Reductive catalytic fractionation: state of the art of the *lignin-first* biorefinery

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Reductive catalytic fractionation (RCF) of lignocellulose is an emerging biorefinery scheme that combines biomass fractionation with lignin depolymerisation. Central to this scheme is the integration of heterogeneous catalysis, which overcomes the tendency of lignin to repolymerise. Ultimately, this leads to a low-M_w lignin oil comprising a handful of lignin-derived monophenolics in close-to-theoretical yield, as well as a carbohydrate pulp. Both product streams are considered to be valuable resources for the bio-based chemical industry. This Opinion article sheds light on recently achieved milestones and consequent research opportunities. More specifically, mechanistic studies have established a general understanding of the elementary RCF steps, which include (i) lignin extraction, (ii) solvolytic and catalytic depolymerisation and (iii) stabilisation. This insight forms the foundation for recently developed flow-through RCF. Compared to traditional batch, flow-through RCF has the advantage of (i) separating the solvolytic steps from the catalytic steps and (ii) being a semi-continuous process; both of which are beneficial for research purposes and for industrial operation. Although RCF has originally been developed for 'virgin' biomass, researchers have just begun to explore alternative feedstocks. Low-value biomass sources such as agricultural residues, waste wood and bark, are cheap and abundant but are also often more complex. On the other side of the feedstock spectrum are high-value bio-engineered crops, specifically tailored for biorefinery purposes. Advantageous for RCF are feedstocks designed to (i) increase the total monomer yield, (ii) extract lignin more easily, and/or (iii) yield unconventional, high-value products (e.g. alkylated catechols derived from C-lignin). Taking a look at the bigger picture, this Opinion article highlights the multidisciplinary nature of RCF. Collaborative efforts involving chemists, reactor engineers, bioengineers and biologists working closer together are, therefore, strongly encouraged.

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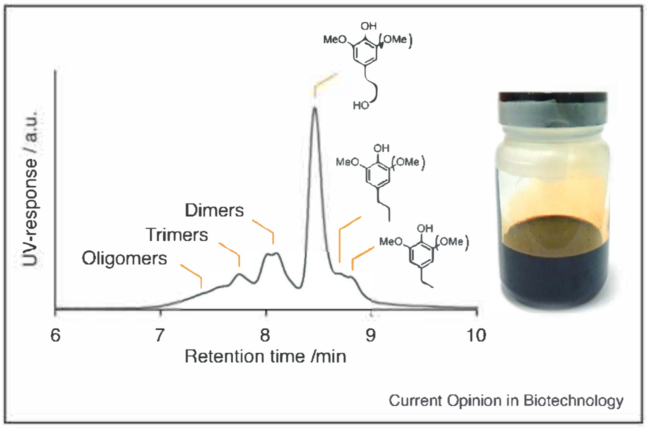
Context and history

Instigated by environmental concerns and resource scarcity, a shift towards a circular, bio-based economy is on the horizon [1–3]. This inevitable transition will hinge on the deployment of alternative technologies that are able to fulfil the needs of our society in a sustainable way. Within this context, lignocellulose biorefining might form a key technology, providing access to renewable chemicals, materials and energy. Over the past few decades, a vast amount of promising biorefinery methods have been disclosed [4–7]. One particular technology that has rapidly emerged in the past couple of years is Reductive Catalytic Fractionation of lignocellulose, abbreviated as RCF. Obviously, redox catalysis plays a central role, which is *the* distinguishing technical feature of the RCF biorefinery.

The roots of RCF go back to studies on native lignin hydrogenolysis from the 1940s (Hibbert) and 1960s (Pepper), which were mainly performed for structural analysis of native lignin [8–11]. Roughly half a century later, research on RCF kick-started (again), but this time in the context of lignocellulose biorefining [12–17]. RCF is a biorefinery approach that integrates biomass fractionation (i.e. delignification) with lignin depolymerisation–stabilisation, the latter being enabled by the redox-active catalyst. Unlike more traditional fractionation approaches (e.g. kraft pulping), RCF yields an uncondensed, low-M_w lignin oil, comprising phenolic monomers in close-to-theoretical yields (Figure 1) [18•].

This Opinion article aims to provide a concise and intelligible overview of the RCF research field, starting from the early proof-of-concept publications through to the most recent innovations such as flow-through operation and the synergy with feedstock engineering. Particular

Figure 1



Current Opinion in Biotechnology

Gel permeation chromatogram of a typical RCF lignin oil (eucalyptus), with signal assignment. Roughly 50 wt% of the lignin oil comprises phenolic monomers. The other fraction comprises dimers, trimers and small oligomers. GPC chromatogram was adapted from Ref. [33].

attention is paid to future research opportunities resulting from these recent advancements, as well as potential hurdles that might obstruct industrial implementation.

How RCF works

The most essential ingredients to operate an RCF biorefinery are (i) lignocellulosic biomass, (ii) an alcohol (or cyclic ether) solvent, and (iii) a heterogeneous redox-active catalyst [12–17,18•]. Often water is used as a co-solvent [19]. These are typically added to a high-pressure batch reactor, which is heated to 180–250°C for 2–6 hours. Heating induces solvolytic extraction of lignin from the biomass (i.e. delignification), followed by partial fragmentation through ether bond cleavage (Figure 2). This initial solvolysis generates reactive, unsaturated fragments that are prone to undergo repolymerisation. The redox active catalyst (e.g. Pd/C) reductively stabilises these unstable species and additionally might effectuate depolymerisation (i.e. hydrogenolysis of residual ether bonds). Although catalytic depolymerisation and stabilisation consume hydrogen, the actual presence of pressurised hydrogen is only optional, as the solvent or hemicellulosic sugars can also be used as hydrogen donors [13–15,20]. Eventually, after filtration and solvent evaporation, RCF yields a stable lignin oil comprising phenolic monomers, dimers and small oligomers (Figure 1). Typically obtained monophenolic products are 4-*n*-propylguaiacol/-syringol [16,17], 4-*n*-propanolguaiacol/-syringol [14,21••] and 4-*n*-propenylguaiacol/-syringol [15], the selectivity being dependent on catalyst and process conditions [4]. In addition, a carbohydrate pulp is obtained, which most often contains the spent catalyst powder. Because in this biorefinery scheme lignin is taken care of before carbohydrate valorisation, the terms 'lignin-first biorefinery' or 'early-stage catalytic conversion of lignin (ECCL)' are often used to indicate the general plan of action [5,22•].

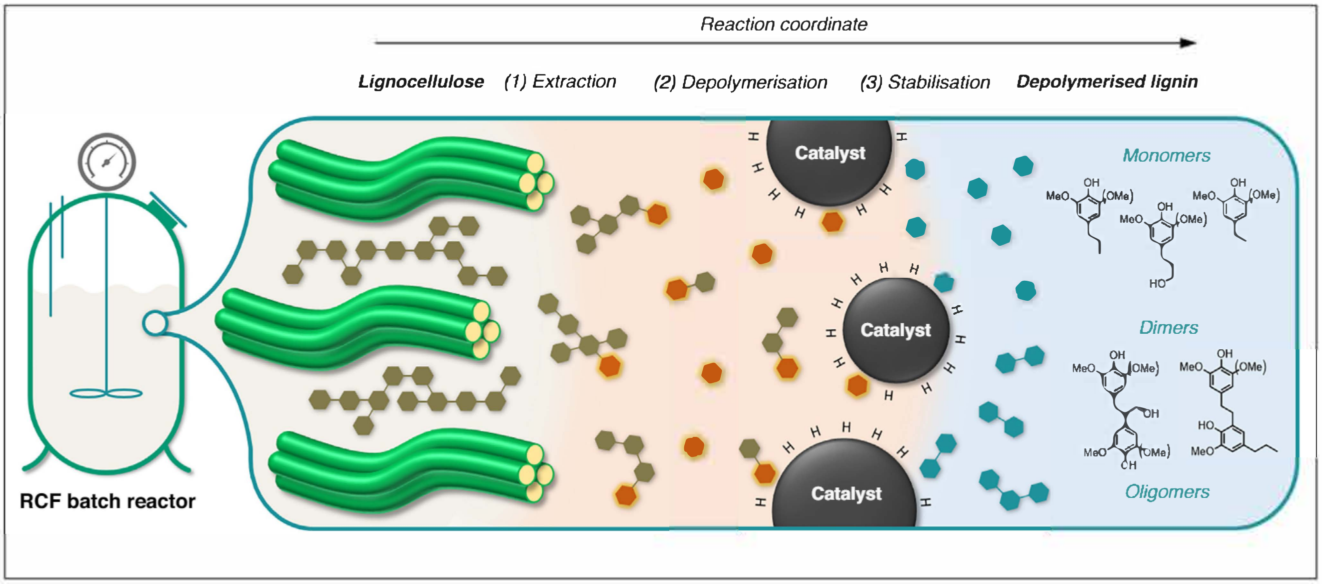
RCF thus comprises three elementary steps: lignin extraction (1), depolymerisation (2) and stabilisation (3) [23••,24••]. Recent studies have established a basic understanding of the relationship between these steps and process parameters. Lignin extraction (1) is solely dependent on the solvolytic conditions and does not require a redox-active catalyst. Contrarily, reductive stabilisation (3) of the unsaturated fragments is exclusively governed by the redox-active catalyst. The situation is less straightforward for the depolymerisation step (2), which comprises two different routes: solvolytic depolymerisation (2a) and catalytic hydrogenolysis (2b) [25•]. Literature indicates that the relative importance of each pathway depends on the '*solvolytic*' severity (i.e. a combination of temperature, pH, solvent polarity). It has been shown that under relatively severe conditions (e.g. methanol, 250°C), lignin depolymerisation occurs primarily solvolytically, generating coniferyl and sinapyl alcohol as reactive intermediates [23••,25•]. These intermediates have also been observed in model compound solvolysis studies, which suggests that coniferyl and sinapyl alcohol are formed *via* homolysis of β–O–4 linkages [26–28]. Under relatively severe RCF conditions, the role of the catalyst is limited to the stabilisation of reactive species [23••]. In contrast, under less severe conditions (e.g. methanol, 190°C), solvolytic bond scission occurs much more slowly, and the catalyst additionally performs hydrogenolysis of inter-unit ether linkages [29••]. Knowing whether ether bonds are primarily cleaved solvolytically or catalytically is of utmost importance for process tailoring. For instance, targeted catalyst design is only possible given a proper understanding of its precise role, which is thus strongly intertwined with the solvolytic severity.

Moving from batch to flow-through reactors

The vast majority of RCF research has been performed using batch autoclaves, with all three elementary steps taking place in one pot. Because the redox-active catalyst is not involved in the lignin extraction (*vide supra*), opportunities arise to physically separate the solvolytic lignin extraction-depolymerisation from the catalytic hydrogenolysis-stabilisation step [15,16,23••]. Recently, two research teams independently performed RCF using a flow-through setup comprising an isolated biomass bed and catalyst bed [25•,29••]. The solvent is first sent through the biomass bed, thereby extracting and partly disassembling the lignin (Figure 3). Next, the liquor flows through the catalyst bed resulting in further depolymerisation and stabilisation of the solubilised lignin fragments [25•,29••]. A back-pressure regulator mounted at the outlet offers control over the total system pressure [25•,29••].

As a result of the physically separated beds, two of the most important advantages of flow-through RCF are that it yields a catalyst-free pulp and allows easy catalyst recuperation, thereby facilitating pulp valorisation as well

Figure 2



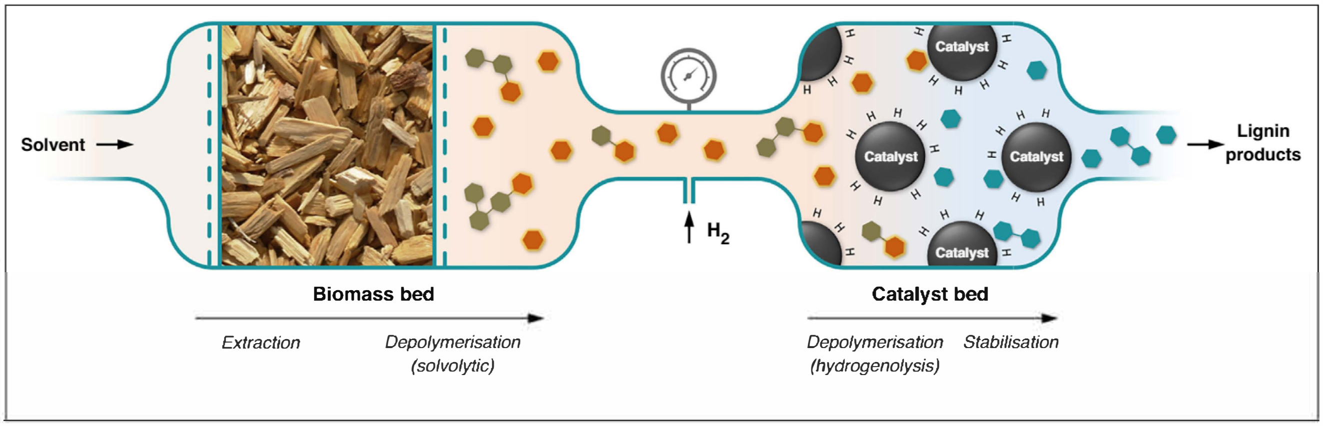
Schematic representation of RCF in batch mode displaying the three elementary steps: lignin extraction, depolymerisation and stabilisation. Depolymerisation can either occur solvolytically or catalytically (hydrogenolysis). The result is a low-M_w lignin oil, comprising monomers, dimers and oligomers, in addition to a carbohydrate pulp. Green hexagons represent native lignin monomer units, orange hexagons correspond to reactive units, and blue hexagons represent stabilised units.

as catalyst reuse [25•,29••]. Samec *et al.* demonstrated that the catalyst-free pulp can be enzymatically hydrolysed to glucose (95% yield based on pulp), without the need for any prior purification [25•]. In a study by Beckham and Roma'n-Leshkov, catalyst reuse in up to four consecutive runs was demonstrated and further investigated [29••]. Moreover, the two confined reaction zones enable a more independent and versatile optimisation of process conditions. The temperature can for instance be set differently for both beds [25•]. Not only this increased flexibility is interesting for process optimisation, but it also allows a better investigation of particular aspects of the RCF process. More specifically, studies inspecting the actual lignin extraction should be performed in a solvolysis-limited regime, as explained by Beckham and Roma'n-Leshkov [30•]. The same applies to studies directed towards catalytic activity and stability, which should occur in a reduction-limited regime [30]. Yet another benefit of the separated beds is the fact that biomass processing can proceed in the absence of pressurised hydrogen, because hydrogen is only useful in the second stage of RCF. Hydrogen can be added to the second, possibly smaller, reactor where the actual hydrogenation takes place, favouring the overall safety and reactor requirements (Figure 3) [29••].

Flow-through RCF is a semi-continuous process; it, therefore, offers better time-resolved data compared to the time-averaged data from batch RCF. By sampling every 10–15 min, it is easier to monitor for instance structural differences between the lignin released in the beginning and at the end of the process, as well as catalyst deactivation [25•,29••,30•]. Another advantage of the semi-continuous nature is that it allows the possibility of changing the process conditions, such as the solvent composition [19] or the concentration of additives [31,32], over the course of the reaction. This could facilitate deeper delignification and/or hemicellulose extraction at the final stages of the process, but remains uncharted terrain thus far. Nevertheless, it should be noted that flow-through RCF is still a batch-wise operation from the perspective of the solid biomass, which has to be (un) loaded between runs. From an industrial point of view, a fully continuous process would be more desirable, but is extremely challenging at first glance.

An inherent drawback of flow-through compared to batch-wise processes is the higher solvent consumption. According to literature, flow-through RCF consumes 90 mL $g_{\mathrm{biomass}}^{-1}$ [29••], being much higher than typical batch processes (4–20 mL $g_{\mathrm{biomass}}^{-1}$) [17,33,34]. Lowering the volumetric flow rate constitutes the most straightforward answer to decreasing solvent use. One should be aware, though, that solvolytic depolymerisation generates unstable fragments, and lowering the flow rate (i) retards these species from reaching the catalyst bed and being stabilised, as well as (ii) increases the average lignin concentration and thus also the concentration of reactive species. Again, the solvolytic severity determines to what extent solvolytic depolymerisation generates reactive

Figure 3



Schematic representation of RCF in flow-through mode. Solvolytic lignin extraction-depolymerisation is physically separated from catalytic depolymerisation–stabilisation, which offers greater flexibility. In addition, flow-through RCF is a semi-continuous process, generating better time-resolved data compared to batch processes.

fragments that can subsequently repolymerise (*vide supra*). For example, when increasing the temperature of the biomass processing stage from 200 to 220°C, Samec *et al.* observed a small yield penalty (11% relative), which was ascribed to increased repolymerisation [25•]. Relatively mild conditions are thus more desirable to lower the extent of repolymerisation. However, mild conditions also impose longer reaction times to satisfactorily delignify the biomass, which in turn has negative consequences for total solvent consumption. A balance should thus be found.

Despite its promising features, the scale at which flow-through RCF has been demonstrated remains limited to 1 g biomass, based on open literature [29••]. For comparison, batch RCF has been demonstrated several times at a 2–5 L scale, with up to 300 g of biomass being processed in a single run [33–35]. Further research is required to evaluate the applicability of flow-through RCF at larger scale. Again, a potential bottleneck could be the time needed for the reactive intermediates to reach the catalyst bed, which can pose constraints on the size and dimensions of the biomass bed. Other considerations for reactor design include the non-uniformity of biomass particles and the possible occurrence of channelling, causing ineffective delignification. Moreover, extracting lignin (and optionally hemicellulose) has been reported to alter the morphological characteristics of the biomass particles [19], which might in turn cause physical changes of the biomass bed over time and consequent deviations from ideal plug flow.

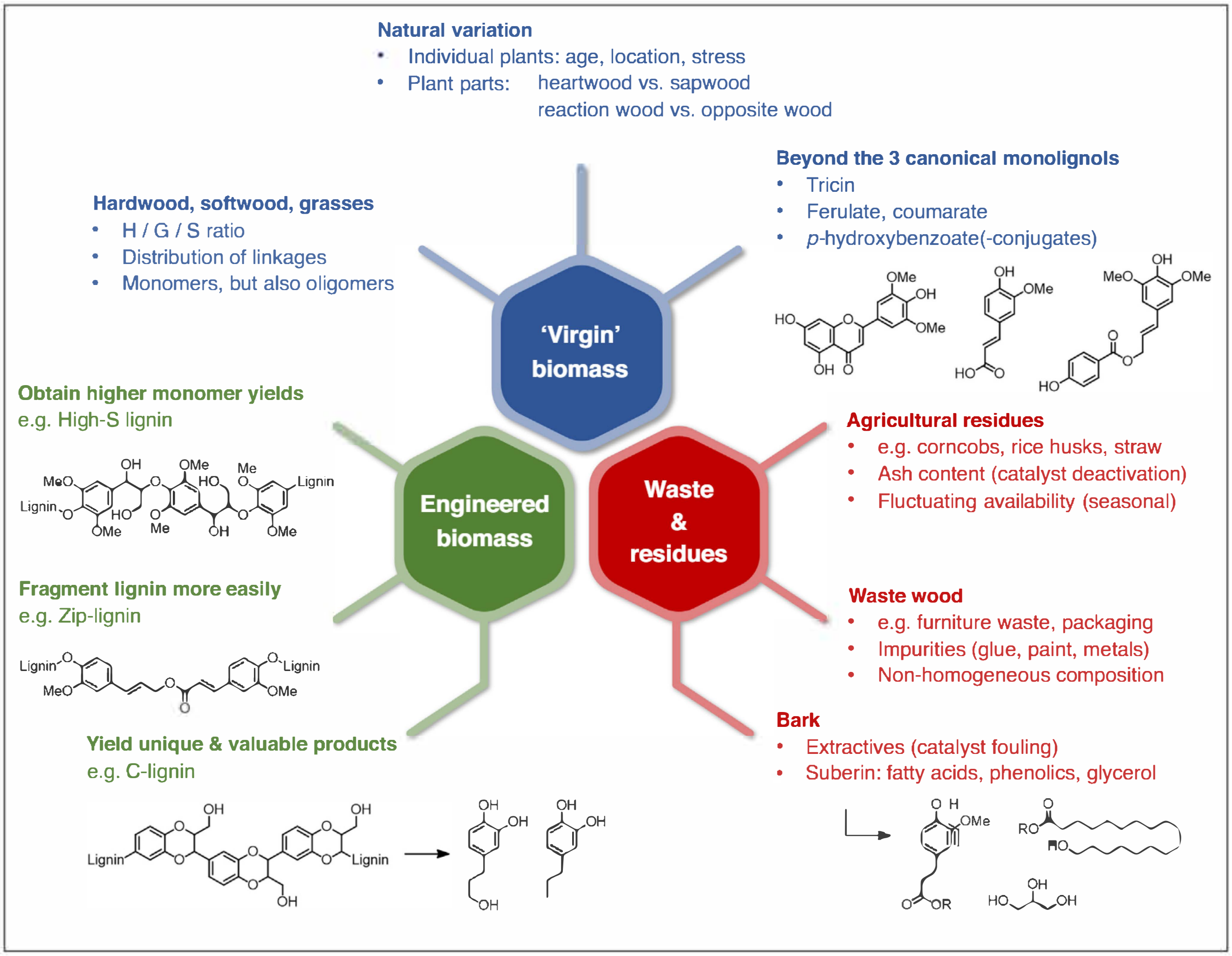
Feedstock scope: opportunities and limitations

'Virgin' biomass

The product outcome of RCF is highly dependent on the nature of the lignocellulosic substrate (Figure 4). Most of the reported studies use a single, virgin lignocellulosic feedstock. Typically, these substrates are divided into hardwoods, softwoods and herbaceous crops. The lignin content, structure and extractability greatly differ between these classes. Lignin content is generally highest for softwoods (21–29 wt%), followed by hardwoods (18–25 wt%) and herbaceous crops (15–24 wt%). Also the relative distribution of precursor monolignols (i.e. lignin building blocks: *p*-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol) varies widely between these classes. Softwood lignin is composed almost exclusively of G units, whereas hardwood lignin contains both S and G units. Herbaceous crops contain H, G and S units, although the amount of 'true' H units is relatively low [36]. Besides the three traditional monolignols, numerous other phenolic compounds are naturally incorporated in the lignin structure [36]. Well-known examples are tricin [37–39], and *p*-coumarate/*p*-hydroxybenzoate conjugates [36]. The RCF biorefinery might benefit from exploiting this natural wealth of potentially valuable lignin building blocks, though current RCF research is mainly focused on the fate of the canonical monolignols.

The lignin structure (viz inter-unit bonds) depends on the relative distribution of H, G and S units (respectively 0, 1 and 2 methoxy groups *ortho* to the phenolic-OH). S units lack a free *ortho*-position and thus cannot form 5–5 and β–5 inter-unit bonds upon radical coupling during lignification. Therefore, lignin rich in S units (hardwoods) contains less stable C–C bonds than lignin rich in G units (softwoods). Because C–C bonds cannot be broken during typical RCF processing, the theoretical maximum lignin monomer yield is roughly proportional to the square of the relative content of cleavable inter-unit ether bonds [5]. In practice, various hardwoods (e.g. birch [17], beech [40], poplar [41], oak [33], eucalyptus [19]), softwoods (e.g. pine [15], spruce [34]) and herbaceous

Figure 4



Overview of feedstock opportunities for RCF biorefineries. RCF has primarily been investigated for 'virgin' biomass. However, potential synergies arise when bioengineered crops are considered, specifically designed for deconstruction. Waste and residual streams in contrast have the advantage of being cheap, but require a robust catalytic system that can deal with some challenging inherent characteristics.

crops (e.g. miscanthus [42]) have been tested in RCF. Lignin monomer yields are generally highest for hardwoods (high S content), followed by herbaceous crops and softwoods (high G content) [4]. Stating that hardwoods are, therefore, inherently better for RCF is an overly simplified and short-sighted conclusion. Besides the aspect of total monomer yield, the fact that softwood lignin is exclusively composed of G units narrows the RCF product distribution, facilitating downstream purification. In addition, a low monomer yield is often accompanied by a high yield of oligomers. The chemical structure of these oligomers is quite unique, given their relatively low M_w (e.g. compared to organosolv lignin [17]) and high content of hydroxyl groups [43]. The RCF oligomer fraction, though, seems to be undervalued, as the major body of literature focusses on monomers. Fortunately, there is inspiring research that exemplifies the valorisation potential of these oligomers, for instance for poly-urethane foams [44] and epoxy resins [45].

Regardless of the general differences among hardwoods, softwoods and grasses, it should also be noted that there is an immense natural variation among individual plants, depending on age, climate, location, endured (a)biotic stress and so on. Even between plant parts (e.g. heartwood, sapwood, twigs, bark, tension/compression/opposite wood) structural variation exists [46–50]. Systematic studies investigating the impact of this natural variation on RCF could offer valuable insight, but are currently lacking.

Waste and residues

In addition to virgin biomass, lignocellulosic waste streams constitute an interesting resource as they are cheap and often abundantly available. A first category comprises residues from agriculture, many of which can be classified as herbaceous crops. Examples that have been investigated in RCF processes include mainly residues from grasses: corn stover [51,52], corn stalks [53,54], corn cobs [55], wheat chaff [56] and rice husks [57]. Often, these agricultural residues are characterised by a high ash content [58]. Ramifications of inorganics, which might accumulate over time, on RCF catalysis remain largely underinvestigated. In addition, some of these agricultural resources are only seasonally available. The impact of storage on feedstock performance is highly relevant within this context. Another class of cheap and abundant biomass is waste wood, originating from packaging, furniture waste, construction wood, saw milling (lumber) operations and so on. In contrast to agricultural residues, waste wood can potentially be much more inhomogeneous and variable over time (e.g. furniture waste). The presence of associated metals, paint, glue or other impregnating components, makes this feedstock highly challenging for RCF. As no dedicated RCF studies have been disclosed to our knowledge, the industrial feasibility is difficult to assess at this stage. Yet another class of residual biomass is bark [59,60,61•], which is a major waste stream from wood processing industries (paper, timber). Bark is a chemically complex material containing components that are not even present in wood, such as suberin. Suberin is a biopolymer composed of two cross-linked domains, an aromatic lignin-like domain and an aliphatic domain [59], the latter being a polyester of (bifunctional) fatty acids, glycerol and hydroxycinnamates (mainly ferulic acid) [62]. When subjecting bark to RCF, as recently disclosed, the suberin (and lignin) is deconstructed yielding phenolics, glycerol and long-chain (C_{16}–C_{26}) aliphatics [59,60,61•]. The latter fraction comprises fatty acids/esters, di-acids/di-esters, alcohols and ω-OH acids/esters, which might be interesting for further upgrading towards fuel applications [61•]. It should be stressed, though, that bark is much more complex than virgin wood. It has a higher ash and extractives content (e.g. waxes, fatty acids, tannins). The combined effect of these components on the catalytic system (i.e. activity, selectivity, stability) remains to be elucidated. Additionally, bark lignin is known to contain more G units than the parent wood lignin, which affects the product distribution and yield (*vide supra*) [47,50,63].

In general, processing low-value waste streams requires a robust catalytic system that is capable of dealing with the inherent presence of contaminants. Research considering this (catalytic) robustness is strongly encouraged. Alternatively, prior feedstock washing or cleaning might be considered, though this will (at least partly) compensate the low feedstock cost.

Engineered crops

On the other end of the feedstock spectrum are genetically engineered crops, having a lignin structure specifically designed for biorefinery purposes. There are multiple ways in which the lignin biosynthesis can be tailored via genetic engineering, as recently reviewed [64••] (see also other papers in this special issue). Lignin can be designed to effectuate a lower polymerisation degree, less cross-linking with structural carbohydrates, increased hydrophilicity and the incorporation of labile linkages or novel lignin building blocks [36,64••]. Designer lignins relevant to RCF are those that either (i) increase lignin monomer yields, (ii) facilitate delignification and/or (iii) provide novel, value-added monomers (Figure 4).

In order to increase the monomer yield obtained upon RCF, lignins should contain a lower fraction of uncleavable carbon-carbon bonds. This can be achieved by increasing the S/G ratio (*vide supra*). More specifically, overexpression of F5H in hybrid poplar resulted in a lignin structure containing nearly 98% S units [65]. Using such a modified substrate with an S-rich lignin clearly offers higher monomer yields upon RCF (up to 77 wt%) [17,66]. The second class of modifications are those that facilitate delignification. This can be accomplished by incorporating labile bonds in the lignin structure. In turn, this might allow lignin extraction and fragmentation under milder conditions, thereby better preserving the carbohydrate fraction and preventing repolymerisation reactions of reactive species (*vide supra*). A well-known example is the so-called *zip*-lignin, in which monolignol ferulate conjugates are used such that labile ester bonds are incorporated into the lignin backbone [67,68]. Other examples are (i) CAD-deficient plants containing hydroxycinnamaldehyde-derived lignins [69,70], (ii) CCR-deficient plants containing ferulic acid [71,72], and (iii) plants modified to contain the Cα-dehydrogenase (LigD) enzyme, and therefore have labile α-keto-β-ether structures in their lignin [73]. The latter approach displays stark resemblance to recent oxidative strategies involving oxidation of the benzylic alcohol to weaken the β–O–4 ether bond [74]. To date, these altered substrates have not thus far been investigated in RCF biorefineries. Finally, the third major strategy is to introduce novel components into the lignin structure that provide added value upon RCF. An intriguing example is lignin built from caffeyl alcohol, or so-called C-lignin [75•,76]. During radical polymerisation, an intramolecular rearomatisation results exclusively in the formation of a benzodioxane inter-unit bond (Figure 4). Consequently, the formation of carbon-carbon bonds is prevented, resulting in linear, ether-rich strains [75•], similar to high S lignin (*vide supra*). C-lignin naturally occurs in vanilla seed coats, which is not a relevant feedstock, but has recently been used as a substrate in RCF to deliver a *proof-of-concept*. This resulted in the formation of catechylpropane or catechylpropanol instead of the traditional guaiacols [77••,78]. The incorporation of C-lignin in bio-energy crops *via* genetic engineering though, remains to be disclosed in open literature [77••]. Alterations in the lignin structure can sometimes negatively affect the plant's health. Dwarfism, a decreased plant stiffness or a delayed growth are common side effects [79]. Yet the extraordinary plasticity of lignin biosynthesis [64••,80,81] has thus far resulted in a rich portfolio of interesting opportunities.

Conclusion

Reductive catalytic fractionation (RCF) evolved from a lignin characterisation tool towards a promising lignocellulose biorefinery scheme that effectively deals with the reactive nature of lignin. Central to the RCF biorefinery is a heterogeneous catalyst, which enables the disassembly of lignin during its extraction from the biomass. Significant progress has recently been made in (i) understanding the elementary steps, (ii) stepping away from all-in-one batch autoclaves, and (iii) considering both low-value waste streams as well as engineered plants as potential feedstocks. Crucial to the further development of RCF are joint research efforts to seize upon multidisciplinary opportunities and to tackle some important challenges that lie ahead.

Conflict of interest statement

Nothing declared.

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- •• of outstanding interest

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PMO), which is used in a second step to also covert the pulp, yielding aliphatic alcohols. Conversion of the pulp allows easy catalyst recuperation. Of note, this work presents several high-value applications for 4-*n*-propanolguaiacol, one of the commonly obtained RCF products.

22. • Renders T, Van den Bosch S, Koelewijn SF, Schutyser W, Sels BF: **Lignin-first biomass fractionation: the advent of active stabilisation strategies**. *Energy Environ Sci* 2017, **10**:1551-1557.

This Opinion article present the general concept of lignin-first biorefining. Mitigating lignin repolymerisation during fractionation is of utmost importance to enable downstream lignin valorisation. Three strategies are presented and discussed, including RCF. In addition, different approaches to integrating hemicellulose valorisation are discussed, as well as opportunities for the pulp.

23. •• Van den Bosch S, Renders T, Kennis S, Koelewijn S-F, Van den Bossche G, Vangeel T, Deneyer A, Depuydt D, Courtin CM, Thevelein J, Schutyser W, Sels BF: **Integrating lignin valorization and bio-ethanol production: on the role of $Ni\text{-}Al_2O_3$ catalyst pellets during lignin-first fractionation**. *Green Chem* 2017, **19**:3313-3326.

This article discloses the utilisation of a catalyst basket in an RCF batch reactor, demonstrating that no physical contact between the biomass and catalyst is required. Furthermore, it is shown that ether bonds are primarily cleaved solvolytically. Under relatively harsh conditions (methanol, 250°C), the major role of the catalyst is to stabilise reactive, unsaturated species such as coniferyl alcohol.

24. •• Ferrini P, Rezende CA, Rinaldi R: **Catalytic upstream biorefining through hydrogen transfer reactions: understanding the process from the pulp perspective**. *ChemSusChem* 2016, **9**:3171-3180.

Whereas the benefits of implementing catalysis during lignocellulose biorefining for lignin valorisation have been numerously demonstrated, this article shows the advantages from the perspective of the pulp. Compared to organosolv pulp, the pulp from an RCF process is characterised by a lower lignin content and a better retention of hemicellulose. See also Ref. 41 for more detailed information.

25. • Kumaniaev I, Subbotina E, Savmarker J, Larhed M, Galkin MV, Samec J: **Lignin depolymerization to monophenolic compounds in a flow-through system**. *Green Chem* 2017, **19**:5767-5771.

This study demonstrates flow-through RCF of birch wood under hydrogen-transfer conditions. The authors investigate the process in the presence and absence of a redox-active catalyst (RCF versus organosolv). A reaction scheme for lignin disassembly is proposed involving solvolytic and catalytic ether cleavage.

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29. •• Anderson EM, Stone ML, Katahira R, Reed M, Beckham GT, Román-Leshkov Y: **Flowthrough reductive catalytic fractionation of biomass**. *Joule* 2017, **1**:613-622.

This article is the first to demonstrate RCF in flow-through mode. The advantages of semi-continuous operation and decoupled solvolysis-catalysis are exploited to study the elementary steps, as well as catalyst deactivation. It is shown that unsaturated intermediates are responsible for repolymerisation.

30. • Anderson EM, Stone ML, Hülsey MJ, Beckham GT, Román-Leshkov Y: **Kinetic studies of lignin solvolysis and reduction by reductive catalytic fractionation decoupled in flow-through reactors**. *ACS Sustain Chem Eng* 2018, **6**:7951-7959.

In this work on RCF, a distinction is made between solvolysis-limited regimes and reduction-limited regimes, required to study either lignin extraction or catalytic activity, respectively. In addition, some intrinsic kinetic data were determined, such as the apparent activation energy for solvolysis. Interestingly, this particular activation barrier measured in batch was half of that measured in flow-through, suggesting that batch RCF is confronted with mass transfer limitations.

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