for lactic acid and lactide production [7,62,63]. It should be noted that the biomass utilization efficiencies from biological and chemical processes cannot be directly compared due to losses resulting from carbon utilization by fermenting microbes for their metabolism (e.g. CO$_2$ emissions). The atoms from water that are incorporated into the monomer during hydrolysis of carbohydrates are considered biogenic, therefore, 100% BUE is calculated on a monomeric sugar basis. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

precursors. The two ventures in the latest stages of development, with the largest commercial partners, are Origin Materials, which is producing bio-based purified terephthalic acid (PTA) for drop-in bio-based poly(-ethylene terephthalate) (PET), and Avantium Chemicals B.V., which is producing 2,5-furandicarboxylic acid (FDCA) for poly(ethylene furanoate) (PEF), a promising renewable PET replacement. We give detailed overviews of their processes using information compiled from various public sources (Figure 1a–b). A key feature that enables their use of non-edible biomass is that their chemocatalytic upgrading processes utilize chloromethyl furfural (CMF) which can be produced in high yields from the cellulosic fraction of lignocellulose *and* can be easily purified from the pretreatment liquor as it is stable, hydrophobic and distillable [22–24]. This enables the generation of a clean, upgradeable stream of CMF directly from lignocellulose and therefore does not require the cost-intensive, intermediate purification of carbohydrates. The heavy commercial investment in these ventures is greatly aided by the drop-in readiness and market demand for the final products (renewable PET replacements). However, with a petroleum-dominated plastics market, this drop-in readiness comes at the cost of producing highly deoxygenated molecules, which when starting from biomass requires a higher number of chemical transformations and ultimately leads to low biomass utilization efficiency (BUE). Although making drop-in plastic precursors is the most sensible solution to reduce fossil-fuel dependence in the short-term, designing plastic precursors based on the structure of biomass, rather than retrofitting biomass chemistry to petroleum structures, could drastically improve BUEs. We outline our group's preliminary efforts to produce lignocellulosic plastic precursors with high BUE, and high value co-products, while also employing these industrial strategies of exploiting a stable, hydrophobic and distillable platform molecule (Figure 1c).

Main text
The CMF process
Over the past few decades, there have been enormous efforts to produce bio-based chemicals (including PTA and FDCA) via 5-hydroxymethyl furfural (HMF). This intermediate is efficiently produced from fructose [25,26] but is notoriously difficult to produce in high yields from biomass, due to its instability in pretreatment conditions [27] (the highest reported reaction yields from lignocellulosic biomass is ~60% [28], as opposed to >95% from edible fructose [29]). To ameliorate the isolation of HMF, Mascal et al., in 2008, dramatically improved the production of CMF, a stable derivative of HMF, from purified sugars. Later, they adapted the process to lignocellulosic biomass [22] with reported isolated yields of CMF from corn stover of up to 80% (molar yield from glucan) [23,24]. The optimized process consists of deconstructing powdered

biomass (grinded and ball-milled) in a closed biphasic reactor between 80 and 120 °C using concentrated aqueous HCl and periodic extraction with an immiscible solvent such as dichloromethane or 1,2-dichloroethane [30]. Aqueous HCl leads to saccharification of cellulose to glucose, isomerisation to fructose, and dehydration to HMF. This is then extracted into the organic phase where the hydroxyl is rapidly replaced by a chlorine from HCl to produce the hydrophobic and more stable CMF. This reactive extraction simultaneously prevents degradation of the unstable HMF and separates CMF from the aqueous pretreatment stream, which can then be easily purified by distillation and upgraded to a wide variety of chemicals [27]. Three extractions over a 3h reaction period (not including heating and cooling cycles) were required to attain >80% yield. At more realistic (powdered) biomass loadings of 10 wt/v %, a 70% molar yield of CMF from glucan was reported with an additional 9% molar yield of levulinic acid as a byproduct in the aqueous phase. After reaction, the remaining solids were filtered and consisted of a highly condensed, de-ashed, black lignin powder that could be potentially burned for energy or used as a source of porous, structured carbon. Hemicellulose yields to furfural are not reported but are likely very low as Mascal recommends pre-extracting the hemicellulose prior to reaction in a biorefinery. The hemicellulose is most probably degraded to polyfuranics and ends up in the solid fraction along with the lignin.

Overall, this technology provides an efficient route to a clean crude stream of CMF directly from lignocellulose in high yields. The hydrophobic and volatile nature of CMF enables its efficient separation from the pretreatment stream by extraction and distillation. Nonetheless, periodic extraction is not feasible at scale, therefore a continuous extraction system with intensive solvent use would likely be needed to maintain high yields (the yield with no periodic or continuous extraction is not reported and was simply described as "unsatisfactory" [23]). Also, the harsh reaction conditions lead to significant degradation of the hemicellulosic and lignin fractions of the biomass, limiting their valorization with the current system. The residual lignin contains high concentrations of covalently bound chlorine, making it less interesting for upgrading or incineration for heat production [31]. Additionally, the use of HCl results in higher capital costs associated with corrosion-resistant equipment [32], and will require very efficient recovery of HCl to guarantee the environmental and economic sustainability of the process— which has been a key barrier in economic production of refined sugars using HCl pretreatments since WW2 [33]. Lastly, toxicologic studies demonstrated higher mutagenicity and cytotoxicity of CMF in bacteria as compared to HMF, which could prove problematic if CMF becomes a widely used platform molecule [34].

Despite these drawbacks, this process enables the production of a clean stream of highly upgradeable CMF directly from low-cost lignocellulose in a scalable fashion and therefore quickly garnered interest from industry [27,35]. Origin Materials is exploiting the CMF pretreatment methods and some of the upgrading methods developed by Mascal et al. to produce renewable PTA [36]. Avantium is now also leveraging CMF to produce FDCA but appears to be using a modified Udic-Rheinau process, initially developed during WW2 [37,38]. Below, we provide detailed technical descriptions of the Origin and Avantium processes, to see how these companies are pioneering industrial routes to lignocellulosic plastics and chemicals. These data are based on publicly available information, therefore the actual processes may contain confidential improvements that are not reflected here.

The Origin Materials process

Pretreatment

Origin Materials has been investigating the synthesis of bio-based p-xylene for PET production via CMF conversion to 2,5-dimethylfuran (DMF) [27]. They disclosed in a patent their design for a biphasic reactor for one-pot lignocellulosic fractionation and CMF synthesis—based on the Mascal approach [39]. In the reported process, they utilize a stirred batch reactor where wood chips or other cellulosic materials, such as cardboard, are loaded into the reactor along with concentrated aqueous HCl and lithium chloride ([Cl−] = 12 M with $\sim$1−2 M [H+] and 10−11 M [Li+]), or another chloride salt, and an organic solvent such as toluene or an alkylbenzene. The reaction is run at around 125−175 °C for 10−60 min. The addition of lithium or other chloride salts greatly increases the partition of HMF/CMF into the organic phase, thereby increasing the driving force for the stabilization reaction and leading to increased reaction yields and lower solvent use. It also acts as a swelling agent for cellulose to enable faster reaction times [30]. From the patent examples, yields of CMF from pure glucose seem to reach a maximum of around 60−65% at full conversion. From corrugated cardboard, a 47% yield at 96% conversion was achieved. Smaller amounts of levulinic acid and furfural are also produced as by-products in the reaction but yields are not reported. These low yields of CMF from cellulose, and even purified glucose, are likely due to the fact that they are not utilizing continuous or periodic solvent extraction, which was likely deemed less practical. After cooling, the aqueous phase is filtered using a filter press to recover the remaining solids (a condensed lignin-rich powder), referred to as hydrothermal carbon (HTC), which Origin Materials is marketing as fuel pellets or as a carbon-black replacement [40]. Levulinic acid is recovered from the aqueous phase and the acidic salts are recycled, both by undisclosed means. The organic phase from the reactor is distilled to recycle the organic solvent and recover furfural and CMF as distillates.

Upgrading

The distilled CMF stream is hydrogenated to DMF with a palladium catalyst, likely in dimethylformamide (DMFD), or a mixture of an organic solvent and urea reagent, at low temperatures (20−40 °C) with yields of up to 84% from CMF in 1−2 h. This reaction pathway is based on a previously disclosed pathway that prevents the formation of the unstable reaction intermediate, 5-methylfurfuryl alcohol, through the use of derivatizing agents and led to increased selectivity and yields of DMF [22]. Origin Materials has rights to two patents regarding this conversion and ran further experiments demonstrating that CMF hydrogenation in either pure DMFD or a mixture of toluene and dimethylpropyleneurea led to the highest yields of DMF (82% and 84% from CMF, respectively) − with pure DMFD appearing to be the most straightforward recipe [41,42]. The resulting DMF is then purified or concentrated and sent to another reactor, where Diels−Alder cyclization is employed with ethylene at $\sim$220 °C and $\sim$50 bar using a Lewis acid catalyst (e.g. Cu(OTf)2) and a solvent (e.g. dioxane), to synthesize p-xylene at 95% yield and 99% conversion [43]. Finally, p-xylene is then partially purified and catalytically oxidized to PTA and purified following the well-established Amoco process where reaction yields to PTA >95% from p-xylene have been reported [44].

Outlook

Origin Materials has assembled a scalable process that enables production of a wide range of products (CMF, HTC, DMF, p-xylene, PTA, FDCA, levulinic acid, and furfural) directly from non-edible biomass with a direct drop-in to the PET market, creating an immediate and massive demand. They have received over $925 million dollars in funding with investors including Danone, Nestlé and PepsiCo, an order book of over $3.5B, and are in the process of building two commercial plants (Origin 1 and Origin 2), with the latter having a projected capacity of processing 1 MMT of biomass per year [45,46]. For this plant, they have selected wood as the feedstock as they have found from past ventures that incentivizing farmers to collect agricultural residues is more complicated [47]. This massive influx of investment is likely due to their strategic decision to target a renewable PET drop-in which is in large demand, and they have a great diversity of products which can be expanded to a wide array of markets. However, achieving drop-in TPA comes at the cost of BUE, process complexity, and sustainability. BUE is defined as "the percentage of initial biomass ending up in the end product based on the molar mass of the monomer of the corresponding biopolymer (e.g. glucose from cellulose) and target bio-based product" and can be used to characterize the process' ability to use natural chemical structures efficiently [48]. The theoretical BUE (at 100% yield), or BUE_S, of PTA from the glucan fraction of biomass via this process is only 42%. Considering that the production of CMF alone has yields ranging from 40 to 80%, the real efficiency is likely

significantly lower. Additionally, the need to hydro-deoxygenate CMF to DMF, couple DMF with ethylene to *p*-xylene, and then re-oxidize to PTA all using different solvent and catalyst systems at high temperatures greatly increases the complexity and diminishes the sustainability of the process. Therefore, the need to retrofit biomass molecules to petroleum-based chemicals comes at a large cost, but is the most sensible and scalable option in the short-term in terms of marketability. Origin's scaling of this process will bring invaluable industrial insight to the biomass valorization community. Hopefully, the large volumes of hydrothermal carbon (HTC) that are co-produced will replace environmentally burdensome fossil-based chemicals to decrease the environmental footprint of the process.

The Avantium process
Pretreatment
Since 2011, Avantium has been producing FDCA from sugars via a catalytic oxidation of 5-(methoxymethyl) furfural (MMF), an intermediate produced from simple sugars, via their YXY technology™ [49]. To move towards second generation feedstocks, Avantium is also exploiting an HCl pretreatment method which appears to be based on the Udic-Rheinau process using a simulated moving bed reactor (SMB) in their pilot biorefinery in Delfzijl (NL), named DAWN technology™ [50]. The sugars extracted in the acidic solutions are then converted to CMF via a biphasic reaction, similar to the Mascal process, which they can then upgrade to FDCA. The main difference in their pretreatment process from the Mascal and Origin processes is that they sequentially depolymerize hemicellulose and cellulose, and separate these steps from the carbohydrate upgrading to CMF and furfural. For the biomass pretreatment, they utilize a SMB reactor with two stages: first the hemicellulose fraction is extracted (pre-hydrolysis) at room temperature with 30 wt.% HCl over 16 h, then the cellulose fraction is hydrolysed (main-hydrolysis) at 30 °C with 42 wt.% HCl over 24 h [31] − leaving behind a condensed lignin residue that is discharged from the reactor beds. At these temperatures the dehydration of the sugars does not occur, enabling them to produce two streams of unmodified sugars in concentrated HCl. From an example in their patent using pine wood [31], the pre-hydrolysate stream contains 2.5 wt.% C6 sugars (0.6 wt.% glucose), 1.3 wt.% C5 sugars and the main-hydrolysate stream contains 7.3 wt.% C6 sugars (5.6 wt.% glucose) and 0.6 wt.% C5 sugars. This corresponds to a ∼91% depolymerization yield of cellulose to glucose, and a near quantitative yield of hemicellulosic sugars− albeit with very long residence times and dilute product streams.

Upgrading
The C6 and C5 sugars in both the prehydrolysate and main hydrolysate streams can then be converted to CMF and furfural, respectively, in a biphasic counter-current reactor operated at 90-100 °C. The reported overall yield of CMF produced and extracted into the organic phases (toluene) in their patent is ∼47% of the theoretical yield on a cellulosic basis from pine wood. The aqueous HCl is then likely recycled using an undisclosed process. Toluene is presumably then evaporated and recycled, and CMF is etherified with methanol to MMF at 50 °C in DCM (Williamson etherification), reaching yields up to 84.6% after 4h [31]. DCM and methanol are then most probably evaporated and MMF is then oxidized at 180 °C and 20 bar with a Co/Mn/Br catalyst in oxygen to yield FDCA and FDCA methyl esters with selectivities above 80% [51]. The purification system for FDCA remains challenging and follows the same procedure as PTA purification in the Amoco process: impurities are hydrogenated to increase their solubility allowing the formation of pure FDCA crystals which are later recovered by centrifugation and drying [52,53].

Outlook
In this process, the sequential pre-hydrolysis and hydrolysis at low temperature allows for production of unmodified sugar streams (in concentrated acid), which Avantium claims is a major improvement over the Mascal process due to greater process and product flexibility. However, this will come at the cost of using high-tech pretreatment reactors (SMB), which are likely difficult to scale, and very long residence times due to the low extraction temperature. An advantage of this process, as compared to Origin, is the lower degree of deoxygenation of the final product, FDCA, as compared to PTA. By maintaining some of the oxygen of the native carbohydrates the process achieves increased BUEs (59% versus 42% for PTA), and requires fewer chemical transformations. Also, stoichiometric reagents such as ethylene are not required. These process benefits come at a major cost in terms of market deployment. The time-to-market for new plastic can be on the order of decades and greatly increases the risk of the financial venture. However, if Avantium manages to produce FDCA at very low cost, its penetration into the market can be greatly accelerated, and would be a promising example that novel bio-based plastics can compete with petroleum-derived alternatives.

Future directions of lignocellulosic plastics
In the short-term, direct drop-in replacements appear to be the "path of least resistance" to reduce the associated emissions of our plastics market and our dependence on fossil fuels. However, it is very difficult to achieve sustainable and economical processes to drop-in, deoxygenated monomers from a highly oxygenated feedstock with numerous C−O bonds [48]. Ideally, we should find monomers that can be produced with high BUE, using an industrially feasible and low-cost process, and that enable the production of marketable materials. From the

success of the CMF pathway, exploiting stable, hydrophobic, and/or volatile platform molecules appears to be a promising strategy to enable industrial implementation. So, how does one create a stable, hydrophobic/volatile molecule while retaining the high degree of oxygenation of lignocellulose? In this context, our group has explored strategies that target products that preserve biomass structure, hence minimizing processing steps and maximizing biomass utilization efficiency, while also targeting stabilized extractable molecules.

The core strategy of the pretreatment technology developed in our group was designed around the fact that biomass degradation systematically proceeds via dehydrations of alcohols to reactive/unstable moieties. By adding one reagent to the pretreatment (an aldehyde), acetals are formed and thereby prevent dehydration and subsequent degradation of the lignin and carbohydrate fractions. The three main fractions of biomass, namely cellulose, lignin (acetal-stabilized) and hemicellulose (in the form of acetal-stabilized xyloses for xylan-rich biomass), can be isolated at high yields, while minimizing condensation [54]. By using an aldehyde with a secondary functionality, we can not only extract a stabilized-lignin and acetalized-xyloses away from cellulose, but can insert targeted functionalities. As an example, we recently published works utilizing a carboxylic acid functionalized aldehyde, glyoxylic acid, to fractionate biomass which leads to a cellulose-rich pulp; a non-condensed, carboxylic acid functionalized-lignin with direct applications in surfactants, cosmetics, and materials [55,56]; and a rigid, tricyclic, diacid acetal-stabilized xylose, called diglyoxylic acid xylose (DGAX) [57]. By converting DGAX to its dimethyl ester, dimethylglyoxylate xylose (DMGX), by simple addition of methanol and heating, the monomer becomes hydrophobic and distillable, enabling its easy separation from the pretreatment liquor. DMGX can then be polymerized with diols to produce polyesters, called poly(alkylene xylosediglyoxylates) (PAX), with thermomechanical and oxygen-barrier properties on par with PET, but more susceptible to degradation by water. The key feature of this process is that the xylose structure remains intact in the structure of DMGX and in the final polymer—leading to a BUE of 97%. By using aldehydes with secondary functionality we can create performance plastic monomers that are stable, hydrophobic, and distillable while maintaining 97% of biogenic atoms, using a scalable and simple two-step, one-pot reaction sequence (using only a mineral acid as catalyst), that also enables full (even enhanced) valorization of the other components of the biomass (namely cellulose and lignin [58]). However, the main tradeoff of this strategy is the addition of an external aldehyde which is incorporated into the final products. In the case of glyoxylic acid ($\sim$\$1/kg), it is currently derived from fossil feedstocks and represents a large fraction of the process' operating costs and greenhouse gas emissions [57]. Fortunately, glyoxylic acid can be produced from bio-derived ethanol or even directly from CO_2. Avantium's Volta process is already demonstrating glyoxylic acid production from CO_2 at pilot scale [59–61], however, selling prices will have to be low to make renewable glyoxylic acid feasible. If low-cost, renewable glyoxylic acid can be realized then PAX plastics could be produced at high efficiency entirely from lignocellulose and carbon dioxide.

Overall, this strategy demonstrates how plastics can be redesigned, while taking inspiration from key chemical production processes for bio-based plastics, including drop-ins, that have already been scaled up. Combining these scaling features with molecular structures that are more sustainable by design could help accelerate a transition towards more renewable and environmentally friendly plastics.

Authors contribution
L.P.M. and M.J.J.: Conceptualization, Formal analysis, Writing - original draft; S.B.: Visualization, Writing - reviewing & editing; J.B.B.: Writing - reviewing & editing; J.S.L.: Conceptualization, Resources, Supervision, Writing - reviewing & editing.

Declaration of competing interest
L.P.M., S.B. and J.S.L. are inventors on a European patent application (EP19203000.5) on methods for producing the renewable monomer and polymer described here. J.S.L. and J.B.B. are part owners in Bloom Biorenewables Ltd, which is exploring commercial opportunities for aldehyde-stabilized lignin and aldehyde-protected xyloses. The remaining authors declare no competing interests.

Data availability
No data was used for the research described in the article.

Acknowledgements

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