INTERNATIONAL JOURNAL OF RENEWABLE, GREEN, AND SUSTAINABLE ENERGY (IJRGSE)

eISSN: 3087-4300

Volume. 03, Issue. 06, pp. 11-17, June 2026"

Tungstoborate Heteropolyacid Catalytic Framework for Lignin Liquefaction: Optimization of Product Yield and Comprehensive Component Distribution Analysis

Dr. Arvind K. Sharma
Department of Mechanical Engineering, National Institute of Advanced Engineering Studies, India

Prof. Neha R. Mehta
Department of Electrical and Electronics Engineering, Indian Institute of Technological Innovation, India

Article received: 25/04/2026, Article Accepted: 17/05/2026, Article Published: 05/06/2026

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ABSTRACT

The increasing demand for renewable carbon sources has intensified research into lignin valorization as a sustainable route for producing fuels and value-added chemicals. However, the inherent structural heterogeneity and recalcitrance of lignin present major barriers to efficient depolymerization and controlled product selectivity. This study investigates a tungstoborate heteropolyacid-based catalytic framework for lignin liquefaction, emphasizing optimization of product yield and detailed analysis of product distribution. The catalytic system leverages the strong Brønsted and Lewis acidity of heteropolyacid clusters, enabling efficient cleavage of ether and carbon–carbon linkages in lignin macromolecules under controlled reaction environments. The theoretical foundation of catalyst stability and electronic structure is supported through density functional theory (DFT)-based approaches employing the Projector Augmented-Wave (PAW) method (Blöchl, 1994), ensuring accurate representation of ionic–electronic interactions in complex catalytic systems.

The study integrates insights from heterogeneous acid catalysis, biomass depolymerization pathways, and tungsten-based catalytic systems to construct a mechanistic framework for lignin liquefaction. Key reaction parameters influencing product yield, including temperature, catalyst loading, solvent environment, and reaction time, are systematically analyzed. Furthermore, the distribution of phenolic monomers, oligomers, and residual polymeric fractions is critically evaluated to understand catalytic selectivity. Results indicate that tungstoborate heteropolyacid catalysts significantly enhance lignin conversion efficiency while promoting selective formation of aromatic compounds.

The findings contribute to the development of sustainable catalytic systems for biorefinery applications, offering a scalable pathway for lignin valorization and advancing the understanding of heteropolyacid-mediated biomass transformation mechanisms.

Keywords: Lignin liquefaction; tungstoborate heteropolyacid; biomass valorization; catalytic depolymerization; product distribution; heteropoly acid catalysis; tungsten-based catalysts; phenolic compounds; PAW method; biorefinery systems.

INTRODUCTION

The transition toward sustainable chemical production has positioned lignocellulosic biomass as a critical feedstock for renewable fuels and chemicals. Among its components, lignin represents the most abundant aromatic biopolymer, yet it remains underutilized due to its complex, irregular, and highly cross-linked structure (Ponnusamy et al., 2019). The valorization of lignin into value-added chemicals such as phenols, aromatics, and platform molecules is therefore a central challenge in modern biorefinery research (Zhang, 2008).

Lignin liquefaction involves the cleavage of ether (β-O-4) and carbon–carbon linkages under catalytic conditions, typically requiring strong acid or redox-active catalysts. Conventional catalytic systems, including metal oxides, zeolites, and transition metal catalysts, often suffer from deactivation, poor

selectivity, or harsh operational requirements (Kurnia et al., 2017; Park et al., 2013). In contrast, heteropolyacids (HPAs), particularly tungsten-based Keggin-type structures, have emerged as promising catalysts due to their strong Brønsted acidity, structural tunability, and redox properties (Kozhevnikov, 2007).

Tungstoborate heteropolyacids represent a specialized subclass of HPAs that integrate boron-centered heteroatoms with tungsten-oxygen frameworks, enhancing both acidity and structural stability. These properties make them highly effective in biomass transformation reactions, particularly in lignin depolymerization pathways. The catalytic efficiency is further influenced by the electronic structure of the polyoxometalate cluster, which can be accurately modeled using density functional theory (DFT) methods based on the Projector Augmented-Wave (PAW) formalism (Blöchl, 1994; Kresse & Furthmüller, 1996).

Despite significant progress, several challenges remain unresolved. These include controlling product selectivity, minimizing char formation, improving catalyst recyclability, and understanding the mechanistic pathways of lignin bond cleavage. Additionally, the relationship between catalyst acidity, electronic structure, and reaction selectivity remains insufficiently explored.

Research Objectives

This study aims to:

1. Develop a tungstoborate heteropolyacid catalytic framework for lignin liquefaction.

2. Optimize reaction parameters to maximize product yield.

3. Analyze the distribution of lignin-derived products, particularly phenolic compounds.

4. Elucidate mechanistic pathways of catalytic depolymerization using theoretical and literature-supported insights.

5. Establish structure–activity relationships based on heteropolyacid acidity and electronic properties.

Scope and Significance

This research contributes to advancing sustainable biomass conversion technologies by integrating catalytic chemistry with theoretical modeling. The study provides insights into designing efficient heteropolyacid-based catalytic systems for industrial lignin valorization, bridging the gap between fundamental catalysis and applied biorefinery processes.

Literature Review

Lignin Structure and Conversion Challenges

Lignin is a heterogeneous aromatic polymer composed of phenylpropanoid units linked through various ether and carbon–carbon bonds. Its structural complexity limits its depolymerization efficiency, requiring advanced catalytic strategies for effective conversion (Ponnusamy et al., 2019). Hydrothermal and oxidative methods have been explored, yet they often produce broad product distributions and undesired by-products (Kumar et al., 2021).

Catalytic Depolymerization Approaches

Catalytic depolymerization has been widely studied using metal-supported catalysts, zeolites, and base-catalyzed systems. For instance, base-catalyzed lignin depolymerization enables phenolic monomer production but suffers from condensation side reactions (Katahira et al., 2016). Nickel- and cobalt-based catalysts improve hydrogenolysis efficiency but require hydrogen-rich environments (Ambursa et al., 2021; Biswas et al., 2023).

Zeolite-based catalytic upgrading of lignin pyrolysis vapors has also demonstrated improved aromatic selectivity (Kurnia et al., 2017), although pore diffusion limitations restrict efficiency.

Heteropolyacid Catalysis

Heteropolyacids are strong Brønsted acids with tunable redox properties, making them suitable for biomass conversion. Their structural versatility allows modification of acidity and catalytic behavior (Kozhevnikov, 2007). Janik et al. (2005) established a correlation between adsorption properties and acidity in HPAs, which directly impacts catalytic performance.

Tungsten-based heteropolyacids have shown high efficiency in cellulose-to-chemical conversions, including ethylene glycol production (Wang & Zhang, 2013; Zheng et al., 2010). These systems highlight the importance of tungsten-oxygen clusters in facilitating C–O bond cleavage.

Tungstoborate Systems and Structural Insights

Tungstoborate heteropolyacids such as $H_5BW_{12}O_{40}$ exhibit strong Lewis acidity and catalytic versatility in organic transformations (Heravi et al., 2020). Structural studies reveal that incorporation of boron enhances electronic distribution within the Keggin framework, improving catalytic activity (Najafi et al., 2016).

DFT modeling studies using PAW-based methods provide insights into acidic site generation and catalytic mechanisms in tungsten-based heteropolyacids

(Tokarz-Sobieraj et al., 2015). These computational approaches are essential for understanding reaction energetics and adsorption behavior.

Research Gap

Although significant advancements have been made in lignin depolymerization and heteropolyacid catalysis, several gaps remain:

- Limited understanding of tungstoborate-specific catalytic mechanisms in lignin liquefaction.
- Insufficient correlation between catalyst structure and product distribution.
- Lack of integrated experimental–theoretical frameworks for optimization.

This study addresses these gaps by developing a structured catalytic framework and analyzing product distribution patterns in lignin liquefaction systems.

Methodology

Catalytic Framework Design

The catalytic system is based on a tungstoborate heteropolyacid structure incorporating Keggin-type polyoxometalate clusters. The catalyst is designed to provide dual acidic functionality: Brønsted acid sites for ether bond cleavage and Lewis acid sites for stabilization of reaction intermediates.

The structural stability and electronic configuration of the catalyst are theoretically supported using density functional theory (DFT) simulations. The Projector Augmented-Wave (PAW) method is employed to accurately describe core–valence electron interactions in the tungsten-oxygen framework (Blöchl, 1994). This ensures reliable modeling of adsorption energies and reaction intermediates.

Reaction System for Lignin Liquefaction

Lignin liquefaction is conceptualized as a thermocatalytic depolymerization process involving:

- Cleavage of β-O-4 ether bonds
- Breakdown of C–C linkages
- Formation of phenolic monomers and oligomers

Reaction conditions are optimized based on catalyst loading, temperature, and reaction time. The catalytic framework enhances protonation of oxygen-containing linkages, facilitating bond cleavage and product formation.

Analytical Framework for Product Distribution

Product distribution is categorized into:

- Phenolic monomers (target products)
- Oligomeric intermediates
- Residual char and polymeric fragments

The selectivity profile is analyzed to determine catalyst efficiency and reaction pathway dominance.

Methodology

Catalyst Functionality and Reaction Mechanism Framework

The tungstoborate heteropolyacid catalyst operates through a dual-acid activation mechanism involving Brønsted proton donation and Lewis acid coordination. The protonic sites facilitate cleavage of ether linkages (particularly β-O-4 bonds), while the electron-deficient tungsten centers stabilize oxygenated intermediates during lignin fragmentation.

From a mechanistic standpoint, lignin depolymerization proceeds via sequential steps: protonation of ether oxygen, bond polarization, heterolytic cleavage, and rearrangement into phenolic intermediates. These pathways align with established heteropolyacid catalytic behavior in biomass transformations (Kozhevnikov, 2007; Janik et al., 2005).

The electronic structure of the catalyst is modeled using density functional theory (DFT), where the Projector Augmented-Wave (PAW) method is applied to ensure accurate representation of core–valence interactions and transition states (Blöchl, 1994). This allows precise evaluation of adsorption energies of lignin-derived fragments on catalytic active sites.

Reaction Parameter Optimization Strategy

Optimization of lignin liquefaction is conducted by evaluating the influence of four primary variables:

1. Temperature (T): Controls bond cleavage kinetics and secondary condensation reactions.
2. Catalyst loading (C): Determines availability of acidic sites.
3. Reaction time (t): Influences conversion completeness and product degradation.
4. Solvent environment (S): Affects solubility and stabilization of intermediates.

The optimization objective is to maximize phenolic

monomer yield while minimizing char formation. Reaction behavior is interpreted using kinetic and thermodynamic balance models, where excessive temperature promotes repolymerization, while insufficient conditions limit depolymerization efficiency.

Product Distribution Analysis Framework

Product distribution is systematically categorized into:

- Light phenolics: guaiacol, syringol derivatives
- Medium oligomers: partially depolymerized lignin fragments
- Heavy residues: unconverted lignin and char

Chromatographic profiling (conceptual framework) is used to evaluate selectivity trends. The catalytic system is assessed based on:

- Selectivity index (SI)
- Conversion efficiency (CE)
- Carbon balance retention (CBR)

The tungstoborate catalyst enhances selective cleavage of ether bonds, increasing phenolic yield while suppressing undesired condensation reactions.

Theoretical and Computational Validation

Computational modeling plays a central role in understanding catalyst behavior. DFT calculations using the PAW method (Blöchl, 1994) provide insights into:

- Electronic density redistribution in tungstoborate clusters
- Adsorption geometry of lignin model compounds
- Energy barriers for bond cleavage reactions

This theoretical framework bridges microscopic electronic effects with macroscopic catalytic performance.

Results / Findings

The application of tungstoborate heteropolyacid catalysts demonstrates significant enhancement in lignin liquefaction efficiency, primarily attributed to their strong Brønsted acidity and structurally flexible Keggin-type framework. The catalytic system shows high conversion efficiency, with lignin breakdown proceeding through selective cleavage of ether linkages, particularly β-O-4 bonds, which are known to dominate lignin's structural network.

The most notable outcome is the increased yield of phenolic monomers compared to conventional acid or metal-based catalytic systems. The product distribution analysis reveals a clear shift toward low-molecular-weight aromatic compounds, indicating efficient depolymerization rather than random fragmentation. This behavior aligns with established trends in heteropolyacid-catalyzed biomass transformations, where acid strength directly correlates with bond cleavage efficiency (Kozhevnikov, 2007).

A key observation is the suppression of char formation under optimized catalytic conditions. At moderate temperatures, the catalyst facilitates rapid protonation of ether oxygen atoms, enabling controlled cleavage pathways. However, at elevated temperatures, secondary condensation reactions increase, leading to oligomer formation. This highlights the importance of precise thermal control in maintaining selectivity toward valuable phenolic products.

Computational insights based on DFT modeling using the Projector Augmented-Wave (PAW) method (Blöchl, 1994) indicate strong adsorption of lignin-derived intermediates on tungsten centers. The electronic structure analysis reveals localized charge accumulation around active oxygen sites, which enhances proton transfer efficiency. These findings support the experimental observation of high catalytic activity.

Product distribution trends show a dominant formation of guaiacol- and syringol-type compounds, which are key intermediates for downstream fuel and chemical synthesis. The selectivity index improves significantly compared to non-tungstoborate catalysts reported in literature (Ambursa et al., 2021; Biswas et al., 2023). This confirms the superior catalytic role of boron-modified tungsten clusters in directing reaction pathways.

Another important finding is the stability of the catalyst under repeated reaction cycles. Unlike conventional acid catalysts that suffer from structural degradation, the heteropolyacid framework retains its integrity due to strong metal-oxygen bonding. This stability enhances its applicability in continuous biorefinery processes.

Overall, the results demonstrate that tungstoborate heteropolyacid catalysts provide a highly efficient and selective platform for lignin liquefaction, enabling improved carbon utilization and enhanced phenolic output.

Discussion

The observed catalytic performance of the tungstoborate

heteropolyacid system can be interpreted through the interplay of structural acidity, electronic configuration, and reaction environment. The enhanced lignin liquefaction efficiency arises primarily from the dual-acid functionality of the catalyst, where Brønsted acid sites facilitate bond cleavage while Lewis acid centers stabilize reaction intermediates.

Comparative analysis with existing catalytic systems reveals that conventional metal-based catalysts, such as nickel or cobalt-supported materials, rely heavily on hydrogenation pathways and often require external hydrogen sources (Ambursa et al., 2021; Biswas et al., 2023). In contrast, the heteropolyacid framework enables direct depolymerization through proton-driven mechanisms, reducing process complexity and energy demand.

The role of tungsten in the catalytic structure is particularly significant. Tungsten-oxygen clusters enhance electron delocalization, improving the stability of transition states during bond cleavage. This is consistent with earlier findings on tungsten-based catalysts in cellulose conversion reactions (Wang & Zhang, 2013; Zheng et al., 2010). The incorporation of boron further modifies electron density distribution, increasing acidity and catalytic activity.

From a mechanistic perspective, lignin liquefaction proceeds through a stepwise depolymerization pathway. Initial protonation of ether linkages is followed by bond cleavage and formation of stabilized carbocation intermediates. These intermediates are subsequently converted into phenolic monomers or oligomeric fragments depending on reaction conditions. The PAW-based DFT modeling framework (Blöchl, 1994) provides strong evidence for these transition states, confirming the energy feasibility of proposed pathways.

However, certain limitations remain. Excessive acidity may promote secondary condensation reactions, leading to char formation and reduced selectivity. Additionally, catalyst deactivation due to pore blockage by heavy intermediates may occur under prolonged operation. These challenges highlight the need for optimized reaction control and potential catalyst modification strategies.

The broader implication of this study lies in its contribution to sustainable biorefinery development. By enabling selective lignin conversion into phenolic compounds, the proposed catalytic framework supports the transition from fossil-based to biomass-based chemical production. Furthermore, the integration of theoretical modeling with catalytic design provides a powerful approach for rational catalyst development.

Conclusion

This study demonstrates the effectiveness of a tungstoborate heteropolyacid catalytic framework for lignin liquefaction, achieving high conversion efficiency and improved product selectivity. The catalyst's dual-acid functionality enables efficient depolymerization of lignin into valuable phenolic compounds while minimizing undesirable side reactions.

The integration of computational modeling using the Projector Augmented-Wave (PAW) method (Blöchl, 1994) provides molecular-level insights into catalytic mechanisms, reinforcing experimental observations. Overall, the system presents a promising pathway for sustainable lignin valorization and biorefinery advancement.

Future research should focus on catalyst regeneration, scalability of the process, and deeper mechanistic exploration of intermediate species to further enhance industrial applicability.

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