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Context-Dependent Effects of PEG Grade on Lignocellulose Fractionation with Deep Eutectic Solvents

Agnes Amelia Tanjung [1], Julinawati Julinawati [1], Widya Fatriasari [2], Zuchra Helwani [3], Andriy Anta Kacaribu [4], and Rinaldi Idroes [1,*]

[1] Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Syiah Kuala, Banda Aceh 23111, Indonesia; agnesamelia.tanjung@gmail.com (A.A.T.); julinawati@usk.ac.id (J.J.); rinaldi.idroes@usk.ac.id (R.I.)
[2] Research Center for Biomass and Bioproducts, National Research and Innovation Agency (BRIN), Cibinong, Indonesia; widy003@brin.go.id (W.F)
[3] Department of Chemical Engineering, Faculty of Engineering, Universitas Riau, Pekanbaru, Indonesia; zuchra.helwani@lecturer.unri.ac.id (Z.H.)
[4] Doctoral Program of Agricultural Science, Postgraduate School, Universitas Syiah Kuala, Banda Aceh 23111, Indonesia; andriyanta72@gmail.com (A.A.K.)

* Correspondence: rinaldi.idroes@usk.ac.id

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Abstract

This structured critical review evaluated how nominal polyethylene glycol (PEG) grade affects lignocellulose fractionation in deep eutectic solvents using an auditable corpus of 42 retained studies, including three within-study PEG-grade series. The eucalyptus studies showed modest PEG400 advantages for selected responses, whereas a sugarcane-bagasse screen gave the highest lignin removal (83.23%), glucose concentration, and glucose yield at PEG600, with lower cellulose retention than at PEG200/400; multivariable optimization subsequently selected PEG400. These contrasts show that nominal grade is a formulation variable rather than an isolated molecular-weight effect: equal PEG mass changes chain and terminal-hydroxyl concentrations, whereas a fixed choline chloride:PEG molar ratio also changes polymer mass and repeat-unit content. Candidate explanations are organized into four pathways—interaction-network modification; viscosity, diffusion, and steric trade-offs; phase behavior and partitioning; and lignin stabilization/carbohydrate protection. Current evidence supports formulation-dependent grade responses but not a universal grade ranking or numerical optimum. MW-REPORT is proposed to standardize grade characterization, normalization, mediator measurements, and product balances needed for reproducible formulation-specific selection.

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1. Introduction

Deep eutectic solvents (DESs) emerged from low-melting choline chloride mixtures and now comprise a broad family of compositionally tunable liquids [1, 2]. Natural deep eutectic solvents extended this concept to metabolites and biologically derived components [3]. Their properties are not determined by component identity alone: molar ratio, water content, acidity, temperature, and the resulting hydrogen-bond and ionic network jointly govern polarity, viscosity, mass transfer, and solute affinity [4, 5]. This responsiveness is important in lignocellulose pretreatment because the solvent must penetrate a heterogeneous cell-wall matrix, disrupt lignin–carbohydrate associations, solubilize lignin, and

retain carbohydrates in a form suitable for downstream conversion. Early biomass applications demonstrated corncob pretreatment and cellulose–lignin separation from eucalyptus, but did not address PEG-grade effects [6, 7]. Reviews of DES-based pretreatment therefore emphasize that performance depends on matching solvent chemistry and process severity to the biomass and intended product, rather than treating DESs as a uniform solvent class [8, 9]. Acidic formulations can provide substantial delignification and recover relatively low-molar-mass lignin, but increasing acidity, temperature, or residence time may also intensify sugar degradation and condensation of reactive lignin fragments [10, 11]. The central formulation problem is therefore a balance among chemical reactivity, transport through the biomass, and stabilization of released products. Additives that influence more than one of these functions are attractive, provided that their effects are evaluated in the specific composition and processing conditions in which they are used.

Polyethylene glycol (PEG) is one such additive. In DES-related media, PEG can contribute ether oxygens and terminal hydroxyl groups to the interaction network, act as a co-solvent, modify viscosity and interfacial behavior, participate in phase formation, and stabilize reactive lignin-derived species. Measurements in reline-, glyceline-, and ethaline-based mixtures containing PEG400 show changes in solvatochromic response and ion-solvation structure, indicating that PEG can reorganize the local liquid environment rather than behave as an inert diluent [12]. Density and viscosity data for other PEG-containing eutectic mixtures likewise show strong dependence on composition and temperature, variables that directly affect diffusion and biomass wetting [13]. PEG-associated lignin stabilization has been observed in selected biomass formulations, consistent with broader strategies that intercept reactive intermediates before recondensation [14–16]. Its practical use in biomass systems now includes near-neutral ternary DES treatment of wheat straw [17], microwave-assisted fractionation of eucalyptus [14], and ternary DES pretreatment of sugarcane bagasse [18]. Recent formulations have also been reported for bamboo, tea stem, and eucalyptus [16, 19, 20]. These studies establish PEG as a relevant formulation component across several biomass types, but the functions ascribed to PEG are not equivalent and should not be transferred uncritically from one solvent system to another.

The distinction becomes more important when PEG grade changes. Commercial labels such as PEG200, PEG400, PEG600, PEG800, and PEG4000 describe nominal average molar-mass ranges, not single monodisperse compounds. Meaningful polymer characterization therefore distinguishes number-average molar mass (M_n), weight-average molar mass (M_w), and dispersity, even when a commercial grade is used as the practical formulation label [21]. Changing that label changes the average chain population and can alter viscosity, hydrodynamic size, terminal-hydroxyl concentration, solvation, steric accessibility, interfacial behavior, and phase compatibility. These changes do not necessarily move in the same direction. A longer PEG chain may provide greater steric shielding around reactive lignin fragments, yet increased viscosity or slower diffusion may reduce contact with the biomass and delay solute transfer. A lower grade supplies more chains and more terminal hydroxyl groups per gram, but may not create the same interfacial or phase behavior. The formulation basis adds another layer of interpretation. At fixed PEG mass, the approximate ethylene-oxide repeat-unit content remains similar while chain and terminal-hydroxyl concentrations decrease as nominal grade increases. At a fixed choline chloride:PEG molar ratio, nominal chain stoichiometry is retained while PEG mass and repeat-unit content rise with grade. These designs answer different questions; neither can be described as an isolated molecular-weight effect unless the changing chemical equivalents and liquid properties are measured and reported. Grade-dependent phase formation and partitioning have also been reported in a PEG-based aqueous biphasic system [22], although that non-biomass setting is used here only as mechanistic context.

The evidence assembled for this review contains three within-study PEG-grade series in native lignocellulose: sugarcane bagasse treated with choline chloride/PEG/hydroxyethyl sulfonic acid mixtures, microwave-assisted choline chloride/lactic acid/PEG treatment of eucalyptus, and eucalyptus fractionation in benzyltriethylammonium chloride/formic acid/PEG [14, 16, 18]. These designs compare formulations rather than isolating chain length. The bagasse series retained a fixed choline chloride:PEG molar ratio, whereas the eucalyptus series used fixed PEG additions. In the bagasse screen, PEG600 gave the highest reported lignin removal, glucose concentration, and glucose yield, but cellulose retention fell relative to PEG200 and PEG400. The eucalyptus series showed modest descriptive advantages for PEG400. These observations do not establish a universal grade ranking or a statistically meaningful advantage without the corresponding uncertainty and tests. Single-grade biomass studies and model systems help identify properties worth measuring, but cannot establish grade-dependent causality in whole biomass. The central gap is

a lack of normalized grade series linking polymer descriptors and solvent properties to both fractionation and product quality.

Accordingly, the objective of this critical review is to determine which nominal PEG-grade responses have been observed in lignocellulose processing, which formulation variables change with grade, and which proposed mechanisms are demonstrated, indirectly supported, or still hypothetical. The three E1 within-study PEG-grade series form the primary empirical backbone, while single-grade PEG biomass studies, PEG model systems, and non-PEG analogues are used only in the supporting roles defined in Section 2.2. The molecular-weight design-lever (MWDL) framework organizes the evidence into M1, interaction-network modification; M2, viscosity, diffusion, and steric trade-offs; M3, phase behavior, partitioning, and crowding; and M4, lignin stabilization and carbohydrate protection. MW-REPORT translates the identified gaps into ten reporting themes and experimental priorities. The intended outcome is a defensible basis for formulation-specific PEG-grade selection, not a universal optimum.

2. Review Methodology

2.1. Literature Search and Study Selection

This review was designed as a structured critical review supported by an auditable evidence database, rather than as a systematic review or meta-analysis. This design is suitable for a small and heterogeneous experimental literature that requires conceptual and mechanistic interpretation while retaining a transparent record of study selection [23–25]. The main search audit was completed on 15 August 2026. Scopus was the main bibliographic source, and ScienceDirect provided complementary platform-level searches. The Scopus query used TITLE-ABS-KEY for DES-, neutral-polymer-, and lignocellulose-related terms and encoded its lower publication-year limit as PUBYEAR > 2009; no upper-year clause was included in the query. Article and Review document-type filters were subsequently applied, without a language or subject-area restriction. The search yielded 154 results before these document-type filters and 147 afterward (141 articles and six reviews); the retrieved years spanned 2010–2026. Three separate ScienceDirect searches in the title, abstract, or author-specified keywords were restricted to 2010–2026 and yielded 26 records for PEG (Query A), 32 for PVA/PVP (Query B), and zero for PPG/poloxamer (Query C). No additional ScienceDirect document-type, language, subject-area, or access-status filters were applied. The four main search executions thus yielded 205 record occurrences before deduplication, not necessarily 205 unique articles. Their complete query expressions, search fields, dates, limits, and retrieved counts are presented in Supplementary Table S1a–S1b.

The 205 accessible records were matched first by normalized DOI and then by normalized title. Removal of 46 duplicates left 159 unique records for title-and-abstract screening. Of these, 113 were excluded. The main reasons were that the polymer was used only in a downstream film, gel, membrane, sensor, adhesive, or phase-change material; no neutral polymer was present in the DES or related processing medium; the reported eutectic or polymer system was outside lignocellulosic biorefining; or the study provided no relevant fractionation, solvent-property, phase-behavior, or transferable mechanistic outcome. Non-eligible publication types and reports whose experimental evidence could not be evaluated were also removed. Forty-six records proceeded to detailed assessment using the main article, abstract, and supporting information as available. Four were excluded at this stage because PVA and/or PAA was introduced only after pretreatment to prepare gels, gel electrolytes, or sensors; their exclusion was not based on open-access status. The resulting evidence database contained 42 studies. A targeted Scopus sensitivity search on 17 August 2026 examined molecular-weight, chain-length, and PEG-grade-specific terms without database-level filters at the retrieval stage. Eight records were exported; after applying the predefined 2010–2026 eligibility window, one 1975 record was excluded. All seven in-window records matched entries in the main Scopus export by DOI, so no additional unique record was identified (Supplementary Table S1c). The selection flow in Table 1 counts only the four main searches; the sensitivity results are documented separately.

To test whether the 2010 lower publication-date limit excluded relevant earlier evidence, the database searches were rerun on 13 October 2026 without a lower publication-year cutoff, while retaining the same search concepts and fields and an upper publication-year limit of 2026. The Scopus rerun, with Article and Review document types and no language or subject-area restriction, returned 156 records; four were published before 2010 (1984, 2000, 2004, and 2009). All four concerned pharmaceutical solid dispersions, drug-delivery formulations, or a pharmaceutical eutectic mixture and did not meet the review eligibility criteria. The corresponding ScienceDirect reruns identified no pre-2010 record for Query A (26 current records) or Query B (33 current records), and Query C remained at zero records. Because these reruns were performed approximately two months after the main audit,

Table 1. Search and screening flow for the present review.

Stage	Records	Interpretation
Records retrieved from four main searches	205	147 Scopus records and 58 ScienceDirect results; raw occurrences before deduplication.
Unique records after deduplication	159	46 duplicates removed using normalized DOI and title.
Excluded at title/abstract screening	113	Downstream polymer use; no polymer-in-DES relationship; non-DES or non-biorefining system; no relevant process, property, or mechanistic outcome; or non-eligible report.
Records assessed in detail	46	Main article, abstract, or supporting information assessed according to availability.
Excluded after detailed assessment	4	PVA/PAA was used only after pretreatment to make gels, gel electrolytes, or sensors; exclusion was unrelated to open-access status.
Final evidence database	42	E1 = 3 within-study PEG-grade lignocellulose series; E2 = 8 PEG-containing native-lignocellulose studies without a verified grade series; E3 = 17 PEG model/process-property studies; E4 = 14 non-PEG mechanistic analogues. E4 is secondary context only.
Targeted sensitivity search	0 new	8 raw records on 17 August 2026 (no year/language limits); 1 excluded by year; 7 matched the main Scopus records by DOI; 0 new unique records.

differences in total database counts were not interpreted as effects of removing the cutoff; the sensitivity assessment was based specifically on records published before 2010. No additional eligible pre-2010 study was identified, and the retained evidence base and conclusions were unchanged (Supplementary Table S1d).

2.2. Eligibility, Data Extraction, and Evidence Classification

Eligibility is defined separately for process evidence and mechanistic context. Process evidence requires PEG to be present during treatment of native lignocellulose in a DES or explicitly described eutectic processing medium, with a reported fractionation, carbohydrate, lignin, or digestibility outcome. A non-biomass or purified-substrate PEG system is retained only when all of the following operational conditions are met: (i) PEG participates in the liquid or eutectic medium rather than being added only after processing; (ii) the study directly measures or calculates a named mediator that maps to M1–M4; (iii) the mediator, formulation, temperature, and physical state can be identified from the source; and (iv) a written transfer limitation is recorded for differences in substrate, polymer chemistry, composition, physical state, and temperature. Eligible mediators include spectroscopic or solvation descriptors, viscosity or diffusivity, phase boundaries or partitioning, and product-structure or coordination measurements. A performance change by itself is insufficient for mechanistic assignment. Systems described as eutectic-like are retained under that designation and are not taken to demonstrate thermodynamic DES formation. Non-PEG gels and materials are eligible only as secondary mechanistic analogues when they directly report a relevant network, transport, phase, or stabilization observation; they never enter the PEG fractionation evidence classes. Studies in which polymer is introduced only to fabricate a downstream film, gel, membrane, sensor, or related material after pretreatment are excluded from process evidence.

The unit of study counting is the article, while the unit of outcome extraction is a specified formulation, grade, and processing condition. The extraction record should link the DOI to component amounts, nominal PEG grade and available molar-mass descriptors, loading basis, water, substrate, solid loading, temperature, time, heating mode, outcome definition, and source location. Each numeric value is distinguished as source-reported, author-calculated, or graph-derived. Replicate number, type of replication, uncertainty definition, and statistical comparison are recorded separately for the grade screen and any subsequent optimization. An inaccessible or unchecked datum is marked not verified (NV), rather than not reported (NR). NR is used only after the relevant main article and supporting information have been checked. Graph-derived values require the figure identifier and an explicit extraction method and precision; they cannot supply unreported replicate numbers or statistics.

Four mutually exclusive article classes define the evidence inventory: E1, within-study PEG-grade series in native lignocellulose; E2, PEG-containing native-lignocellulose studies without a verified within-study grade series; E3, PEG model or process-property studies outside native lignocellulose, including purified substrates and non-biomass liquids; and E4, non-PEG mechanistic analogues. If an article covers more than one setting, its article-level class is assigned in the order E1, E2, E3, E4, while individual observations retain their system labels. Foundational or methods references are cited separately and are not automatically counted as retained experimental studies. Applying these rules to the 42 retained studies yielded E1 = 3, E2 = 8, E3 = 17, and

E4 = 14. The three E1 articles are [14], [16], and [18]. Two E2 records, [26] and [27], remain provisional because only partial source material could be verified; neither is used to rank PEG grades. E1 demonstrates within-study formulation responses rather than an isolated molecular-weight effect, whereas E4 is used only as secondary mechanistic context. The study-level assignments and transfer boundaries are provided in Supplementary Table S4.

MW-REPORT is proposed as a polymer-specific reporting checklist organized into ten themes corresponding, in order, to the ten gap-to-action rows: (1) PEG identity and molar-mass distribution; (2) formulation basis and chemical-equivalent normalization; (3) water content and its determination; (4) PEG-grade comparison design, including an additive-free control; (5) rheology and transport properties under relevant processing conditions; (6) phase state and polymer partitioning; (7) fractionation mass balance and product quality; (8) PEG recovery and solvent-composition changes during reuse; (9) accessible numerical grade-response data, replication, uncertainty, and statistical analysis; and (10) mediator measurements for testing proposed mechanisms. Temperature and process severity should be reported alongside the relevant property measurements and fractionation outcomes. This explicit correspondence connects each identified gap to a reporting or experimental action and distinguishes performance measurements from evidence needed to evaluate their mechanistic interpretation.

Evidence distance controls the wording used throughout the review. The three E1 articles are referred to as within-study PEG-grade series because they compare grade-labelled formulations within the same study but do not isolate molecular size as an independent variable. E2 and E3 studies can support process variables or candidate mechanisms, whereas E4 provides only secondary mechanistic analogy. None of E2-E4 can establish a PEG-grade ranking in native lignocellulose, and even E1 supports only within-formulation grade responses unless the changing chemical equivalents and solvent properties are independently controlled. For mechanistic coding, Supplementary S4 separates pathway assignment from mediator verification: a pathway is classified as mediator-supported only when the source reports the corresponding interaction, transport/rheology, phase/partitioning, or stabilization measurement; a literature explanation without that mediator is retained only as a hypothesis code and is not counted as mechanistic proof.

2.3. Methodological Limitations

The primary Scopus and ScienceDirect search audit reflects records available through 17 August 2026; the separate lower-date sensitivity rerun on 13 October 2026 was conducted only to test the effect of removing the 2010 cutoff and did not alter the retained evidence base. Web of Science Core Collection was not accessible through the institutional or account access available during the primary search period and was therefore not included. This restriction may have reduced database coverage; absence from the retained corpus should not be interpreted as absence from the wider literature. Screening, eligibility decisions, and data extraction were performed by one reviewer and were not independently duplicated. To reduce interpretation drift, the reviewer applied predefined eligibility rules, DOI- and title-based deduplication, a standardized extraction form, explicit recording of missing information, evidence-distance classification, and page-, section-, table-, figure-, or supporting-file locators for decisive claims. The targeted PEG-grade sensitivity search, the lower-date sensitivity check, and subsequent source-locator audits were used to revisit potentially eligible records and verify the three E1 within-study PEG-grade series. These safeguards improve traceability and consistency but are not equivalent to independent dual screening; residual selection and extraction error therefore remain possible.

No review protocol was registered, and no universal risk-of-bias score was assigned across these heterogeneous experiments. Instead, the three E1 within-study PEG-grade series [14, 16, 18] were audited separately for replication reporting, matched controls, grade-specific statistical testing, completeness of grade-resolved measurements, major formulation/process confounders, and numerical traceability (Supplementary S2). The audit found that all three studies used within-study comparison structures, but the strength of reporting differed. Liu et al. [14] documented triplicate component analysis in the supporting information and compared glycol, PEG200, PEG400, and PEG4000 at a fixed 2.5 g third-component addition, but no inferential test for the between-grade screen was located, and grade-resolved solvent-property measurements were incomplete. Zhou et al. [16] reported three-repeat analytical measurements and five viscosity readings per sample, used a single-variable PEG-grade comparison with a no-PEG binary-DES reference, and provided grade-resolved yield/composition figures; however, the source inspected did not provide a traceable inferential test supporting the statement that grade did not significantly affect fractionation. Huang et al. [18] reported grade-resolved composition and retention/removal values with

uncertainty and included an untreated control; its response-surface analysis formally tested PEG molecular weight as a factor for glucose concentration and yield, but those ANOVA models used PEG400/600/800 rather than the full PEG200/400/600/800 single-factor screen and did not constitute pairwise tests among all grades.

Across all three E1 studies, the principal reliability limitation is design confounding rather than absence of a within-study comparison. The two eucalyptus studies changed nominal PEG grade at fixed PEG mass or mass fraction, which necessarily changed chain number and terminal-hydroxyl concentration, whereas the bagasse study held ChCl:PEG at 1:4 on a molar basis, causing PEG mass fraction and overall formulation composition to change with grade. None of the three studies reported the full grade-resolved combination of measured PEG Mn, Mw, dispersity, water content, viscosity, and diffusivity required to isolate molecular size from composition and transport. Accordingly, Supplementary S2 reports domain-level judgments rather than a pooled quality score, and the synthesis treats these studies as evidence of within-formulation PEG-grade responses rather than proof of an isolated molecular-weight effect. Two supporting records also remain provisional: S. Yu et al. [26] lacks a verified PEG400-specific result, and D. Zhao et al. [27] lacks a verified PEG grade and complete processing conditions; neither record is used to determine grade ranking.

3. Nominal PEG Grade as a Formulation Variable

3.1. Terminology and Molar-mass Basis

The expression 'PEG molecular weight' is widely used as a commercial grade label, but it should not be treated as an exact molecular mass. Commercial PEG contains a distribution of chain lengths, and the number in PEG200, PEG400, PEG600, PEG800, or PEG4000 denotes a nominal average molar-mass grade rather than a single molecule. Polymer terminology distinguishes the number-average molar mass Mn, the mass-average molar mass Mw, and dispersity Đ = Mw/Mn [21]. Accordingly, this review uses 'nominal PEG grade' for supplier labels and reserves Mn, Mw, and Đ for experimentally measured distributions of PEG, lignin, or other polymers. The older references in this paragraph are retained only as foundational sources for polymer and PEG terminology [21, 28].

3.2. Experimental Normalization and Chemical-equivalent Basis

Controlled-grade comparisons have not used a single normalization basis. Z. Liu et al. [14] compared ethylene glycol, PEG200, PEG400, and PEG4000 at a fixed 2.5 g addition, whereas S. Zhou et al. [16] compared PEG200, PEG400, PEG600, and PEG800 at a specified PEG mass fraction. The following values are therefore an author calculation that makes the chemical consequence of a fixed-mass design explicit, not molar-mass measurements. For an illustrative 5 wt% PEG formulation, equivalent to 50 g PEG kg^{-1} solution, the nominal number of PEG chains is approximated by $n_{chain} = m_{PEG}/M_{grade}$. It decreases from 0.250 mol kg^{-1} for PEG200 to 0.125, 0.083, 0.0625, and 0.0125 mol kg^{-1} for PEG400, PEG600, PEG800, and PEG4000, respectively. For linear $HO–(CH_2CH_2O)_n–H$, the corresponding terminal-hydroxyl amount is approximately $2n_{chain}$ and therefore falls from 0.500 to 0.025 mol kg^{-1}.

The repeat-unit basis behaves differently. Using 44.05 g mol^{-1} for $–CH_2CH_2O–$ and 18.02 g mol^{-1} for the two terminal groups, the same 50 g kg^{-1} example contains approximately 1.03–1.13 mol of ethylene-oxide repeat units kg^{-1} across PEG200–PEG4000. Thus, the repeat-unit amount changes by only about 9%, while the chain and terminal-hydroxyl amounts change by a factor of 20. A response observed at fixed PEG mass may consequently reflect chain number or end-group concentration as well as chain length.

Huang et al. [18] used a different design: ChCl and PEG200, PEG400, PEG600, or PEG800 were combined at a ChCl:PEG molar ratio of 1:4 before hydroxyethyl sulfonic acid was added. On the nominal-grade basis, four moles of PEG per mole of ChCl correspond to approximately 0.80 kg PEG for PEG200 and 3.20 kg PEG for PEG800. Using 139.62 g mol^{-1} for ChCl, the PEG fraction of the binary ChCl–PEG mixture therefore rises from approximately 85.1 to 95.8 wt%. If the total solvent mass is then held at 50 g, the absolute amounts of both ChCl and PEG chains decrease as grade increases, while the PEG mass fraction and repeat-unit contribution increase. This series changes nominal grade, PEG:ChCl mass ratio, end-group concentration, and overall formulation simultaneously; it cannot isolate chain length alone.

Fixed-mass and fixed-molar designs are both informative, but they answer different questions and should not be pooled without normalization. Future grade-comparison studies should report supplier and grade, measured M_n, M_w, and Đ when available, PEG mass, moles of chains, terminal-hydroxyl and repeat-unit equivalents, water content, and formulation viscosity. These descriptors are required to determine whether an apparent grade response originates from molecular size, end-group density, transport, or composition.

3.3. Formulation-dependent Functions of PEG

PEG functions in eutectic and eutectic-like media cannot be inferred from nominal grade alone. In direct property studies, PEG400 changed solvatochromic response and ion-solvation structure when added to several DESs [12], while the density and viscosity of a PEG400/1,3-propanediamine DES depended strongly on composition and temperature [13]. These studies demonstrate formulation-dependent solvent behavior, not a universal PEG-grade effect. More broadly, hydration studies show that water can reorganize DES interaction networks rather than act as a purely inert diluent [29, 30]; this is relevant context, but neither study compared PEG grades.

At the process level, the evidence also separates loading effects from grade effects. Increasing PEG200 loading was associated with lower viscosity in a K_2CO_3–glycerol system [31], which supports a transport role for PEG200 in that formulation but does not predict the behavior of PEG400 or PEG800. Conversely, PEG-grade effects on lignin dissolution in polar aprotic/poly-DES systems were non-monotonic and depended on the lignin substrate [32]. A single label such as 'viscosity modifier' or 'lignin solvent' is therefore insufficient without formulation-specific measurements.

Adjacent systems clarify narrower pathways but require explicit evidence-distance limits. PEG grade affected phase formation and RNA partitioning in PEG-based aqueous biphasic systems [22]. In a controlled Zn-based cellulose solvent, PEG–Zn coordination was linked to competitive protection of glycosidic bonds [33]. These results support phase-behavior and coordination hypotheses, respectively, but neither directly demonstrates the same mechanism during native lignocellulose fractionation. D. Zhao et al. [27] further reported Lewis-acid catalysis coupled with PEG stabilization of lignin; however, because the present audit could verify only the abstract and supporting information for that record, it is not used here as decisive grade-specific evidence.

Taken together, PEG may contribute through interaction-network modification, transport control, solvation, phase formation, coordination, or chemical stabilization, but the active contribution is system dependent. Mechanistic claims should therefore be tied to the measured formulation variable and evidence level. Nominal grade by itself cannot identify which pathway produced an observed biomass or product response.

4. Within-study PEG-grade Series in Lignocellulose Processing

Three articles in the assembled corpus compare multiple nominal PEG grades during native lignocellulose processing: two eucalyptus studies and one sugarcane-bagasse study [14, 16, 18]. Table 2 displays each tested grade side by side. Exact numerical values are reproduced only when they were tabulated or stated explicitly by the source. When a grade-screen outcome is available only graphically, the table states that it is graph-reported and that the exact numerical value was not tabulated, rather than digitizing the plot. Replication, uncertainty, and statistical testing are reported only when traceable in the source. Differences in biomass, chemistry, heating, loading basis, and outcome definitions prevent a pooled grade ranking. Selected optimized conditions are kept separate from the grade-screen comparison.

NR means not reported after inspection of the available main article and supporting information. Exact numerical values are reproduced only when they were tabulated or stated explicitly in the source. For Huang et al. [18], the lignin-removal and cellulose-retention values and the ± terms are source-reported; the single-factor replicate number and definition of ± were not stated in the inspected text. Its later RSM formally tested PEG molecular weight as factor B for glucose concentration ($p = 0.0224$) and glucose yield ($p = 0.0031$), but the RSM used PEG400/600/800 and is not a pairwise test of the full four-grade screen. For Liu et al. [14], the grade-screen fractionation outcomes are presented graphically and exact grade-resolved numerical values are not tabulated; the original article separately reports grade-resolved recovered-lignin Mw/Mn/PDI values. For Zhou et al. [16], grade-resolved CRS/SR yields and viscosity are presented graphically rather than as numerical tables; therefore, Table 2 does not assign digitized values to those plots. The exact grade-resolved CrI values available in the supporting information are reported instead. † denotes the selected PEG400 A5M400T130 TDESL lignin product, not a grade-resolved GPC series. Supplementary S3a reconciles source-reported PDI with Đcalc = Mw/Mn, and Supplementary S3b records data availability and original-source locators. CRS = cellulose-rich solid; CrI = crystallinity index; GC = glucose concentration; GY = glucose yield; SI = Supporting Information; TDESL = recovered lignin from the selected ternary-DES condition.

4.1. Comparability of the Controlled-grade Designs

The three studies manipulated nominal grade under two different formulation bases. The eucalyptus experiments held PEG addition constant: 5 wt% for PEG200–PEG800 in

Table 2. Grade-resolved outcomes in the three within-study PEG-grade series.

Study and Grade	Primary Grade-screen Outcome	Secondary Grade-screen Outcome	Lignin Mw / Mn (g mol-1)	PDI / Đcalc	Replication / Uncertainty / Grade Statistics
[18] PEG200	Lignin removal 59.06 ± 0.51%	Cellulose retention 85.19 ± 0.75%	NR	NR	Single-factor n NR; ± reported but definition NR; no pairwise grade test located.
[18] PEG400	Lignin removal 59.23 ± 0.30%	Cellulose retention 85.43 ± 0.49%	NR	NR	Single-factor n NR; ± reported but definition NR; RSM factor B tested separately.
[18] PEG600	Lignin removal 83.23 ± 0.55%	Cellulose retention 73.63 ± 0.75%	NR	NR	Single-factor n NR; ± reported but definition NR; RSM factor B: GC p=0.0224, GY p=0.0031 (not pairwise; PEG400/600/800 levels).
[18] PEG800	Lignin removal 59.95 ± 0.73%	Cellulose retention 50.50 ± 0.53%	NR	NR	Single-factor n NR; ± reported but definition NR; no pairwise grade test located.
[14] PEG200	Delignification: graph only; exact value NR	Cellulose recovery: graph only; exact value NR	5682 / 2683	2.17 / 2.12	Component analysis n=3 (SI); error bars shown; no grade-wise test.
[14] PEG400	Delignification: graph only; PEG400 slightly higher; exact value NR	Cellulose recovery: graph only; exact value NR	5613 / 2730	2.14 / 2.06	Component analysis n=3 (SI); error bars shown; no grade-wise test.
[14] PEG4000	Delignification: graph only; exact value NR	Cellulose recovery: graph only; exact value NR	6365 / 3142	2.17 / 2.03	Component analysis n=3 (SI); error bars shown; no grade-wise test.
[16] PEG200	CRS yield: graph only; exact value NR	CrI 70.36% (SI)	NR for grade screen	NR	Experiments n=3; error bars shown; no traceable grade-wise test.
[16] PEG400	CRS yield: graph only; PEG400 slightly higher; exact value NR	CrI 70.98% (SI)	NR for grade screen; selected PEG400 product 4978 / 3434†	NR for grade screen; selected PEG400 product 1.44 / 1.45†	Experiments n=3; viscosity n=5/sample; no traceable grade-wise test.
[16] PEG600	CRS yield: graph only; exact value NR	CrI 68.86% (SI)	NR for grade screen	NR	Experiments n=3; error bars shown; no traceable grade-wise test.
[16] PEG800	CRS yield: graph only; exact value NR	CrI 66.51% (SI)	NR for grade screen	NR	Experiments n=3; error bars shown; no traceable grade-wise test.

the TEBAC-formic-acid system and 2.5 g for PEG200, PEG400, and PEG4000 in the microwave-assisted lactic-acid/choline-chloride system [14, 16]. The bagasse study instead held ChCl:PEG at 1:4 on a molar basis while changing PEG200–PEG800 [18]. Thus, the two-eucalyptus series decreased chain and terminal-hydroxyl concentrations as grade increased, whereas the bagasse series increased the PEG mass fraction and repeat-unit contribution.

These designs do not isolate polymer size as a single independent variable. None of the three studies reported the full combination of measured PEG M_n, M_w, dispersity, grade-resolved water content, viscosity, and diffusivity needed to separate chain length from composition and transport. Their supplier labels should therefore be interpreted as nominal formulation grades. The valid causal statement is that changing grade changed the response within each reported formulation, together with the chemical-equivalent changes imposed by its normalization basis.

4.2. Cross-study Response Patterns

The eucalyptus series show shallow, non-monotonic grade responses, but the original reports do not tabulate the principal fractionation values for every grade. Liu et al. [14] describe delignification as similar for PEG200, PEG400, and PEG4000, with PEG400 slightly higher; exact

grade-resolved fractionation values are therefore reported as not tabulated rather than digitized from the plot. Zhou et al. [16] likewise describe a modest grade effect, with PEG400 giving a slightly higher CRS yield than the other tested grades; exact grade-resolved CRS/SR values are not tabulated. The study reports repeated experiments and visual uncertainty bars, but the reliability audit did not identify a traceable grade-wise inferential test. These two studies therefore support qualitative within-study response patterns rather than numerical claims of statistical superiority.

The fixed-molar-ratio bagasse experiment produced a clearer separation among grades. Lignin removal was 59.06%, 59.23%, 83.23%, and 59.95% for PEG200, PEG400, PEG600, and PEG800, respectively, while cellulose retention was 85.19%, 85.43%, 73.63%, and 50.50% [18]. In the single-factor enzymatic-hydrolysis screen reported by Huang et al. [18], both glucose concentration and glucose yield reached their maxima at PEG600 and declined at PEG800. Thus, PEG600 maximized specific lignin-removal and glucose responses but did not maximize cellulose retention. Response-surface optimization subsequently selected PEG400 under different combinations of acid concentration, time, and temperature. The shift from PEG600 to PEG400 reflects factor interaction and the chosen response; it is not evidence of a universal optimum.

4.3. Process Performance and Product Quality

Selected-condition performance must be separated from the between-grade contrast. For the PEG400 TEBAC/formic-acid formulation, the submitted extraction lists 53.32% cellulose-rich-solid yield, 82.79% lignin recovery, cellulose degree of polymerization 1611, alpha-cellulose content 86.75%, crystallinity index 70.98%, water-retention value 214%, and Fock reactivity 80.82% [16]. These values describe that condition. Inspection of the original article confirms that the selected TDESL product reports Mw = 4978 g mol^{-1}, Mn = 3434 g mol^{-1}, and PDI = 1.44. The quotient of the displayed molar masses is 1.4496, giving Đcalc = 1.45 to two decimal places. We therefore distinguish the source-reported PDI of 1.44 from this calculated ratio. The supporting information includes molecular-weight distribution data, but provides no corrected or unrounded values that reconcile the discrepancy. Its cause remains unresolved, and no rounding explanation or correction to the original measurement is assumed (Supplementary Table S3a).

For the microwave study, 89.73% delignification describes the selected PEG400 condition and does not measure its advantage over another grade [14]. Inspection of the original article confirms Mw/Mn pairs of 5682/2683, 5613/2730, and 6365/3142 g mol^{-1} and source-reported PDI values of 2.17, 2.14, and 2.17 for PEG200, PEG400, and PEG4000, respectively, under the reported microwave grade-screen conditions. The corresponding ratios of the displayed molar masses are 2.1178, 2.0560, and 2.0258, giving Đcalc = 2.12, 2.06, and 2.03. Thus, the differences are already present in the source data rather than arising from transcription into this review. Table 2 and Supplementary Table S3a distinguish source-reported PDI from calculated ratios. The supporting information describes the GPC procedure but provides no corrected or unrounded values that reconcile these discrepancies. Their cause remains unresolved, and the inconsistent dispersity values are not used to rank PEG grades. The reported increase in lignin solubility from 22.71 to 29.73 wt% concerns PEG400 addition relative to the binary solvent and cannot establish a grade effect.

4.4. Mechanistic Limits and Experimental Implications

The three studies are consistent with a balance among liquid mobility, biomass contact, solvation, and product stabilization, but none resolves these contributions by grade. The TEBAC-formic-acid study linked PEG incorporation at lignin side-chain alpha positions with lower condensation, and the microwave study linked PEG400 addition with changes in acidity, polarity, lignin solubility, and cellulose protection [14, 16]. The bagasse study attributed part of the response to biomass swelling and reduced non-productive cellulase adsorption [18]. These mechanisms are plausible within the reported formulations, but the papers did not test whether their magnitude changes systematically with nominal grade.

Accordingly, the three E1 within-study PEG-grade series do not support a monotonic 'higher grade is better' rule or establish a numerical design window. They support context-dependent formulation responses whose apparent optimum depends on normalization basis, biomass, process severity, and the response selected for optimization. A decisive experiment should compare the same grades on parallel equal-mass and equal-chain bases; for linear PEG with two hydroxyl ends per chain, equal-chain and equal-terminal-hydroxyl normalization are proportional rather than independent. Water content, viscosity, density, polarity or acidity, phase state, fractionation mass balances, and cellulose and lignin quality should be measured for every grade. Isolating end-group chemistry additionally requires matched end-capped or otherwise functionality-controlled polymers. These measurements would help distinguish chain size from end-group density, bulk transport, and composition effects.

5. Supporting Process and Adjacent System Evidence

The within-study lignocellulose series in Section 4 identify empirical formulation responses. Single-grade PEG biomass studies (E2) identify relevant process variables; PEG model systems (E3) test selected interactions or phase phenomena; and non-PEG analogues (E4, Section 8) supply secondary context. None of these supporting classes adds a new E1 study or establishes a PEG-grade ranking in native biomass.

5.1. PEG Loading and Solvent Property Effects

At a fixed nominal grade, changing PEG amount can alter fluidity enough to affect fractionation. In a K_2CO_3–glycerol DES containing PEG200, additions of 0, 5, 10, and 20 mL gave room-temperature viscosities of 76.24, 26.48, 9.90, and 2.87 Pa·s, respectively. The 10 mL formulation removed 81.93% xylan and 96.37% lignin and gave a cellulose yield of 73.65% [31]. Because all formulations used PEG200, this series demonstrates a loading effect. The volumetric additions should not be converted to mass fractions unless PEG density is reported or measured.

A related co-solvent effect appears in purified cellulose. Adding 5 wt% PEG400 to a choline chloride-imidazole DES increased cotton-linter cellulose solubility from 2.48 to 4.57 wt% and reduced the crystallinity index of regenerated cellulose from 41.6% to 21.83% [34]. These results support PEG-mediated changes in accessibility and decrystallization, but neither whole-biomass fractionation nor a grade series was tested.

Composition-dependent measurements confirm that PEG can change the solvent environment. Varying the PEG400 mole fraction in reline, glyceline, and ethaline altered solvatochromic parameters and chloride solvation [12]. A PEG400-1,3-propanediamine DES also showed composition- and temperature-dependent density, viscosity, refractive index, and spectroscopic interactions [13]. These findings justify measuring viscosity, density, and polarity at the actual processing composition and temperature. They do not establish how those properties change across PEG grades.

Adjacent PEG-containing liquid systems identify measurements relevant to M1–M3, but they do not constitute E1 within-study PEG-grade evidence for lignocellulose fractionation. Composition-dependent CO_2 solubility in PEG–water–choline chloride/ethylene glycol mixtures illustrates that multicomponent liquid behavior cannot be inferred from a nominal PEG label alone [35]. Choline chloride-based binary and ternary DESs used for pyrazinamide likewise showed formulation-specific solubility enhancement [36]. Studies of griseofulvin and ethionamide further demonstrate solute- and composition-dependent behavior in PEG-containing media [37, 38]. A PEG–sugar DES used to extract potato protein also linked hydrogen-bond regulation to recovered-product functionality [39]. These adjacent studies support measurements and hypotheses, not grade ranking in native biomass.

5.2. Controlled-grade Evidence from Purified Cellulose and Isolated Lignin

Purified-cellulose experiments provide the closest controlled evidence outside whole biomass. In a $ZnCl_2{\cdot}3H_2O$–H_3PO_4 eutectic solvent, PEG200, PEG600, PEG1000, and PEG2000 were compared together with PEG loading. A formulation containing 1 g PEG200 per 20 g DES dissolved 7 wt% cellulose in about 2 h and preserved a regenerated-cellulose degree of polymerization near 745. Higher grades reduced the dissolution ratio, while calculations supported preferential PEG–Zn^{2+} coordination that protected glycosidic bonds [33]. The controlled grade response is relevant to cellulose protection, although purified cellulose lacks native lignin-carbohydrate architecture.

Controlled grade series on isolated lignins reveal a different response. Poly-DESs prepared from levulinic acid and PEG or PEG diacrylate grades 200, 400, and 600 became less viscous as nominal grade increased, but lignin solubility was non-monotonic and depended on lignin type. Polar aprotic co-solvents increased solubility to as high as 96.82%, while Kamlet-Taft α and π* generally decreased with PEG grade and β showed no simple grade relation [32]. Thus, viscosity and solvation descriptors did not predict a single grade ranking across lignins.

Loading effects can produce a similar composition-specific optimum without changing grade. In choline chloride-glycerol-PEG400 mixtures, a 1:2:2 molar formulation gave an ethoxylated hardwood lignin solubility of 66.70 g per 100 g solvent at 60 °C. Regenerated lignin retained most of its β-O-4 content, and the solvent recovered more than 98% of its mass [40]. This study links solvent composition with lignin solubility and product structure, but the use of PEG400 alone prevents a grade-specific inference.

5.3. Phase Behavior and Transferable Controlled-grade Evidence

Within-study grade series in aqueous biphasic systems show that improved phase formation need not improve target partitioning. At a fixed TBAC:PEG molar ratio of 1:2, increasing nominal grade from PEG200 to PEG4000 strengthened phase-forming ability but progressively reduced RNA extraction efficiency [22]. This opposing

response demonstrates that phase separation and solute affinity must be evaluated as distinct outcomes. It does not establish the direction of lignin partitioning in a biomass-derived liquor.

A second controlled series compared PEG200, PEG400, PEG600, and PEG800 in TBAB-PEG solvents for asphalt desulfurization. PEG400 gave the strongest extraction performance, whereas both shorter and longer grades performed less effectively; the authors related the decline at higher grades to steric hindrance and changes in hydrogen-bond interactions [41]. The non-monotonic pattern supports an interaction-transport trade-off, but petroleum sulfides and asphalt do not reproduce lignocellulose chemistry.

Fixed-grade separation studies identify additional process variables. A TBAB-PEG200 DES in circular channels showed that flow and contact conditions govern extraction and volumetric mass transfer [42]. A choline chloride-PEG400-glycerol three-phase system linked multistage selectivity to phase distribution [43]. Dielectric and fluorescence measurements in a nonionic PEG-based DES further revealed several relaxation timescales rather than a single viscosity-controlled response [44]. Hydrodynamics, phase distribution, and molecular relaxation are therefore plausible mediators, but these non-biomass studies do not demonstrate grade-dependent lignin recovery.

5.4. Implications for Lignocellulose Grade Studies

Two conclusions are consistent across the supporting evidence. First, PEG amount and solvent composition can change viscosity, polarity, coordination, and substrate accessibility even when nominal grade is fixed. Second, controlled grade series outside biomass can produce non-monotonic or opposing responses across dissolution, phase formation, and target partitioning. These observations strengthen the physicochemical basis for context-dependent grade effects, but they do not increase the count of E1 within-study PEG-grade series in native lignocellulose.

A future causal grade experiment should connect each process outcome to an intermediate property. Grade series should report the PEG normalization basis and measure water content, rheology at treatment temperature, density, polarity or acidity, phase boundaries, and substrate solubility. Fractionation mass balances should be paired with cellulose degree of polymerization or digestibility and with lignin recovery, molar-mass distribution, β-O-4 abundance, and residual PEG. This design would distinguish an empirical grade response from a response caused by loading, composition, or transport.

6. Evidence-derived Mechanistic Framework for PEG Molecular-weight Effects in DES Biorefining

Nominal PEG grade may alter several coupled properties of DES-based fractionation, with the direction and magnitude depending on loading basis and composition. The proposed MWDL framework separates four candidate pathways so that each can be tested through a measured mediator. A change in fractionation performance alone cannot identify the active pathway. The within-study series compare grade-labelled formulations; they do not independently establish molecular size as the cause of the response.

Figure 1 summarizes the proposed MWDL logic. Nominal PEG grade is not treated as an independent causal descriptor; it is interpreted together with loading basis, DES composition, water content or activity, temperature, biomass, and process severity. These variables may influence the system through M1–M4, whose combined effects are expressed in fractionation, product quality, solvent and polymer recovery, and sustainability outcomes. The diagram is an evidence map for organizing measurements, not a validated predictive model.

The four pathway names are used consistently throughout: M1, interaction-network modification; M2, viscosity, diffusion, and steric trade-offs; M3, phase behavior, partitioning, and crowding; and M4, lignin stabilization and carbohydrate protection. Their labels organize measurements and interpretations rather than ranking mechanism strength. Crowding, steric effects, and grade-dependent stabilization remain hypotheses unless the relevant mediator is measured in a suitable comparison.

The pathway assignments are linked to observations rather than inferred solely from high process performance. Supplementary S4 now reports all 42 retained articles study by study, including evidence class, assigned M1–M4 pathway(s), the coded mediator or source-level observation, verification status, classification basis, and the inference boundary. A pathway is marked as mediator-supported only when the required intermediate property is reported: interaction/solvation for M1, rheology/transport for M2, phase/partitioning for M3, or structural stabilization/carbohydrate protection for M4. If a paper proposes a pathway from performance without measuring the mediator, S4 labels that assignment as hypothesis-only. A study may support more than one pathway when separate observations justify each assignment. This matrix separates evidence-distance classification (E1–E4) from mechanistic coding and permits the reader to identify where a mechanism is measured, transferred, provisional, or unverified.

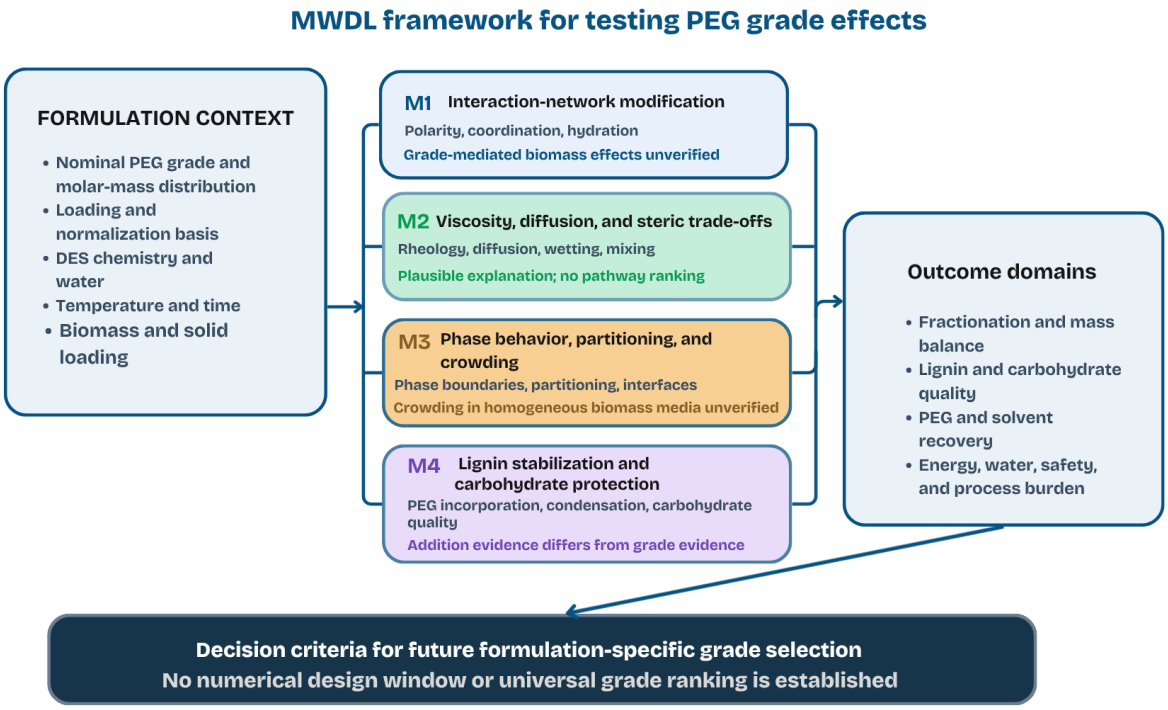


Figure 1. Proposed MWDL framework for testing PEG-grade effects. Formulation context can influence several candidate mediators, which must be measured alongside process and product outcomes. Pathways are not ranked; arrows indicate hypotheses for testing rather than demonstrated causation. Future selection requires explicit response thresholds and uncertainty.

Examples informing the framework include measured solvatochromic and coordination behavior for M1 [12, 33], fixed-grade loading–viscosity data for M2 [31], grade-dependent phase formation and a fixed-grade multiphase interpretation for M3 [22, 45], and structural evidence of PEG incorporation and reduced condensation for M4 [16, 45]. Non-monotonic biomass outcomes are compatible with several of these pathways and cannot distinguish them. Table 3 states the current inference limit and the measurement needed to test each pathway. No comparative score or validated ranking of M1–M4 is claimed.

6.1. M1: Interaction-network Modification

M1 concerns changes in hydrogen bonding, ionic association, polarity, acidity, and metal coordination caused by PEG participation in the liquid network. In reline, glyceline, and ethaline mixtures, varying the mole fraction of PEG400 changed solvatochromic descriptors and chloride solvation [12]. Because the grade remained PEG400, that study demonstrates a composition effect. A controlled PEG200/600/1000/2000 series in a $ZnCl_2{\cdot}3H_2O$–H_3PO_4 solvent further showed grade-dependent cellulose dissolution and preferential PEG–Zn^{2+} coordination [33]. This provides controlled evidence of a grade-dependent coordination effect, although the purified-cellulose system does not reproduce the structural complexity of native lignocellulose.

Isolated-lignin experiments also show that interaction descriptors need not move together. In levulinic-acid poly-DESs based on PEG or PEG diacrylate grades 200, 400, and 600, Kamlet–Taft α and π* generally decreased as grade increased, whereas β showed no simple grade relation and lignin solubility remained dependent on lignin type [32]. The E1 lignocellulose series did not measure α, β, π*, water activity, or spectroscopic interaction markers for every grade. Thus, the observed grade responses are formulation specific, and the available data are not sufficient to attribute them directly to M1.

Water must also be treated as part of M1 because it competes for hydrogen-bonding sites and can reorganize DES structure rather than act as an inert diluent [29, 30]. At the same gravimetric water content, longer PEG grades contain a higher proportion of internal ether oxygens relative to terminal hydroxyl groups and may distribute strongly associated and more mobile water differently from short oligomers. This could alter water activity (aw), local polarity, and network relaxation, but the retained literature does not directly compare these quantities across PEG grades in lignocellulose DESs. Grade-specific hydration should therefore be treated as a testable mediator rather than an established explanation. Matched grade series should report both total water content and aw after equilibration at the treatment temperature.

Table 3. Evidence basis, current limitations, and recommended measurements for the four mechanistic pathways discussed in this review.

Label and Proposed Pathway	Derivation from Retained Evidence	Current Evidence Status	Measurements Needed for Further Evaluation
M1 Interaction-network modification	Measured solvatochromic and chloride-solvation changes at varying PEG400 fraction, plus grade-dependent PEG–Zn^{2+} coordination in a purified-cellulose solvent [12,33].	PEG addition and composition effects are demonstrated. Controlled-grade evidence is outside whole biomass; the E1 biomass series lack grade-resolved interaction descriptors.	Compare equal-mass and equal-chain formulations; control end groups. Measure water activity, solvent descriptors, acidity, spectra, and coordination.
M2 Viscosity, diffusion, and steric trade-offs	Zhou et al. [16] report grade-resolved viscosity alongside the PEG200/400/600/800 fractionation screen, while fixed-grade loading-viscosity data [31] and isolated-lignin grade series [32] provide additional transport context.	One E1 study reports a grade-resolved rheological descriptor, but the measurement temperature and a formal mediator-response analysis are not established in the inspected report. Liu [14] and Huang [18] do not provide grade-resolved transport mediators. M2 is therefore plausible, not ranked as the strongest pathway.	Measure process-temperature rheology, diffusivity or validated penetration, wetting, density, and mixing for every grade; test whether the mediator changes reproducibly with grade and predicts the response after formulation and severity are controlled.
M3 Phase behavior, partitioning, and crowding	Controlled grade effects in an aqueous biphasic system and a depletion interpretation in fixed-grade multiphase biomass microextraction [22,45].	Transferable evidence only for the central question. Crowding or depletion is not established in homogeneous PEG200–PEG800 biomass DESs.	Determine phase diagrams, cloud points, concentration relative to c*, interfacial composition, and polymer and lignin partitioning.
M4 Lignin stabilization and carbohydrate protection	PEG incorporation at lignin α-positions, reduced condensation, and retained lignin structures in PEG-containing systems [16, 45].	PEG-associated stabilization is directly supported at selected grades. Grade-dependent stabilization and the role of terminal-group density remain unresolved.	Quantify PEG incorporation, β-O-4 and C-C linkages, carbonyls, phenolic OH, M_w/M_n/dispersity, residual PEG, and mass balance across matched grades.

Future studies of M1 should carefully control the basis used to compare PEG grades. At equal PEG mass, shorter grades supply more chains and terminal hydroxyl groups; at equal PEG molar amount, higher grades supply more PEG mass and ether repeat units. Comparisons based on equal PEG mass, chain concentration, and terminal-OH concentration would help separate molecular-size effects from changes in chemical equivalents. Relevant measurements include water content or activity, Kamlet–Taft parameters, acidity, spectroscopic features, and ion or metal speciation at the processing temperature. A stronger case for M1 would require a consistent relationship between PEG grade, these interaction descriptors, and the resulting fractionation or product-quality response.

6.2. M2: Viscosity, Diffusion, and Steric Trade-offs

M2 links nominal grade to fluid transport, biomass wetting, interfacial contact, and the steric environment around dissolved fragments. Zhou et al. [16] provide the clearest E1 mediator measurement: grade-resolved viscosity was measured for the PEG200/400/600/800 formulations, with five measurements per sample, alongside grade-resolved CRS/SR responses. Because the viscosity values are presented graphically rather than tabulated and the measurement temperature is not sufficiently clear for a process-temperature interpretation, we do not reproduce digitized viscosity values. No mediation analysis links the viscosity differences statistically to fractionation. Liu et al. [14] report viscosity for PEG400 loading changes but not across PEG200/400/4000, while Huang et al. [18] report grade-response outcomes without grade-resolved rheology or diffusion. The E1 evidence is therefore compatible with M2 but does not establish a causal transport sequence.

Independent property evidence shows why grade alone cannot serve as a viscosity proxy. At fixed PEG200 grade, increasing PEG addition lowered the room-temperature viscosity of a K_2CO_3–glycerol DES from 76.24 to 2.87 Pa·s, a change of more than one order of magnitude [31]. In the isolated-lignin poly-DES series, viscosity decreased rather than increased as PEG or PEG-diacrylate grade rose [32]. A nonionic PEG-based DES also displayed several dielectric and fluorescence relaxation timescales [44]. These findings show that composition, temperature,

and molecular relaxation can override a simple higher-grade-higher-viscosity expectation.

M2 is a plausible explanation for part of the non-monotonic E1 response, but the present evidence does not justify ranking it above M1, M3, or M4. Only Zhou et al. [16] couple the grade screen to a grade-resolved rheological descriptor, and even there the causal linkage is not isolated. Future comparisons should measure rheology at the treatment temperature together with diffusion or validated penetration, density, biomass wetting, mixing characteristics, and time-resolved lignin/carbohydrate release. A stronger M2 claim would require a reproducible grade effect on the mediator and a corresponding process response after formulation, water, and severity have been controlled.

6.3. M3: Phase Behavior, Partitioning, and Crowding

M3 separates three related but distinct phenomena: formation of a second liquid phase, partitioning of a target between phases, and crowding or depletion forces that may operate when polymer coils and interfaces are present. In an aqueous biphasic system at fixed TBAC:PEG molar ratio, increasing grade from PEG200 to PEG4000 strengthened phase-forming ability but progressively reduced RNA extraction efficiency [22]. This controlled series demonstrates that PEG grade can change phase behavior in an adjacent system. It also shows that stronger phase formation does not establish favorable partitioning of a particular solute.

A PEG400/oxalic-acid/MIBK microextraction system for switchgrass attributed interfacial stabilization partly to PEG-associated depletion interactions [45]. The evidence is relevant to a deliberately multiphase process, but only PEG400 was used; it therefore cannot be extended directly to depletion-driven lignin precipitation in homogeneous PEG200–PEG800 pretreatment systems. PEG200–PEG800 are short oligomeric liquids, and a nominal grade does not by itself establish polymer overlap, entanglement, or a depletion regime. Foundational PEO-solution measurements show that long-range behavior must be interpreted jointly from molecular size and concentration [46].

M3 is therefore best regarded as a plausible phase-behavior mechanism that still requires direct validation in homogeneous biomass systems. Future studies could address this by measuring phase diagrams, cloud points, PEG concentration relative to the overlap concentration (c*), and the distribution of PEG and lignin between phases. Water and salt contents, temperature, turbidity, interfacial composition, and the timing of phase formation must be reported. Without this information, changes in lignin recovery cannot be confidently attributed to crowding or depletion effects.

6.4. M4: Lignin Stabilization and Carbohydrate Protection

M4 concerns chemical interception or passivation of reactive lignin fragments and the associated preservation of carbohydrate and lignin quality. In PEG400-based switchgrass microextraction, the authors reported formation of an α-PEG-β-O-4 structure together with PEGylation of lignin [45]. In the selected PEG400 TEBAC-formic-acid condition, a new HSQC cross-peak at δC/δH 69.76/3.53 ppm was assigned to PEG substitution at the α-position of a β-O-4 derivative, and the ternary system showed less lignin condensation than the binary system [16]. These are direct observations of PEG-associated stabilization in biomass processing, but neither study compared the structural response across grades.

The microwave eucalyptus study likewise found that adding PEG400 increased alkali-lignin solubility from 22.71 to 29.73 wt% and inhibited condensation relative to the binary solvent, while product analyses were centered on the PEG400 formulation [14]. A PEG400-based isolated-lignin system retained much of the β-O-4 structure, but it tested loading and composition rather than grade [40]. Abstract and supporting-information evidence from a Lewis-acid system is consistent with PEG stabilization, although the unverified grade and full formulation make that record provisional [27]. General chemical-functionalization studies explain why trapping reactive intermediates can suppress condensation, but they do not establish a PEG-grade effect [15, 47].

However, whether the magnitude of this stabilization depends systematically on PEG grade remains unclear. At equal mass, a shorter grade supplies more PEG chains and terminal hydroxyl groups that could act as trapping sites, whereas a longer grade supplies fewer chains with a larger steric volume and slower diffusion. Clarifying this relationship will require grade-resolved measurements of PEG incorporation, β-O-4 abundance, condensed C–C linkages, carbonyl and phenolic-OH contents, molar-mass distribution, residual PEG, and lignin and carbohydrate mass balances. These measurements would help determine whether structural stabilization is actually responsible for the observed grade response.

The evidence is uneven. M1 and M4 are supported for PEG addition or selected PEG-containing formulations, but grade causality has not been isolated. M2 has one grade-resolved rheology data set in an E1 study [16], while the other E1 series lack the corresponding transport mediator; this is insufficient to rank M2 as the dominant explanation. M3 is demonstrated for phase behavior in adjacent systems, whereas crowding and

depletion remain untested in homogeneous PEG200–PEG800 biomass media. Accordingly, Figure 1 and Supplementary S4 should be read as an auditable map of measured, transferred, and hypothesis-only pathways, not as a validated hierarchy or predictive grade-selection model.

7. Context-dependent PEG-grade Selection

The current literature does not define a quantitative or universal optimum PEG-grade window. A more defensible interpretation is context-dependent grade selection: a formulation is preferable only when several process and product criteria are satisfied simultaneously for a stated biomass, DES composition, normalization basis, severity, and objective. The three E1 within-study PEG-grade series support this interpretation because none establishes a monotonic relationship between nominal grade and all relevant outcomes, and they differ in substrate, solvent chemistry, heating mode, normalization basis, and primary response.

The three E1 within-study PEG-grade series also show why a single optimum PEG grade is difficult to define. In a fixed-mass PEG200/400/600/800 series for eucalyptus fractionation, the overall grade response was weak and non-linear, with PEG400 providing only a small descriptive advantage in the reported balance of cellulose and lignin outcomes [16]. A microwave-assisted eucalyptus study using fixed masses of PEG200, PEG400, and PEG4000 reported slightly greater delignification with PEG400, whereas PEG4000 was associated with a higher molar mass of the recovered lignin [14]. In sugarcane-bagasse pretreatment at a fixed choline chloride-to-PEG molar ratio, the PEG200/400/600/800 series also produced non-monotonic responses, but the principal outcomes were glucose yield and concentration rather than lignin quality [18]. Thus, a grade that performs well for one response or formulation should not be regarded as universally optimal.

The mechanistic interpretation of these trends also remains limited. Lower nominal grades provide more chains and terminal hydroxyl groups at equal PEG mass and may increase mobility or specific interactions. Higher grades may provide a larger steric domain or promote phase separation, but they may also change penetration and relaxation behavior. Because the E1 biomass series did not measure interaction descriptors, viscosity, diffusion, phase behavior, and structural outcomes for every grade, the mechanisms behind these trends remain uncertain. Evidence from related systems further illustrates this uncertainty: viscosity, Kamlet–Taft parameters, and lignin solubility changed in different directions across PEG-based poly-DES formulations and lignin types [32], while a PEG200/600/1000/2000 series in purified cellulose showed that dissolution performance and preservation of cellulose degree of polymerization need not select the same condition [33]..

The basis used to normalize PEG also affects how a grade comparison should be interpreted. At equal PEG mass, increasing nominal molecular weight reduces the molar concentration of chains and terminal hydroxyl groups. At an equal PEG molar amount or fixed choline chloride-to-PEG molar ratio, increasing grade raises the total PEG mass and ether-repeat-unit content. Commercial PEG grades also represent molecular-weight distributions rather than single, precisely defined molecular weights. Consequently, the fixed-mass designs used by S. Zhou et al. [16] and Z. Liu et al. [14] cannot separate chain length from chain-number and end-group effects, whereas the fixed-molar-ratio design used by Huang et al. [18] introduces a changing polymer-mass basis. These studies are therefore useful for comparing formulations, but they do not isolate chain length as the only variable.

A defensible grade-selection criterion should therefore consider several process and product responses rather than relying on a single performance metric. Relevant fractionation responses include lignin removal and recovery, cellulose and hemicellulose retention, and the formation of soluble degradation products. Product quality can be assessed through lignin interunit linkages, condensation, phenolic hydroxyl content, molar-mass distribution, cellulose degree of polymerization, and, where relevant, enzymatic digestibility. The same experiments would also benefit from measurements of water content or activity, acidity, rheology at the processing temperature, phase behavior, solvent recovery, polymer loss, and energy demand. Once comparable data become available, Pareto-front or multi-criteria analysis may provide a balanced basis for formulation-specific grade selection.

Future studies could begin by comparing at least four PEG grades within the same DES chemistry under identical water content and processing severity, together with an additive-free control. Repeating the comparison on equal-chain and equal-terminal-hydroxyl bases would help distinguish chain-length effects from changes in chemical equivalents. Once the influence of the normalization basis is better understood, polymer loading, water content, temperature, and treatment time can be examined as additional interacting factors. Any resulting grade-response range should be reported as formulation specific and tied to the biomass type, DES composition, normalization basis, water content, processing conditions, selected outcome, and uncertainty. The present literature does not support a

universal preference for PEG400, PEG600, or any other nominal grade.

8. Secondary Mechanistic Analogues beyond PEG (E4; n = 14)

The 42 retained articles are not equally close to the central PEG-lignocellulose question: E1 = 3 within-study PEG-grade series in native lignocellulose, E2 = 8 PEG-containing native-lignocellulose studies without a verified grade series, E3 = 17 PEG model/process-property studies, and E4 = 14 non-PEG mechanistic analogues. This section discusses E4 only as secondary context. E4 articles are not pooled with E1 when describing PEG-grade effects and do not contribute evidence for the direction or magnitude of a PEG molecular-weight response. The M1–M4 framework can be transferred beyond PEG only when the level of inference is explicit: a phenomenon may be transferable when both systems show the same measured intermediate property, but the direction and magnitude of a molecular-weight effect are not transferable across polymer chemistries without a controlled target-system grade series.

8.1. E4 Transferable Evidence from Eutectic Systems Containing Neutral Polymers

The retained corpus outside PEG is dominated by PVA-containing eutectogels rather than pretreatment liquids. A cellulose/HEC/PVA eutectogel retained low-temperature conductivity and non-flammability within a hydrogen-bonded polymer matrix [48]. Molecular-dynamics analysis of a lignin-infused PVA eutectogel quantified hydrogen bonding, radial distribution, and lithium-ion diffusivity as functions of network composition [49]. These observations support the M1 proposition that a neutral polymer can reorganize a DES interaction network and the M2 proposition that network composition can alter transport. They do not show that PVA molecular weight changes biomass wetting, lignin diffusion, delignification, or carbohydrate retention. Ion motion in an equilibrated gel is also not equivalent to macromolecular transport through a reacting plant-cell-wall matrix.

Other PVA studies establish similarly limited forms of transfer. Coordination and hydrogen bonding influenced the properties of metal-salt and PVA/CMC deep-eutectic gel electrolytes [50, 51]. DES/water-induced microphase separation was accompanied by PVA-rich structure formation and lignin nanoparticle assembly in a double-network material [52]. A related system linked biphasic separation to formation of demethylated-lignin micro- and nanoparticles [53]. These results make M3 experimentally plausible in polymer-containing media, but they concern material fabrication after components have been combined under conditions selected to form a gel. They cannot establish that a second phase forms during homogeneous DES pretreatment or that increasing polymer grade will improve lignin recovery.

Process timing creates another boundary. Solvent exchange with a DES induced crystallization and reprogrammed the shape of a printed PVA ionogel [54]. That observation is relevant to polymer-chain reorganization, yet it occurs after a preformed object is exposed to a new solvent. In biomass fractionation, the relevant sequence is solvent formation, biomass contact, bond cleavage or solubilization, phase evolution, and product recovery. Evidence generated at the last stage cannot be assigned automatically to the reaction stage. Across the retained literature, no controlled molecular-weight series for PVA, PVP, PPG, poloxamers, HEC, or dendritic polyols directly measured lignocellulose fractionation outcomes under otherwise identical conditions. This absence defines an evidence gap; it does not imply that these polymers lack molecular-weight effects.

Polymer-containing eutectogels provide additional, but deliberately indirect, evidence that polymer chemistry and architecture can reshape network organization and transport. Lignin-containing eutectogels have been developed for ion-conductive supercapacitor electrodes and dynamic-network strain sensors [55, 56]. Cellulose-based systems have likewise been evaluated as wearable strain sensors, self-healing multisensing materials, and self-calibrating human–machine interfaces [57–60]. Other studies report cellulose-enhanced eutectic hydrogels and supramolecular cellulose-based bioplastics with ionic conductivity, mechanical robustness, and recyclability [61, 62]. These endpoints show that polymer–eutectic interactions can influence network strength and ion transport. However, they arise in formed gels or solids and therefore support only mechanistic plausibility, not nominal-grade causality in liquid-phase biomass fractionation.

8.2. Polymer Chemistry and Architecture beyond Nominal Molar Mass

PEG is a flexible, linear polyether with two terminal hydroxyl groups. At equal PEG mass, a higher nominal grade reduces the number of chains and terminal hydroxyl groups while increasing average contour length. The same interpretation does not apply to PVA, whose hydroxyl groups occur along a carbon-carbon backbone and whose hydrolysis level and crystallization behavior introduce additional variables. HEC has a substituted polysaccharide backbone; the degree and pattern of substitution influence its interaction-site density. PVP

presents pendant lactam groups, whereas PPG contains methyl-substituted oxypropylene units. Poloxamers combine poly(ethylene oxide) and poly(propylene oxide) blocks, and dendritic polyols concentrate many terminal groups within a branched architecture. These structures may engage M1–M4, but nominal molar mass does not place them on a common physicochemical scale.

A cross-polymer comparison must therefore separate at least three variable classes. The first is chemistry: donor and acceptor site identity, functional-group density, hydrophobicity, and possible reactivity. The second is architecture: linear, branched, or block structure; terminal-group number; and the potential for crystallization, association, or micellization. The third is molar-mass distribution, which requires measured number-average and weight-average molar masses and dispersity rather than a single commercial grade label [21]. Evidence that PEG-based DESs exhibit multiple relaxation times and viscosity-dependent dynamics illustrates why transport descriptors must be measured directly [44]. A controlled PEG series in cellulose dissolution further shows that dissolution and carbohydrate preservation can favor different grades [33]. Neither result supplies the direction of a PVA, PVP, or poloxamer grade effect.

The normalization problem also becomes more severe across chemistries. Equal polymer mass does not equalize chain number, repeat-unit concentration, terminal-group concentration, hydrodynamic volume, or occupied volume. Equal chain concentration may require very different polymer masses, whereas equal hydroxyl concentration is not meaningful for a polymer whose dominant interaction site is a lactam group. General comparisons of PEG with alternative hydrophilic polymers are useful for identifying candidate chemistries, but their behavior in another application cannot substitute for DES-specific measurements [28]. A defensible study should report both the formulation basis and the chemical-equivalent basis used for comparison.

8.3. Rules for Transfer and Direct Validation

Three rules define a defensible transfer. First, a mechanistic pathway should be transferred only when the proposed intermediate property is observed directly in both contexts. For example, phase separation and lignin-particle formation in PVA-containing eutectogels can motivate measurements of cloud points and polymer-rich phases in biomass-processing solvents, but these observations cannot predict which PVA grade will maximize lignin recovery [52, 53]. Second, a descriptor should be transferred only after its definition, composition, temperature, and physical state have been matched. Viscosity or transport behavior measured in a room-temperature gel cannot represent automatically the rheology of a reacting DES at the processing temperature because relaxation and viscosity-dependent dynamics vary with temperature and solvent composition [44]. Third, neither the direction of a molecular-weight response nor an optimum grade should be transferred without a controlled grade series in the target system. The controlled PEG series reported for cellulose dissolution demonstrates that dissolution performance and carbohydrate protection may favor different grades [33]. These rules distinguish mechanistic analogy from grade-specific evidence.

Accordingly, we propose that direct validation should begin within one polymer family. At least four well-characterized grades and a polymer-free control should be compared within one DES chemistry while maintaining identical water content, solvent-to-solid ratio, temperature–time history, and product-recovery procedure. An equal-mass series should be paired with a second normalization basis selected for the polymer, such as equal chain concentration or equal accessible functional-group concentration. Each polymer should be characterized using number-average and weight-average molar masses, dispersity, architecture, end-group chemistry or substitution level, and purity because a commercial grade represents a molecular-weight distribution rather than a single molecular species [21]. Measurements should connect solvent state to process response through spectroscopy, water activity, rheology at the processing temperature, diffusion or penetration proxies, phase diagrams, and polymer partitioning. Fractionation data should include lignin removal and recovery, carbohydrate retention, soluble degradation products, and the structural quality of the recovered fractions.

Cross-polymer comparisons should be conducted only after within-family effects have been resolved. PEG and a candidate alternative should be evaluated using more than one normalization basis, followed by testing whether the same intermediate descriptor predicts the response in both polymer systems. A shared relationship would support transfer of the proposed pathway, whereas different relationships would indicate that polymer chemistry or architecture changes the causal sequence. Current PVA- and HEC-containing eutectic materials support selected interaction, transport, and phase-behavior concepts [48, 49]. However, they do not establish molecular-weight-dependent fractionation behavior. PEG should therefore remain the principal evidence base for molecular-weight engineering in DES

biorefining, while PVA, PVP, PPG, poloxamers, HEC, and dendritic polyols should be treated as prospective test families. The available literature does not support a universal molecular-weight rule across neutral polymers.

9. Process, Sustainability, and Scale-up Implications

Assessment of scale-up must distinguish measured process behavior from consequences inferred from polymer physics. The retained literature includes single-grade recycle studies and supporting studies that relate formulation to viscosity or lignin solubility. It does not include a controlled PEG-grade series that reports pumping power, heat duty, solvent loss, toxicity, cost, or life-cycle indicators under matched conditions. Section 9 therefore uses published measurements to define the variables and system boundaries required for process assessment. It does not rank nominal PEG grades for industrial suitability.

9.1. Operational Consequences of Nominal PEG Grade

A nominal grade may affect operation because changing average chain length at a fixed PEG mass also changes chain concentration and the concentration of terminal hydroxyl groups. The grade label nevertheless cannot predict viscosity by itself. At fixed PEG200 grade, increasing the amount added to a potassium-carbonate/glycerol DES reduced the reported room-temperature viscosity from 76.24 to 2.87 Pa·s, demonstrating a strong composition effect rather than a grade effect [31]. In an adjacent controlled series based on isolated lignin, viscosity decreased as the nominal grade of PEG or PEG diacrylate increased, while lignin-solubility responses depended on lignin type and co-solvent [32]. These findings rule out a general higher-grade-higher-viscosity assumption.

Temperature and physical state further limit extrapolation. A PEG-based nonionic DES showed several dielectric and fluorescence relaxation timescales and a temperature-dependent relation between molecular relaxation and viscosity [44]. A viscosity value measured at room temperature, or in a gel, therefore cannot be inserted directly into a design calculation for a reacting biomass slurry. Pumpability, mixing, biomass wetting, and heat and mass transfer should instead be evaluated using flow curves at the treatment temperature and relevant solid loading. Density, heat capacity, thermal conductivity, yield stress where present, mixing power, heat-up time, temperature uniformity, and residence-time distribution should be measured for each formulation. Microwave processes additionally require grade-resolved dielectric properties and absorbed-power measurements because the present biomass studies do not isolate a PEG-grade effect on field coupling.

Operational comparison also requires a common process basis. Equal PEG mass, equal chain concentration, and equal terminal-hydroxyl concentration create different solvent compositions as grade changes. Water content, acid or salt concentration, solvent-to-solid ratio, mixing speed, reactor geometry, and temperature-time history must remain fixed or be included explicitly in the experimental design. The practical endpoint is not the lowest neat-solvent viscosity. It is stable handling of the reacting slurry at the target biomass loading without compromising fractionation or product quality. A grade should therefore be considered operationally favorable only when its rheology, energy use, wetting or penetration response, and material balances are measured in the same experiment as lignin removal, carbohydrate retention, and product-quality indicators.

9.2. Solvent Recovery and Recycle Stability

The strongest recycle evidence is formulation-specific. A bamboo study used a PEG400-containing ethylamine hydrochloride/malic acid solvent that maintained 79.34% lignin removal and an 85.29% glucose yield after the seventh pretreatment cycle without fresh DES addition [19]. A choline chloride/glycerol/PEG400 solvent recovered more than 98% of its mass and retained high lignin-solubilization performance through three cycles in an isolated-lignin system [40]. These results show that two PEG400-containing formulations can be recovered under their reported procedures. They do not establish that PEG400 is easier to recycle than PEG200, PEG600, PEG800, or a higher grade, and they should not be presented as evidence of grade-independent recovery.

Recovered solvent mass is an incomplete measure of recycle stability. Water, antisolvent, dissolved carbohydrates, organic acids, salts, lignin fragments, and the polymer may be retained or lost at different rates. The recovered mixture can consequently differ from the fresh formulation even when its total mass appears stable. In the bamboo study, the authors associated sustained performance partly with accumulation of formic acid generated from carbohydrate degradation [19]. That observation illustrates why repeated performance can result from composition drift rather than exact solvent restoration. Claims of stable recycling should therefore pair a closed component-specific mass balance with solvent-property measurements and product outcomes for every cycle.

A minimum grade-resolved recycle protocol should quantify PEG, hydrogen-bond acceptor, hydrogen-bond donor, water, degradation products, and dissolved biomass components in the recovered solvent, product fractions, wash streams, and waste. PEG concentration

and molar-mass distribution should be measured before use and after recovery to detect selective loss or chain degradation. Water and antisolvent makeup, evaporation duty, wash volume, recovery yield, and composition-adjustment steps should be reported per unit of dry biomass. The recycled formulation should then be compared with a freshly prepared control using rheology, acidity or basicity, water activity, spectroscopy, phase behavior, fractionation performance, and product-quality measures. Until this protocol is applied to matched grades, the literature cannot identify a grade with superior retention or functional recycle life.

9.3. Sustainability and Scale-up Assessment

The term green should not be assigned to a DES solely from low volatility or the reputation of its components. Experimental studies have shown that the toxicity and biodegradability of choline-chloride-based DESs depend on the complete formulation, concentration, pH, and biological endpoint [63, 64]. Proposed testing guidance likewise emphasizes that solvents must be evaluated across relevant organisms, exposure concentrations, and environmental compartments [65]. A PEG-containing DES used for biomass processing therefore requires formulation-specific safety and fate data. A benign result for one binary DES cannot be transferred to a ternary acidic or alkaline formulation, and toxicity data do not establish low life-cycle impact.

Life-cycle assessment should include polymer production, manufacture of the hydrogen-bond acceptor and donor, biomass preparation, solvent preparation, heating or microwave electricity, mixing, fractionation, solid-liquid separation, water and antisolvent use, product washing and drying, solvent recovery, wastewater treatment, and management of unrecovered material. Reviews of DES-based lignocellulose processing identify solvent recovery, water demand, energy input, and scale-up as system-level constraints [8, 9]. A recent process review similarly treats recyclability and techno-economic viability as requirements for industrial application [11]. These sources define assessment priorities; they do not provide grade-resolved inventory data. Results should be reported per unit of dry biomass processed and, where product quality is specified, per unit of recovered lignin or carbohydrate fraction meeting that specification.

Techno-economic analysis should use measured rather than assumed grade effects. Relevant inputs include the purchase price and purity of each polymer grade, solvent preparation losses, energy for heating and agitation, equipment capacity constrained by slurry rheology, cycle time, water and antisolvent demand, evaporation and drying loads, component-specific recovery, solvent makeup, wastewater treatment, and product yields. Revenue assumptions should reflect lignin and carbohydrate quality instead of treating all recovered mass as equivalent. Polymer grade, recovery efficiency, effective solvent lifetime, solvent-to-solid ratio, and biomass throughput should be tested as interacting sensitivity variables. This structure can reveal whether a more expensive or more viscous formulation is offset by improved recovery or product value, but such a result must be calculated from grade-resolved data.

Scale-up decisions should therefore pass four evidence checks. The formulation must remain pumpable and adequately mixed at the intended solid loading and treatment temperature. Heat and mass transfer must remain sufficiently uniform to reproduce the laboratory severity profile. Recovery operations must close component balances and prevent unacceptable accumulation of impurities. Recovered cellulose, lignin, and liquid products must meet residue and quality specifications after repeated cycles. Corrosion and material compatibility should be tested for the complete solvent at operating temperature rather than inferred from individual ingredients. The current literature does not show that any nominal PEG grade meets these requirements more consistently than another. The defensible conclusion is that grade should be treated as an explicit process-design and sensitivity variable until matched operational, recycle, safety, economic, and life-cycle measurements are available.

10. Research Gaps and MW-REPORT Priorities

The remaining evidence gaps are linked rather than independent. An undefined commercial grade prevents chemical-equivalent normalization; incomplete water and rheology data prevent transport comparisons; and missing phase, product-quality, and polymer-recovery measurements prevent a causal or process-level interpretation. Table 4 consolidates these dependencies into ten gap-to-action pairs. Its first four rows define the polymer and formulation that must be compared, the next two define the solvent state under process conditions, and the final four connect fractionation performance to material balance, data quality, recovery, and mechanism testing. The proposed MW-REPORT items are therefore a polymer-grade-specific extension of established DES reporting practice. They are not presented as the first universal DES checklist, and completion of the checklist would improve comparability rather than prove that a particular nominal grade is

Table 4. Research gaps and minimum MW-REPORT actions.

Gap	Why It Prevents Comparison	Minimum Reporting or Experiment
PEG identity is reported only as a commercial label	Nominal grade does not define Mn, Mw, dispersity, water, or end-group chemistry.	Report supplier, product code, nominal grade, measured/certificate Mn and Mw if available, dispersity, water content, and end groups.
Formulation basis is ambiguous	Fixed mass, fixed PEG moles, fixed repeat units, and fixed terminal-OH equivalents test different hypotheses.	Report all component masses and moles; calculate chain, repeat-unit, and terminal-OH equivalents.
Water is incompletely defined	Water strongly changes hydrogen bonding, acidity, viscosity, and phase behavior.	Report initial component water, added water, water after equilibration, and analytical method.
Only one PEG grade is used	A loading effect cannot be interpreted as a grade effect.	Use at least four grades spanning oligomeric and, where processable, longer-chain PEG; include an additive-free control.
Rheology is reported at one temperature	Pretreatment occurs under different viscosity and mixing conditions.	Report flow curves and temperature-dependent viscosity at the actual composition; add density and diffusion/conductivity indicators.
Phase state is assumed	Crowding or depletion claims require evidence of overlap, demixing, or interfaces.	Measure phase diagrams/cloud points, c/c*, interfacial composition, and polymer distribution between phases.
Fractionation and product quality are separated	High removal may coincide with cellulose loss or lignin condensation.	Report full carbon/mass balance, lignin recovery and structure, cellulose retention/DP/digestibility, hemicellulose fate, and degradation products.
Recovery is reported without polymer balance	Selective PEG loss changes the solvent in later cycles.	Quantify PEG recovery, degradation, residual PEG in products, composition after every cycle, and makeup demand.
Grade-response values appear only in figures	Exact effect sizes and uncertainty cannot be audited or pooled.	Provide machine-readable tables with replicates, uncertainty, statistical model, and raw-condition identifiers.
Mechanism is inferred from performance	Several pathways can yield the same fractionation trend.	Pair performance with spectroscopy, solvatochromism, rheology, phase analysis, and product-structure measurements for every grade.

optimal. The priorities below explain how the actions in Table 4 can be implemented in a staged experimental programme.

10.1. Reporting Priorities for Comparable Grade Studies

A commercial PEG grade represents a molar-mass distribution, so the nominal label should not substitute for number-average molar mass, weight-average molar mass, or dispersity [21]. Supplier, product code, lot or certificate information, water content, architecture, and end-group chemistry should accompany the nominal grade. The formulation basis must then identify the scientific contrast. The two eucalyptus E1 studies used a fixed PEG mass or mass fraction, which altered chain concentration and terminal-hydroxyl equivalents across grades [14, 16]. The sugarcane-bagasse E1 study used a fixed choline-chloride-to-PEG molar ratio, which altered PEG mass and repeat-unit content [18]. These designs answer different questions. Table 4 therefore requires reporting of component masses and moles together with calculated chain, repeat-unit, and terminal-hydroxyl equivalents so that readers can identify the quantity held constant and the quantities allowed to vary.

Water content, temperature, polymer loading, and solid loading should be treated as state variables rather than secondary details. At fixed PEG200 grade, changing PEG loading and formulation produced a large change in measured viscosity and fractionation performance, demonstrating that composition can dominate the response attributed informally to grade [31]. Independent measurements in a PEG-based nonionic DES also show that relaxation and viscosity-related dynamics vary with temperature [44]. A single room-temperature viscosity value cannot therefore represent the rheology of a reacting biomass slurry. Each grade series should report water before and after equilibration, flow curves at the processing temperature, density, and a transport proxy such as diffusion, conductivity, or validated penetration measurements. Phase state, cloud point, and polymer distribution should be recorded at the same composition and temperature used for fractionation.

The performance endpoint should close the material balance and preserve product identity. Lignin removal alone can conceal lignin loss, carbohydrate degradation, polymer carryover, or structural damage. The minimum dataset in Table 4 therefore links delignification to recovered-lignin yield and structure, cellulose retention and degree of polymerization, enzymatic digestibility, hemicellulose fate, soluble degradation products, and carbon or mass closure. Recovery claims require the same discipline. A PEG400-containing bamboo solvent retained substantial performance through seven cycles, while a different PEG400 formulation gave high solvent-

mass recovery in an isolated-lignin system [19, 40]. Neither study compares grades. Future recycle experiments should quantify PEG and every solvent component in the regenerated solvent, product fractions, washes, and waste, and should measure whether the PEG molar-mass distribution changes during use.

10.2. Priority Experiments for Causal Validation

The first priority is a controlled grade screen within one DES chemistry. At least four well-characterized grades and a polymer-free control should be processed at identical water content, solvent-to-solid ratio, biomass particle-size distribution, mixing history, and temperature-time severity. Where longer-chain PEG remains physically processable, a series such as PEG200, PEG400, PEG600, PEG800, and PEG4000 would connect the ranges used in the two eucalyptus E1 series [14, 16]. The experiment should not rely on one normalization basis. Parallel series based on equal PEG mass and equal chain concentration are needed to separate backbone length from the chemical equivalents that change with grade; for linear PEG with two hydroxyl ends per chain, equal terminal-hydroxyl concentration is proportional to equal chain concentration. A fixed-molar-ratio series may be added to reproduce the design used for sugarcane bagasse, but its simultaneous change in PEG mass must be analysed explicitly [18]. Primary outcomes and exclusion rules should be specified before the experiment.

The second priority is to test the proposed pathways using grade-resolved mediators. For M1, spectroscopy, solvent descriptors, water activity, and coordination measurements should determine whether grade changes the interaction network before biomass response is interpreted. Controlled work with purified cellulose supports PEG-grade-dependent coordination and carbohydrate protection, while isolated-lignin poly-DES systems show grade-dependent viscosity and solvent-property changes [32, 33]. These studies justify the measurements but do not establish a whole-biomass grade effect. For M2, process-temperature rheology should be paired with wetting, penetration, diffusion, mixing-power, and time-resolved fractionation data. Evidence for grade causality would require a reproducible grade effect on the proposed mediator and a corresponding response after formulation, water, and severity have been controlled.

The third priority is to distinguish phase-mediated partitioning from chemical stabilization. For M3, PEG concentration should be related to overlap concentration and measured phase boundaries, followed by direct quantification of PEG, lignin, water, and other solvent components in each phase. Controlled aqueous biphasic systems establish that PEG grade can alter phase formation and solute partitioning, but the transferred hypothesis must be tested with lignocellulosic substrates [22]. For M4, time-resolved lignin samples should be analysed for interunit linkages, condensation, molar-mass distribution, functional groups, and PEG incorporation. A fixed-grade multiphase biomass study supports PEG-associated lignin stabilization and a depletion interpretation, but it cannot identify a grade dependence [45]. Sampling before treatment, during solubilization, before quenching, and after precipitation would reveal whether the observed grade response arises during penetration, dissolution, intermediate stabilization, or product recovery.

10.3. Reproducibility and Decision Criteria

Grade-response data should be released as machine-readable tables rather than only as plotted values. Every condition requires a stable identifier linking formulation, polymer characterization, pretreatment, analytical method, replicate, and recovered fraction. Biological and technical replication should be distinguished, uncertainty should accompany each estimate, and the statistical model should include grade-by-process interactions when the design permits them. Non-monotonic responses should be estimated with planned contrasts or a suitable response-surface model rather than inferred from the highest observed mean. These practices address the data-access gap in Table 4 and allow later meta-analysis without digitizing figures or reconstructing undocumented conditions.

Interlaboratory replication should follow, rather than replace, within-system mechanism testing. A shared reference biomass, harmonized analytical methods, and at least one common DES formulation would establish whether a grade response survives differences in reactor geometry and laboratory practice. A second biomass with contrasting lignin and hemicellulose composition would then test transferability. Reviews of DES pretreatment identify solvent recovery, water use, energy input, and scale-up as persistent system constraints [8, 11]. Replication should therefore extend beyond fractionation yield to process-temperature rheology, energy use, component-specific recovery, solvent lifetime, and product specifications. Safety, techno-economic, and life-cycle assessment should use the measured grade-resolved inventories rather than generic assumptions for PEG-containing DESs.

The decision output should be a conditional molecular-weight window, not a universal optimum. Before analysis, the study should define acceptable thresholds for lignin

recovery and structure, carbohydrate retention or digestibility, solvent handling, polymer carryover, recovery demand, and uncertainty. A grade is preferable only within the stated biomass, DES composition, normalization basis, severity, and objective, and only if its gain in one response does not create an unacceptable loss in another. Table 4 provides the minimum information needed to audit that decision; it does not guarantee causality or industrial viability. Completion of the staged programme would allow the present M1–M4 framework to be rejected, refined, or combined into a predictive model. Until matched studies are available, nominal PEG grade should remain an explicit experimental and sensitivity variable rather than a stand-alone design rule.

11. Conclusions

The available literature supports treating nominal PEG grade as a conditional formulation variable rather than an intrinsic performance ranking. Only three of the 42 retained studies contained E1 within-study PEG-grade series in native lignocellulose. PEG400 showed modest descriptive advantages in two eucalyptus formulations. In the bagasse single-factor screen, PEG600 gave the highest lignin removal (83.23%), glucose concentration, and glucose yield, but cellulose retention fell to 73.63% versus 85.19% and 85.43% for PEG200 and PEG400; subsequent multivariable optimization selected PEG400 under different conditions. Because the comparisons used different solvent chemistries and normalization bases, chain length cannot be separated from chain population, terminal-OH concentration, polymer mass, and repeat-unit content. The present evidence therefore does not define a universal optimum.

The M1–M4 synthesis separates evidence that a process occurs from evidence that nominal grade controls it. Supplementary S4 further separates measured mediators from hypothesis-only assignments. M2 has one grade-resolved viscosity data set in the eucalyptus series [16], but a causal mediator-response relationship has not been demonstrated and M2 is not ranked above the other pathways. Interaction-network changes (M1) and lignin stabilization (M4) are supported for selected PEG-containing media without complete grade-resolved mediator series. Phase formation is grade dependent in adjacent systems, whereas crowding and depletion under homogeneous biomass-treatment conditions remain hypotheses.

Progress now depends on matched experiments rather than additional single-grade optimizations. At least four characterized grades and a polymer-free control should be compared on more than one normalization basis while water, severity, and recovery procedures are held constant. Solvent state, grade-resolved mediators, fractionation mass balance, lignin and carbohydrate structure, and PEG recovery should be measured in the same experiment. MW-REPORT provides the minimum record for determining a formulation-specific grade-response range tied to a stated biomass, formulation, process, and product objective, rather than a universal molecular-weight window.

Supplementary Materials: The evidence database used in this review is available in the supplementary material accompanying the article. Supplementary Table S1 documents the database search strategies, and Supplementary Table S3a presents the dispersity audit with source locations. Supplementary Table S4 provides the article-level evidence-class inventory and the study-by-study pathway/mediator coding matrix, including verification status and transfer boundaries. Supplementary materials can be accessed at https://heca-analitika.com/ljes/article/view/457/309.

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