Cleave and Couple: Sustainable Routes to Bio-based Amines

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Global aim and grand challenges

Achieving energy efficiency, resource security and preventing environmental pollution are great societal challenges that need to be urgently tackled. To address these key points, the chemical industry has to undergo an essential transition from a fossil-based to a renewables-based enterprise, while—at the same time—significantly improving practices related to sustainability and green chemistry.[1,2,3] This would bring significant environmental and economic benefits overall, while creating revenues for the agricultural and chemical industry sectors and various other stakeholders in the European Bioeconomy.[4]

But how to achieve this transition when our conventional methodologies, developed in the past centuries, were designed to gradually add functionality to simpler petroleum-based molecules (typically alkanes, alkenes, simple aromatics)? In contrast to fossil resources, renewables are highly oxygenated biopolymers; therefore, their implementation would require finding efficient depolymerisation and controlled deoxygenation strategies in order to access usable chemical building blocks.[5] And what kinds of consumer products can we and should we produce from renewables? Undoubtedly, great efforts should be devoted to connecting the initial depolymerisation strategies with accessing bio-based products that spread a wide value-range: from fuels to fine chemicals. Notably, we need to design, simultaneously, for improved performance of products as well as minimising their adverse effects on human health and the environment.

Lignocellulose

Lignocellulose is a non-edible, renewable starting material consisting of lignin, cellulose and hemicellulose. An estimated 136Mt of lignocellulose waste was generated in 2015 by agricultural and forestry activities in the EU[6]. This waste could serve as valuable input into biorefineries for the sustainable production of bio-based fuels, chemicals, materials. However current approaches are largely inefficient, especially concerning the efficient depolymerisation and valorisation of the lignin constituent. Moreover, besides second-generation biofuels, other product portfolios, especially higher-value molecules, have not been explored.

Connected to these global challenges, and in full accordance with the principles of green chemistry, this project aims to develop entirely new catalytic processes and sustainable waste-to-value chains with a focus on lignin depolymerisation and the production of bio-based amines. This approach will open possibilities for the implementation of lignocellulosic biomass as renewable raw material for innovative, environmentally beneficial and economically feasible lignocellulosic biorefineries.[7]

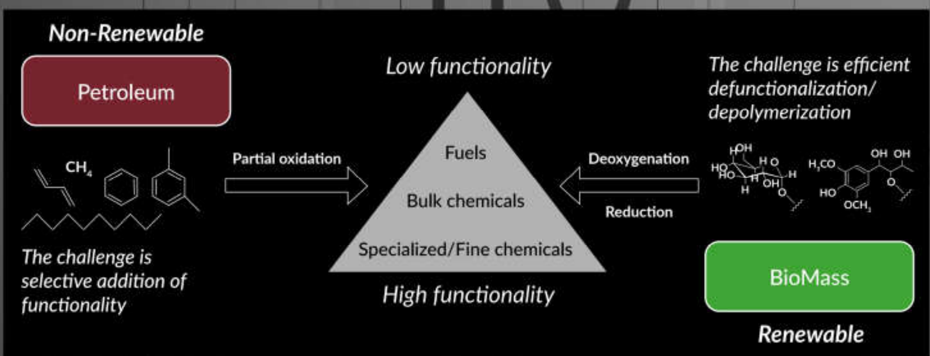


Figure 1: Contrasting challenges in the area of petrochemicals versus renewables.

Cleave and couple: amines from renewables

Amines are crucially important classes of chemicals, widely present in pharmaceuticals, agrochemicals and surfactants or polymers.[8] Yet, surprisingly, ***systematic*** approaches to obtaining this essential class of compounds from lignocellulosic biomass in a waste-free manner have not yet been realised. Ammonia is produced on a large scale and can even be obtained from renewables. In principle, the shortest and most sustainable route to amines would be the *direct coupling* of ammonia[9] with biomass-derived alcohols and water as the only by-product.[10,11] Lignocellulosic biomass and molecules derived therein, is already abundant in alcohol moieties. Moreover, carefully designed depolymerisation and defunctionalisation strategies should deliver specific alcohol functionalities in platform chemicals.

Project aim

The central aim of this project is to enable chemical pathways for the production of amines through alcohols from renewable resources, preferably lignocellulose waste. Two **key scientific challenges** are addressed:

a. The development of efficient lignocellulose processing strategies (upstream) by inventing new catalysts, and methods to enable efficient **cleavage/ depolymerisation reactions, maximising the value gained from all chemically different components of lignocellulose.**

b. The development of new catalysts and methods based on abundant metals, for the atom-economic **coupling** of the derived alcohol building blocks directly with ammonia and for further coupling reactions, in order to access value-added amines that may find application in various areas such as polymers, fine chemicals, pharmaceuticals.

The extensive *defunctionalisation of renewable*

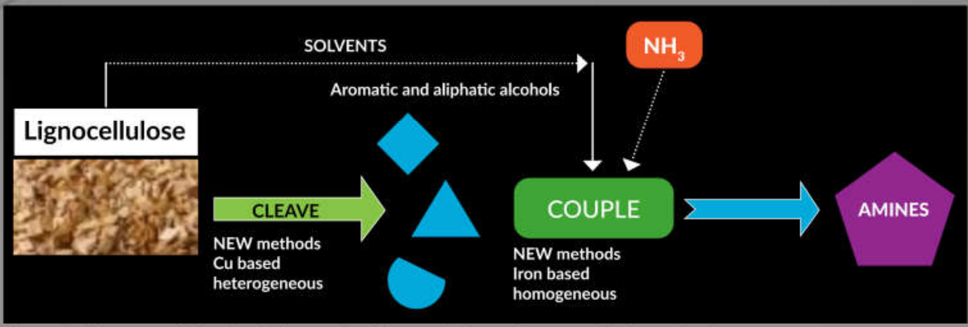


Figure 2: Cleave and Couple: fully sustainable catalytic pathways to bio-based amines

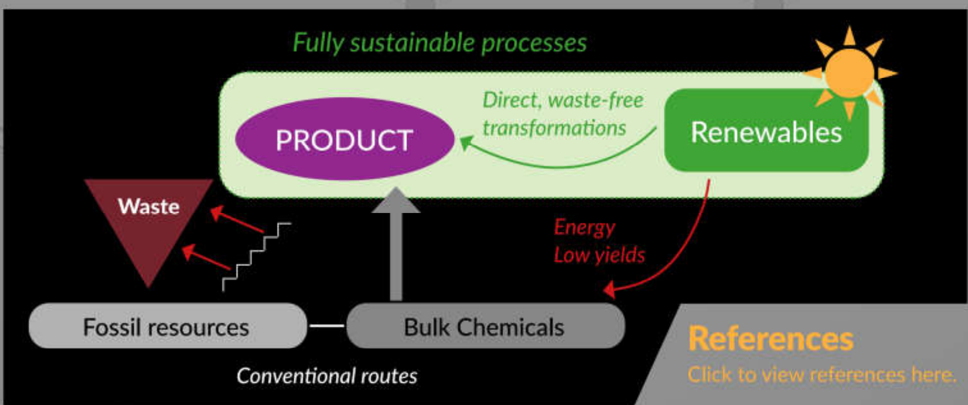
starting materials to obtain simple bulk aromatics (e.g. BTX), necessitates breaking strong C-C and C-O bonds and as a *consequence, requires large energy input.*[6] However, these simple molecules would be subjected again to multi-step, frequently wasteful syntheses when structurally more diverse products are desired. In other words, an approach that destroys functionality in renewable feedstocks just to build it back up again is certainly neither efficient nor environmentally friendly. In contrast, this project presents novel, **mild depolymerisation and controlled defunctionalisation strategies**, which require less energy and retain part of the structural complexity inherent to the renewable substrate. Careful design of the depolymerisation pathways delivers platform chemicals of unprecedented structure, which have multiple handles for further functionalisation—preferably in an atom-economic[12] manner. Such reactions of choice are, for example, the direct coupling of alcohols with ammonia, and further diversification of these primary amines, preferably using catalyst containing only Earth-abundant metals.

This unique balance between cleavage and coupling pathways allows access to value-added products directly, minimising the number of overall reaction steps required, and significantly reducing the amount of waste formed in the overall process.[1,2] The rapid conversion to higher-value products—such as functionalised amines that can enter the chemical supply chain at a much later stage than bulk chemicals derived from petroleum—offsets the relatively high initial energy costs associated with lignocellulose processing.

Impact

The project, which started in 2016, has already delivered several breakthroughs in the area of lignocellulose conversion,[13,14] sustainable catalysis,[15,16,17] and lignin chemistry.[18] Significant advances in lignin valorisation include the stabilisation of reactive intermediates during acidolysis in order to minimise undesired recondensation phenomena and to access aromatic platform chemicals that have not previously been obtained.[18] Furthermore, a perfect illustration of the 'cleave and couple' concept is the work on **complete lignocellulose** conversion.[13] This 'model biorefinery' is able to convert the main constituents of lignocellulose to aromatic and aliphatic alcohol intermediates.

- An interdisciplinary concept for the complete utilisation of renewable lignocellulose.
- Specific, completely waste-free routes from lignocellulose to valuable amines.
- A unique balance of cleavage/coupling pathways, which minimise the number of reaction steps and increase overall sustainability.
- Fundamental concepts in lignin chemistry.
- New catalysts and methods based on inexpensive Erath abundant metals.



References

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Figure 3: Embracing complexity in renewable resources allows to develop waste-free routes to high-value products.

SUMMARY

The multidisciplinary ERC Starting Grant project "Cleave and Couple" encompasses research in sustainable catalysis. 'Cleave' refers to finding novel catalytic depolymerisation approaches for renewable biopolymers, focussing on lignin. 'Couple' signifies the diversification of the obtained chemical building blocks to access products, in particular bio-based amines, with potential future application in various areas, e.g. pharmaceuticals, materials, polymers.

PROJECT LEAD PROFILE

Dr Barta started her independent career in 2013 at the Stratingh Institute for Chemistry in Groningen and is currently Full Professor at the University of Graz. She is a member of the Young Academy of Europe, secretary of EuChemSoc - GSC division and 2022 co-chair of the Gordon Research Conference in Lignin valorisation. Her awards include: ERC Starting Grant 2015, VIDI Grant 2015, ERC Proof of Concept Grant 2019, the 2019 NCCC Award and the 2020 ACS Sustainable Chemistry & Engineering Lectureship award.

PROJECT PARTNERS

The CatASus project is based at the University of Graz, Austria and the Stratingh Institute of Chemistry, University of Groningen, the Netherlands. Collaboration partners include groups from Germany, Switzerland, UK, and the USA.

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