DEVELOPMENT OF NOVEL SYNTHETIC ROUTES AND INTENSIFIED PROCESSES FOR BIOMASS-DERIVED CHEMICALS

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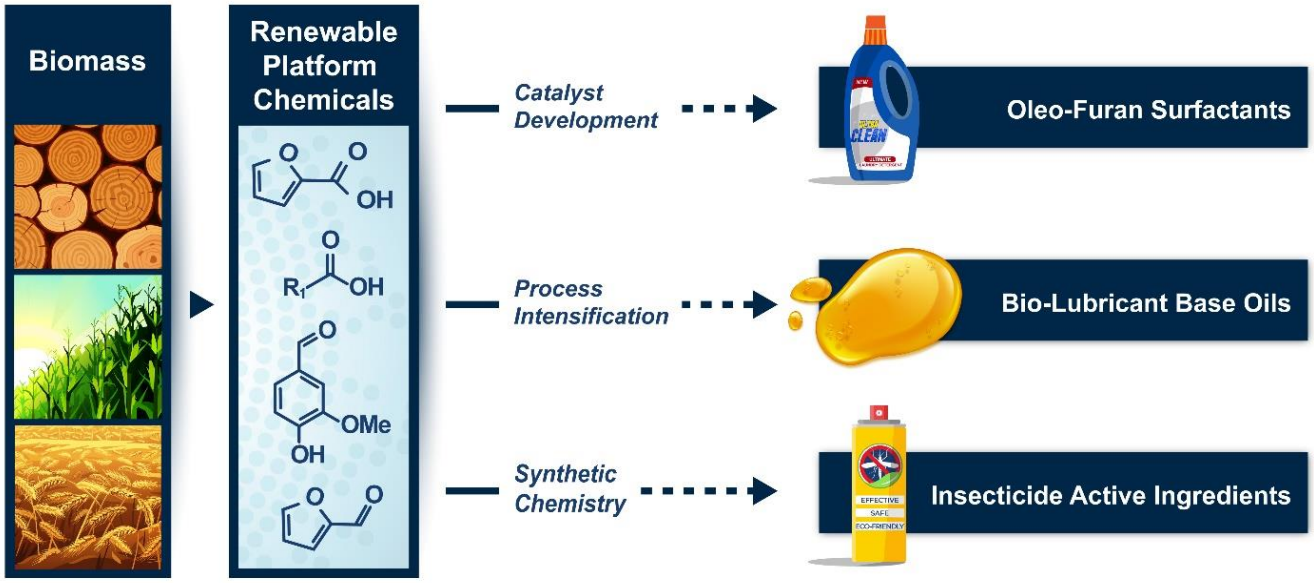
CCM 106 | https://udel.zoom.us/j/92824146574| (Password: biomass)



Fossil fuels are not only sources of energy but also serve as the primary feedstock for over 95% of specialty chemicals. Petroleum refineries provide a continuous supply of aromatic building blocks, such as benzenes, phenols, and naphthalenes, which are essential for the synthesis of surfactants, lubricants, and agrochemicals. However, the synthetic utility of these compounds comes with significant drawbacks, including poor biodegradability, performance limitations, and environmental toxicity. These issues are particularly prominent in the sectors mentioned, which comprise 45% of the specialty chemicals market.

Biomass offers an abundant and renewable alternative that is increasingly being used to produce similar chemicals. However, current biobased processes face several challenges, including inefficient catalysis, excessive reliance on costly raw materials, energy-intensive separations, and limited product performance. Addressing these diverse challenges requires a versatile approach. This thesis introduces innovative strategies in catalysis, process intensification, and synthetic chemistry to overcome the key obstacles in the production of renewable surfactants, lubricants, and agrochemicals from biomass feedstocks.

Thrust 1: Renewable Surfactants from Biomass and Hybrid Feedstocks

This thrust explores two complementary routes to oleo-furan sulfonate (OFS) surfactants, renewable analogs to linear alkylbenzene sulfonates (LAS). The first route improves OFS precursor yields via cross-ketonization of 2-furoic acid and fatty acids using magnesium oxide (MgO), which achieved 86% yield by minimizing decarboxylation. Mechanistic studies (XRD, FTIR, TGA) revealed that metal–carboxylate complexation governs selectivity, and the catalyst was recyclable over multiple cycles.

The second route introduces a hybrid-feedstock approach by combining biomass-derived 2-furoic acid with alcohols obtained from plasma-oxidized polyethylene. Process conditions were optimized to minimize side reactions and accommodate real plastic waste. This strategy offers a novel path to surfactants from dual waste streams, reducing reliance on fatty acids.

Thrust 2: Process-Intensified Lubricant Production via Self-Ketonization in Flow

A continuous, solvent-free flow process was developed for the production of 12-tricosanone, a key lubricant precursor, via self-ketonization of lauric acid. A custom trickle-bed reactor was designed to operate at industrially relevant flow rates and achieved 90% selectivity, enabling monthly production of up to 25 kg, a 20 x increase from the previous reported scale. Catalyst deactivation from carbonate formation was fully reversible through calcination. Techno-economic

analysis revealed a 29% reduction in the minimum selling price relative to commercial polyalphaolefins (PAOs), while life cycle assessment indicated an 8.9% reduction in global warming potential under carbon-neutral assumptions.

Thrust 3: Long-Chain Oxygenates from Cellulosic Feedstocks via MOF Catalysis

This thrust explores the use of amine-functionalized UiO-66-NH_2 metal-organic frameworks (MOFs) to catalyze the aldol condensation of furfural and acetone, enabling the direct synthesis of long-chain oxygenates from cellulosic feedstocks. The single-step process eliminates reliance on fatty acids and highlights the importance of tuning MOF properties, such as defectiveness, surface area, and acid modulator to optimize catalytic performance. HCl-modified samples exhibited higher reactivity due to improved acid-base balance and pore structure. This work demonstrates the potential of MOFs as platforms for biomass valorization.

Thrust 4: Biobased Insecticides through Synthetic Innovation and Structure-Guided Design

This thrust develops a strategy for creating safer, biobased alternatives to commercial insecticides. The initial effort focused on synthesizing novel carbamate active ingredients from biomass-derived monomers, specifically furfural and vanillin. These were upgraded using Rh/Al_2O_3 catalyzed reductive amination, followed by $La(OTf)_3$ catalyzed carbonylation. The resulting furfural carbamate matched the insecticidal potency of carbofuran but exhibited lower predicted ecotoxicity and bioaccumulation, techno-economic analysis also confirmed the economic feasibility of the pathway.

Building on the advantages of the biobased core discovered, the next stage introduced a case study for biobased insecticide discovery. A library of 72 furan- and tetrahydrofuran-based carbamates was generated via SMARTS-based molecular enumeration. The molecules underwent pre-synthesis ecological screening using QSAR and DFT models (fathead minnow LC_{50} and photodegradation). Ten candidates were synthesized and tested against *Alphitobius diaperinus*,

leading to the identification of two lead compounds. This demonstrated how early integration of ecological constraints can streamline the discovery of high-performing, safer insecticides.

The final progression expanded the molecular space to include diammide and benzoyl urea insecticides. These compounds were synthesized by replacing halogenated aromatic scaffolds with furan and vanillin-based cores while maintaining key functional groups for receptor binding. Insecticidal assays are pending, but the resulting molecules could represent a new generation of bioinsecticides that combine biodegradability and receptor specificity.

In summary, this thesis provides solutions to key bottlenecks in the valorization of biomass into biobased chemicals.