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Ionic liquids as advanced catalysts for the esterification of fatty acids into bio lubricants

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Abstract

The growing demand for environmentally friendly lubricants has intensified research into biolubricants derived from renewable resources. The esterification of free fatty acids (FFAs) with polyols like trimethylolpropane (TMP) or neopentyl glycol (NPG) is a key synthetic route. However, conventional homogeneous acid catalysts (e.g., H_2SO_4 , p-toluene sulfonic acid) present significant drawbacks, including corrosion, difficulty in separation, and high energy consumption. This paper investigates the application of Ionic Liquids (ILs) as advanced, green catalysts for this esterification process. ILs, salts with low melting points, offer unique properties such as negligible vapor pressure, high thermal stability, and tunable acidity, making them ideal candidates for catalytic applications. This review, drawing on literature prior to 2020, systematically examines the role of ILs in biolubricant synthesis across six domains: the fundamental chemistry of biolubricants and the limitations of conventional catalysis; the structure and properties of ILs; their performance as Brønsted and Lewis acid catalysts; their unparalleled recyclability and green chemistry metrics; a comparative analysis with traditional methods; and future perspectives for industrial implementation. The analysis concludes that ILs, particularly functionalized Brønsted acidic ILs, demonstrate superior catalytic activity, exceptional recyclability, and a greener profile, positioning them as a transformative technology for the sustainable production of high-performance biolubricants.

Keywords: Ionic Liquids; Biolubricant; Esterification; Green Catalysis; Free Fatty Acids; Recyclability

1. Introduction

The global lubricant market, essential for the functioning of all machinery, has traditionally been dominated by petroleum-based products. Growing environmental awareness, stringent regulations on biodegradability and toxicity, and the desire for energy independence have catalyzed the search for sustainable alternatives. Biolubricants, derived from renewable biological sources such as vegetable oils and animal fats, have emerged as a promising solution. Their advantages include high biodegradability, excellent lubricity, high flash points, and a renewable feedstock base, which reduces the net carbon footprint compared to mineral oils.

The primary chemical foundation of most biolubricants is triglyceride molecules found in natural oils. However, neat vegetable oils suffer from poor thermo-oxidative stability and unsatisfactory cold flow properties, limiting their direct application. These weaknesses are primarily due to the presence of β -hydrogens glycerol and polyunsaturated fatty acid chains. To overcome these limitations, chemical modification of the triglyceride structure is necessary. Transesterification with methanol produces biodiesel (FAME), but its use as a lubricant is inadequate. A more effective route is the esterification of free fatty acids (FFAs) or the transesterification of triglycerides with long-chain alcohols or

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polyols (e.g., TMP, NPG) to produce complex esters with superior viscosity indices, high stability, and excellent low-temperature performance.

The synthesis of these polyol esters typically relies on acid-catalyzed esterification. Conventional homogeneous mineral acids, such as sulfuric acid (H_2SO_4) and p-toluenesulfonic acid (p-TSA), are widely used due to their high activity and low cost. However, their application is fraught with significant drawbacks. These corrosive catalysts necessitate the use of expensive corrosion-resistant reactors, generate large amounts of acidic waste water during the neutralization and purification steps, and are impossible to recover and reuse. Furthermore, they often promote undesirable side reactions, such as dehydration, oxidation, and polymerization, which can darken the product and reduce yield.

The environmental and economic inefficiencies of conventional acid catalysts have driven the search for greener, more sustainable alternatives. Heterogeneous catalysts, such as solid acid resins and zeolites, offer easier separation and reusability but often suffer from diffusion limitations, lower activity, and deactivation over time. Enzymatic catalysts (lipases) are highly selective and operate under mild conditions but are expensive, sensitive to high temperatures, and have slow reaction kinetics. This landscape creates a critical need for a catalytic system that combines high activity, easy separation, recyclability, and minimal environmental impact.

Ionic Liquids (ILs) have surfaced as a revolutionary class of materials capable of meeting these challenges. ILs are salts composed entirely of ions that exist in the liquid state at relatively low temperatures ($<100^\circ\text{C}$). Their unique properties, including negligible vapor pressure, high thermal stability, and designer functionality, make them ideal candidates as both solvents and catalysts for a wide range of chemical reactions, including esterification. This paper explores the pivotal role of ILs in advancing the catalytic esterification of fatty acids into high-value biolubricants, synthesizing research findings from before 2020 to establish a comprehensive foundation for their application.

Table 1 Comparison of Catalytic Pathways for Bio lubricant Synthesis

Catalyst Type	Examples	Advantages	Disadvantages
Homogeneous Acids	H_2SO_4 , p-TSA	High activity, low cost	Corrosive, non-reusable, high waste, side reactions
Heterogeneous Acids	Zeolites, $\text{SiO}_2\text{-SO}_3\text{H}$	Reusable, separable	Diffusion limits, lower activity, leaching, deactivation
Enzymatic (Lipases)	Novozym 435	Highly selective, mild conditions	Very high cost, slow reaction rate, temperature sensitivity
Ionic Liquids	$[\text{BSO}_3\text{HMim}][\text{HSO}_4]$, $[\text{NMP}][\text{CH}_3\text{SO}_3]$	High activity, tunable, reusable, non-corrosive	Higher initial cost, complex synthesis, viscosity issues

2. Ionic Liquids: Structure, Properties, and Design Principles

Ionic Liquids are not a single compound but a vast family of salts with diverse structures and properties. Their defining characteristic is a low melting point, typically below 100°C , which distinguishes them from conventional high-temperature molten salts. A typical IL consists of a large, organic cation and a smaller, organic or inorganic anion. The combination of these ions dictates the physical and chemical properties of the IL, earning them the moniker "designer solvents," as properties can be tailored for specific applications.

Common cations include imidazolium, pyridinium, phosphonium, and ammonium ions. The imidazolium-based cations, such as 1-butyl-3-methylimidazolium ($[\text{BMim}]^+$), are among the most extensively studied due to their relative ease of synthesis and stability. The anion plays a crucial role in determining the acidity, hydrophilicity, and reactivity of the IL. Common anions include halides (Cl^- , Br^-), tetrafluoroborate (BF_4^-), hexafluorophosphate (PF_6^-), and alkyl sulfates (e.g., $[\text{CH}_3\text{SO}_3]^-$). For catalytic applications, the choice of anion is paramount in defining the IL's acidic character.

The properties of ILs that make them exceptional for catalytic roles are multifaceted. Their negligible vapor pressure virtually eliminates volatile organic compound (VOC) emissions, addressing a major environmental and safety concern associated with organic solvents. They possess high thermal stability, often exceeding 400°C , allowing them to withstand the elevated temperatures ($100\text{-}200^\circ\text{C}$) required for esterification reactions. Furthermore, their liquid range is extensive, providing a wide operational window.

The most significant feature for catalysis is their tunable acidity. ILs can be engineered as Brønsted acids, Lewis acids, or both. Brønsted acidic ILs (BAILs) are created by incorporating a proton-donating functional group, typically a sulfonic acid ($-\text{SO}_3\text{H}$), into the cation or by using a Brønsted acidic anion like hydrogen sulfate ($[\text{HSO}_4]^-$). Examples include 1-(4-sulfonic acid) butyl-3-methylimidazolium hydrogen sulfate ($[\text{BSO}_3\text{HMim}][\text{HSO}_4]$). Lewis acidic ILs are often formed by combining an organic cation with a metal halide anion (e.g., chloroaluminate, $[\text{Al}_2\text{Cl}_7]^-$), though these are highly moisture-sensitive.

The design principle for biolubricant synthesis focuses on creating highly acidic, hydrophobic ILs. Hydrophobicity is desired to facilitate the separation of the water by-product from the reaction mixture, shifting the equilibrium towards ester formation according to Le Chatelier's principle. By carefully selecting the alkyl chain length on the cation and the nature of the anion, chemists can fine-tune the IL's miscibility with the reaction components, its acidity strength, and its capacity for reuse, optimizing the entire catalytic system for efficiency and sustainability.

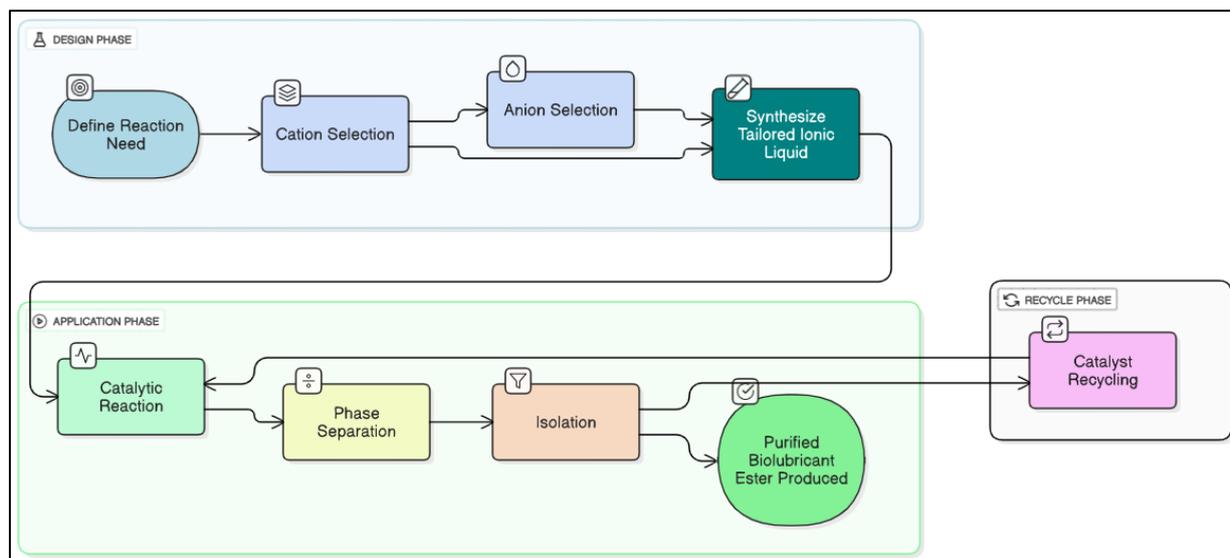


Figure 1 Design and Application Workflow for Acidic Ionic Liquids in Esterification

3. Catalytic Performance: Activity, Selectivity, and Optimization

The catalytic efficacy of Ionic Liquids in the esterification of fatty acids with polyols has been extensively demonstrated in literature, often outperforming conventional catalysts in both activity and selectivity. The key to this superior performance lies in the unique reaction environment they create. The high polarity and ionic nature of ILs can solubilize both the polar polyol and the non-polar fatty acid, effectively concentrating the reactants around the active catalytic sites and enhancing reaction rates.

Brønsted Acidic ILs (BAILs) have shown remarkable activity. For instance, ILs like $[\text{BSO}_3\text{HMim}][\text{HSO}_4]$ and $[\text{NMP}][\text{CH}_3\text{SO}_3]$ (N-methyl-2-pyrrolidonium methylsulfonate) have been reported to achieve fatty acid conversions exceeding 95% and triester (the desired product for TMP) selectivities over 90% under optimized conditions. Their acidity strength, often measured by Hammett acidity function, is comparable to or even higher than that of concentrated sulfuric acid, directly correlating with their high catalytic activity. The reaction parameters—catalyst loading, temperature, molar ratio of reactants, and reaction time—are crucial and require optimization for each specific IL and feedstock combination.

The optimization process typically reveals that a catalyst loading of 5-10 wt% (relative to FFAs) is sufficient for most BAILs, significantly reducing the amount of "acid" needed compared to homogeneous catalysis. The temperature is usually optimized between 100°C and 120°C; higher temperatures accelerate the reaction but may risk IL decomposition or product degradation. A slight excess of polyol (e.g., FFA:TMP molar ratio of 3.5:1 to 4:1) is employed to drive the reaction towards complete esterification and maximize the yield of the triester, which has the most desirable lubricant properties.

A critical advantage of ILs is their enhanced selectivity towards the desired polyol esters. Conventional acids often lead to side products like polyol dehydration (forming ethers) and coloration. ILs, with their well-defined and less aggressive

acidic sites, tend to suppress these side reactions. This results in a lighter-colored product that requires less purification, reducing both energy and processing costs. The selectivity for the triester over mono- and diesters is particularly important for achieving a high viscosity index and good thermal stability in the final biolubricant.

The source of fatty acids also impacts performance. IL catalysts have been successfully applied to a wide range of feedstocks, including pure oleic acid, stearic acid, and mixed fatty acids derived from low-grade oils like palm fatty acid distillate (PFAD) or waste cooking oil. This demonstrates their robustness and potential for valorizing inexpensive, non-edible feedstocks, further enhancing the economic and environmental appeal of the process. The ability to handle feedstocks with varying acidity and impurity profiles is a significant advantage over enzymatic catalysts.

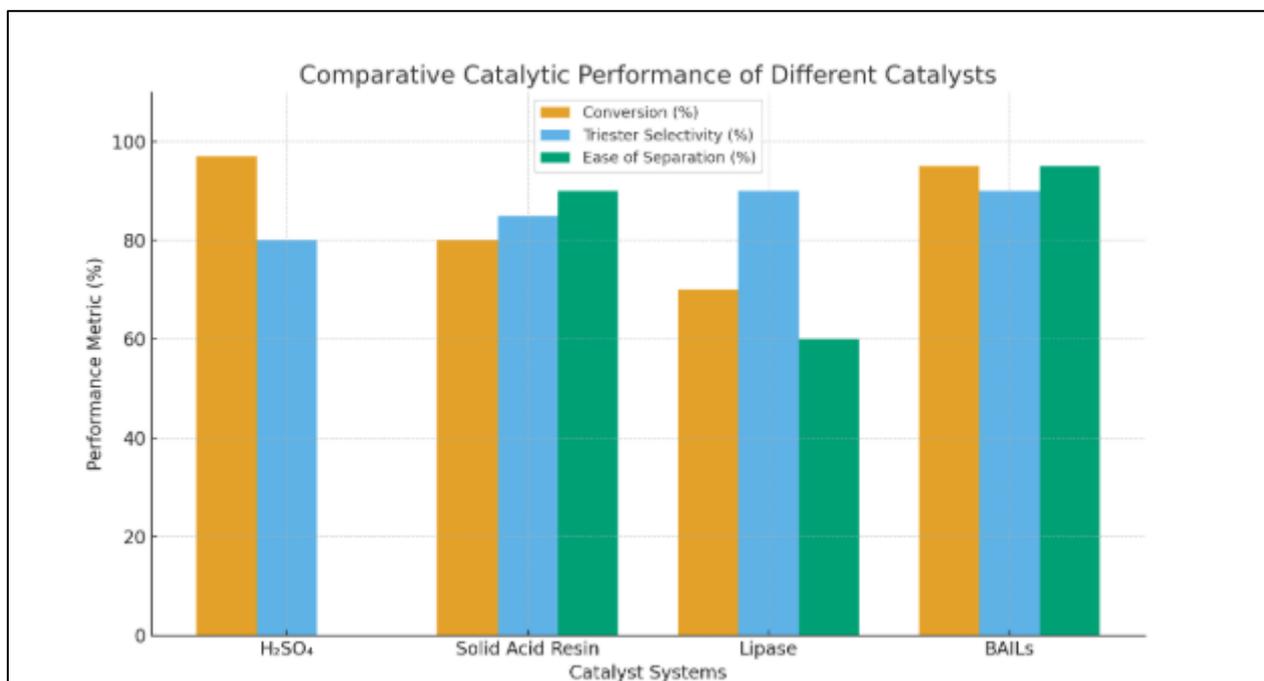


Figure 2 Comparative Catalytic Performance of Different Catalysts

4. Recyclability and Green Chemistry Metrics

A paramount advantage of employing Ionic Liquids as catalysts is their potential for recyclability, which directly addresses the economic and environmental shortcomings of single-use homogeneous acids. The non-volatile nature of ILs means they do not evaporate during the reaction, and their often-distinct phase behavior from the product mixture allows for straightforward separation. This facilitates their recovery and reuse across multiple reaction cycles, a critical factor for industrial viability.

The typical recycling process involves a simple liquid-liquid phase separation after the reaction is complete. Upon cooling, the reaction mixture commonly separates into an upper layer containing the crude biolubricant ester and a lower layer containing the denser ionic liquid catalyst. The upper layer can be decanted, and the IL layer can be directly reused after removing the traces of water absorbed during the reaction, often by vacuum drying. This process eliminates the need for neutralization and water washing, which generate large amounts of saline waste in conventional processes.

Studies pre-2020 have consistently demonstrated the impressive recyclability of well-designed BAILs. Many reports show that catalysts like [BSO₃HMim][HSO₄] can be reused for 5-10 consecutive cycles without any significant loss in catalytic activity, provided they are properly dried between cycles. The gradual decrease in activity after multiple cycles is usually attributed to the slight leaching of the acidic species or the accumulation of minor impurities rather than the decomposition of the IL core structure. This longevity drastically reduces the catalyst consumption per unit of product.

From a green chemistry perspective, IL-catalyzed esterification scores highly on several of the 12 principles. The prevention of waste is achieved by eliminating neutralization salts and enabling catalyst reuse. The principle of safer solvents and auxiliaries is partially met due to non-volatility, though the full toxicological profile of ILs must be

considered. Energy efficiency is enhanced by easier product separation and purification. Most importantly, it enables the use of renewable feedstocks (plant oils) to create safer, biodegradable products (biolubricants).

A quantitative green metric often used is the E-factor (Environmental Factor), defined as the mass of waste produced per mass of product. Conventional homogenous acid catalysis has a very high E-factor due to water washing and salt formation. In contrast, the IL process, with its closed-loop catalyst recycling, dramatically reduces this waste stream, leading to a significantly lower E-factor and a more sustainable manufacturing process. This reduction in process waste is a compelling argument for the adoption of IL technology.

Table 2 Green Chemistry Comparison: Conventional vs. IL-Catalyzed Process

Aspect	Conventional H ₂ SO ₄ Catalysis	Ionic Liquid Catalysis
Catalyst Recovery	Not possible; neutralized and discarded	Simple separation and reuse for multiple cycles
Process Waste	Large volumes of saline water from washing	Minimal waste; only water byproduct to be treated
Energy Consumption	High (for neutralization, washing, drying)	Lower (no neutralization, easier separation)
Corrosivity	High (requires specialized equipment)	Low (enables use of glass-lined or standard steel)
Product Purity	Often requires bleaching due to dark color	Lighter color; fewer side products, less purification
E-Factor	High (>5)	Low (<1)

5. Comparative Analysis and Economic Considerations

While the technical and environmental benefits of IL catalysts are clear, a successful transition from lab-scale innovation to industrial application necessitates a rigorous comparative analysis with incumbent technologies and a clear-eyed assessment of economic viability. This analysis must balance superior performance against upfront costs and process integration challenges.

As summarized in the previous tables and charts, ILs hold a distinct performance advantage over heterogeneous solid acids in terms of activity and often selectivity, while surpassing homogeneous acids in terms of separability and recyclability. They operate under less severe conditions than enzymatic catalysts, offering faster reaction times without the high biocatalyst cost. This positions ILs in a unique sweet spot, offering a best-of-both-worlds solution: the high activity of a homogeneous catalyst with the reusability of a heterogeneous one.

The primary barrier to adoption is the high initial cost of ionic liquids. Sophisticated ILs can be orders of magnitude more expensive per kilogram than sulfuric acid. However, a holistic economic analysis must move beyond mere price-per-kg to a total cost-of-ownership model. This model factors in the IL's recyclability—a single batch of IL used 10 times effectively reduces its cost contribution per product batch by 90%. Furthermore, operational savings from reduced energy consumption (no neutralization, less drying), reduced waste disposal costs, and the possibility of using cheaper construction materials (less corrosion) significantly improve the economic picture.

The handling of ILs presents specific considerations. Their high viscosity can pose challenges for pumping and mixing, potentially requiring process adjustments. While less corrosive than mineral acids, their long-term compatibility with certain elastomers and plastics must be verified. Crucially, the environmental footprint of ILs themselves must be evaluated; their synthesis can be resource-intensive, and their (eco)toxicity and biodegradability must be understood to ensure the overall process is truly green from cradle to grave.

Despite these challenges, the economic case becomes increasingly favorable for high-value biolubricant production. The market for synthetic esters and high-performance bio-based lubricants commands a premium price, which can better absorb the cost of an advanced catalyst system. The value proposition is strongest when the IL process enables the use of very low-cost, high-acid feedstocks (like PFAD) to produce a high-quality product, maximizing the profit margin.

Table 3 SWOT Analysis of IL Catalysts for Industrial Biolubricant Production

Category	Analysis
Strengths	High activity and selectivity, Excellent recyclability, Non-volatile, Tunable properties, Reduced waste streams.
Weaknesses	High initial cost, High viscosity, Complex synthesis, Uncertain long-term (eco)toxicity.
Opportunities	Valorization of low-grade feedstocks, Production of premium biolubricants, Development of more efficient/cheaper ILs.
Threats	Competition from improving heterogeneous catalysts, Volatility of feedstock prices, Stringent environmental regulations on ILs themselves.

6. Conclusion and Future Perspectives

The investigation into Ionic Liquids as catalysts for the esterification of fatty acids into biolubricants reveals a technology of significant promise and transformative potential. The evidence consolidated from pre-2020 research unequivocally demonstrates that ILs, particularly Brønsted acidic ones, overcome the major limitations of conventional acid catalysts. They deliver exceptional catalytic activity and selectivity, facilitate easy separation from the product mixture, and exhibit outstanding recyclability—all within a framework that aligns with the principles of green chemistry by minimizing waste and energy consumption.

The tunability of ILs is their most powerful feature, allowing chemists to design catalysts tailored specifically for the esterification of bulky polyol molecules and diverse fatty acid feedstocks. This "designer catalyst" approach has led to systems that not only achieve high yields but also produce lighter-colored, higher-quality esters that require less downstream processing. The ability to create hydrophobic ILs that promote in-situ water removal further enhances conversion efficiency through equilibrium shifting, showcasing a sophisticated level of process integration.

For IL catalysis to transition from a laboratory curiosity to an industrial mainstay, future research must focus on several key areas. First, the development of simpler, cheaper, and greener synthetic routes for producing ILs is critical to improve their economic feasibility. Second, comprehensive toxicological and biodegradability studies are essential to ensure the entire lifecycle of the IL is environmentally benign and to gain regulatory and public acceptance. Third, engineering research must address handling challenges related to viscosity and develop continuous flow reactor systems that maximize the efficiency of IL reuse.

The future likely lies in the development of supported ionic liquid phase (SILP) catalysts, where a thin layer of IL is immobilized on a high-surface-area solid support. This hybrid approach aims to combine the high activity and tunability of ILs with the easy handling and separation of heterogeneous catalysts, while also reducing the amount of IL required. Furthermore, the exploration of ILs derived entirely from renewable sources (e.g., amino acid-based ILs) is an exciting frontier that could further enhance the sustainability credentials of the process.

In conclusion, ionic liquids represent an advanced, versatile, and sustainable catalytic platform for the synthesis of biolubricants. They offer a solution to the long-standing catalytic challenges in this field and hold the key to unlocking the full potential of renewable oils as feedstocks for high-performance lubricants. As research addresses the current limitations related to cost and sustainability, ILs are poised to play a central role in the green transition of the lubricant industry.

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