Sustainable Production of Value-added Chemicals

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Over 80% of global energy and more than 90% of chemical products are derived from fossil fuels, making them a dominant driver of greenhouse gas emissions. The escalating demand for energy and chemicals, alongside increasing environmental awareness and stringent greenhouse gas emission regulations, highlights the critical need for renewable alternatives. Forest residues and food waste (FW) are promising resources to meet these demands sustainably. In addition to feedstock selection, a sustainable biorefinery relies on conversion technology, and high-value products while maintaining cost-effectiveness, energy and carbon efficiency. In this thesis, we investigate conversion of FW and forest residues into value-added chemicals via economic and environment-friendly processes.

Traditional FW treatment methods, such as disposal into landfills and composting, are environmentally unfriendly. Intensive exploration of other methods that selectively utilize the diverse composition of FW to high commercial value chemicals is a key to alleviating this challenge. Extraction of antioxidant and antimicrobial activity providing chemicals (flavonoids, phenolic acids, etc.) from FW feedstocks is one such economically lucrative option to valorize FW. This work first targets three pivotal challenges in enhancing the extraction of bioactive compounds from FW, thereby advancing the circular economy and fostering sustainable waste management.

First, the choice of solvent is a critical parameter that affects the extraction efficiency. However, there is an insufficient fundamental understanding of the solvent selection process for

FW extraction applications, with ethanol, methanol, and their mixtures with water being common choices. A vital consideration is their safety for human consumption due to the application of target extractives in the pharmaceutical, cosmetic, and food industries. In this study, I develop a blueprint for solvent selection revealing more than 150 solvents providing up to 15-fold solubility enhancement than ethanol and methanol *via* ADF-COnductor like Screening MOdel for Real Solvents (COSMO-RS).[1] Further, Hansen Solubility Parameters in Practice (HSPiP) is used to identify replacements for high-performing but toxic solvents with high-solubility green solvent mixtures, and this approach is demonstrated on real FW.

Second, microwave-assisted extraction (MAE) is a versatile and selective approach that offers high yields and employs less time, solvent, and energy making it environmentally and economically advantageous compared to traditional methods. However, mixed FW have received limited attention as most studies focus on pure single feedstocks. Herein, I characterize different FW feedstocks and study MAE of phenolic acids.[2] This library of materials unravels the relationship of FW composition and physical properties with dielectric properties, heating, and extractive yields. Moisture, extraction temperature, time, and the interplay of these factors affect the phenolics' yields. In contrast, the specific target acid yields are determined by the amount of extractives present and their interaction with other extracted components. Interestingly, intermolecular interactions among different FW components enhance phenolics' yields in mixed FW above a simple additive model.

Finally, purification of natural phenolics is critical to replace toxic synthetic antioxidants. However, the separation and purification of these phenolics is challenging owing to their similar chemical nature, high boiling points, and low concentrations in FW. This study directly addresses this issue by proposing a scalable and extensible methodology for conducting selective separation of the target molecules using molecular imprinted polymers.[3] Experiments revealed that polymer synthesized using a bio-based monomer (itaconic acid) provides the highest reported separation factor. The polymer exhibits superior selectivity towards chlorogenic acid, and its high sensitivity to various functionalities enables effective sequential separation of all target phenolic acids.

Fourier transform infrared studies revealed polymer-solvent interaction as the critical factor influencing its performance. The approach, validated using coffee and potato peel waste extracts, outperforms traditional industrial purification techniques, delivering significant economic value and reducing carbon emissions.

Next, we direct our attention to reductive catalytic fractionation of forest residues of three tree parts (bark, twigs/branchlets, leaves) collected in four phenophases (senescence, leafless, emergence, and leafed for deciduous trees) from four co-occurring species (*Betula lenta* L., *Fagus grandifolia* Ehrh., *Liriodendron tulipifera* L., and *Pinus rigida* Mill). We examine the impact of phenophases, species and tree part on the lignin content, total phenolic monomer, S, and G units yields. Generally, bark has the highest lignin content, followed by twigs/branchlets and leaves. Further, the forest residues collected in leafed phenophase provide the highest total phenolic monomer yields, making them more effective for lignin valorization. This work introduces simple harvesting strategies for targeting specific monomers and products for biorefineries.

References

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