

Optimizing a Green Stoichiometry for Quadruple-Function Modified Hemp Lignin (QF-MHL) Synthesis: Maximizing Functionalization and Yield via Controlled Mannich Amination

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November 2025

Abstract

The Quadruple-Function Modified Hemp Lignin (QF-MHL) is the pivotal component of the Hempoxies vitrimer system, providing the dynamic covalent chemistry sites (imine bonds) necessary for catalyst-free reprocessability. The current synthesis protocol for the QF-MHL via Mannich amination relies on an unoptimized, high molar excess of formaldehyde and amine reagents (a 10.0:1.0:1.0 proxy ratio), which drastically increases the **Process Mass Intensity (PMI)** and violates the platform’s core green chemistry mandate. This study proposes a systematic investigation to determine the minimum effective reagent stoichiometry. We hypothesize that the inherent site-selectivity of the Mannich reaction on the lignin’s guaiacyl units will permit a substantial reduction in reagent excess without a corresponding loss in crucial amine functionalization (DV1) or degradation of the maleate cross-linker (DV4). The optimal treatment will be determined by the highest **Multi-Criteria Optimization Score (MOS)**, balancing chemical quality with process efficiency.

1 Introduction

The Hempoxies platform is a novel, 100% bio-based vitrimer designed to replace traditional petroleum-based epoxies. Its key innovation is the **catalyst-free dynamic imine exchange network**, achieved through the integration of the Quadruple-Function Modified Hemp Lignin (QF-MHL) component. The QF-MHL must successfully integrate four critical chemical functionalities: a primary amine source (for imine formation), an aldehyde source (for imine formation), an epoxy-amine cross-linker (via maleate groups), and a carbon nanofiller compatibilizer.

The synthesis of QF-MHL involves a **Mannich amination reaction** onto maleated hemp lignin (M-HL). The current baseline protocol utilizes a 10.0-fold molar excess of formaldehyde, leading to a large amount of unreacted reagents that must be removed via extensive water washing. This results in significant time, energy, and water consumption, dramatically increasing the cost and environmental footprint of the final material. To ensure scalability and maintain the carbon-negative status, this synthetic step must be optimized.

Gap and Hypothesis

The key scientific gap is the lack of quantitative data linking reduced reagent stoichiometry in the Mannich reaction to the final chemical quality and process efficiency of the QF-MHL.

The **Mannich reaction** is known to be selective, primarily attacking the reactive C-5 position of guaiacyl lignin units. Given the finite and quantifiable density of available phenolic hydroxyl active sites on the hemp lignin backbone, a large stoichiometric excess of reagents is chemically inefficient.

Hypothesis (H_a): Reducing the molar excess of formaldehyde from the baseline (T1) to the low-excess proxy (T4: 3.0:1.0:1.0) will not result in a statistically significant decrease in the critical ****Amine Functionalization (%N)**** or ****Maleate Retention****, but will yield a statistically significant reduction in ****Wash Water Volume**** (dH_2O), leading to a higher ****Multi-Criteria Optimization Score (MOS)**** for the lower-excess treatments.

Null Hypothesis (H_0): There is no statistically significant difference in the Multi-Criteria Optimization Score (MOS) between the four tested reagent stoichiometries (T1-T4).

2 Materials and Methods

2.1 Materials

Maleated Hemp Lignin (M-HL) feedstock, formaldehyde solution (37 wt% in H_2O), and diethylamine (DEA) were used as received. Deionized water (dH_2O) was used for purification.

2.2 Experimental Design: Mannich Reaction Stoichiometry

The Mannich amination reaction was carried out in four treatment groups (T1-T4), varying the molar ratio of Formaldehyde : Diethylamine : Phenolic Hydroxyl Sites. The amount of M-HL was held constant for all batches.

Table 1: Experimental Molar Ratio Treatments for QF-MHL Synthesis

Treatment Group	Formaldehyde (F) (Molar Ratio)	Diethylamine (A) (Molar Ratio)	Phenolic Hydroxyl (PH) (Molar Ratio)
T1 (Baseline Proxy)	10.0	1.0	1.0
T2 (Medium-High Excess)	7.5	1.0	1.0
T3 (Medium-Low Excess)	5.0	1.0	1.0
T4 (Low-Excess Proxy)	3.0	1.0	1.0

2.3 Synthesis and Purification Protocol

The synthesis involves standard stirring and heating for a defined duration. Upon completion, the resulting QF-MHL product in each batch is purified by washing with dH_2O until the filtrate reaches a neutral pH ($pH = 7.0$).

2.4 Dependent Variables and Analytical Techniques

Triplicate samples ($n = 3$) were prepared for each treatment group (T1-T4).

1. **Amine Functionalization (%N):** Measured via ****Elemental Analysis (CHNS)****. This quantifies the incorporation of the diethylamine group, a critical component for the dynamic imine network.
2. **Maleate Retention ($mmol/g$):** Measured via ****Quantitative H^1 NMR Spectroscopy****. The maleate cross-linker group must be retained to ensure proper cross-linking with the epoxy matrix.
3. **Wash Water Volume (L):** The total volume of dH_2O required to neutralize the filtrate to $pH = 7.0$. This is the proxy for ****PMI**** and process scalability.

4. **Glass Transition Temperature (T_g) ΔT (Validation Check):** Measured via ****Differential Scanning Calorimetry (DSC)**** on the final cured Hempoxies composite derived from each QF-MHL batch.

2.5 Multi-Criteria Optimization Score (MOS) Calculation

The primary comparison metric is the MOS, calculated by weighting and normalizing the critical dependent variables. The goal is to maximize quality (functionalization/retention) and minimize waste (wash water volume).

$$\text{MOS} = (W_1 \cdot \text{Norm}(\%N)) + (W_2 \cdot \text{Norm}(\text{Maleate Retention})) - (W_3 \cdot \text{Norm}(\text{Wash Water Volume}))$$

Where W_1 , W_2 , and W_3 are the assigned weighting factors (e.g., $W_1 = 40\%$, $W_2 = 30\%$, $W_3 = 30\%$). $\text{Norm}(X)$ represents the min-max normalized value of X across all treatments. The treatment with the highest MOS is deemed optimal.

3 Statistical Analysis

All quantitative results will be reported as mean $\pm$ standard deviation. A ****One-way Analysis of Variance (ANOVA)**** will be conducted on the mean values of $\%N$ and MOS for the four treatments to determine statistical significance ($p < 0.05$). The ANOVA will confirm whether the reduction in reagent ratio has a statistically non-significant effect on functionalization while having a statistically significant effect on the MOS, confirming the hypothesis.

4 Results

[Placeholder: Raw and analyzed data tables for %N, Maleate Retention, Wash Water Volume, and MOS] [Placeholder: Figure 1: Comparative Bar Charts of %N and Wash Water Volume by Treatment] [Placeholder: Figure 2: Multi-Criteria Optimization Score (MOS) Ranking] [Placeholder: Statistical Analysis Output (ANOVA table and p-values)]

5 Discussion

[Placeholder: Interpretation of the MOS results and its implication for Green Chemistry and scalability.] [Placeholder: Analysis of the relationship between reagent excess and the kinetics of the Mannich reaction.] [Placeholder: Discussion of whether the ΔT_g validation check confirms the maintenance of crosslink quality.]

6 Conclusion

[Placeholder: Final determination of the optimal reagent stoichiometry for QF-MHL synthesis and confirmation of the achievement of the green chemistry mandate.]

7 References

References

- [1] Hempoxies Master Technical SOP Suite (8 Protocols) + Expert-Level Technical Report.
- [2] Liu, F., et al. Bio-Based and Solvent-Free Epoxy Vitrimers Based on Dynamic Imine Bonds with High Mechanical Performance. *Polymers*, 2023.

- [3] Sheldon, R. A., Green Chemistry and Catalysis. *Pure Appl. Chem.*, 2000.