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# A Lignin-First Perspective on Biomass Dissolution: Molecular Dynamics Insights into Deep Eutectic Solvents

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## INTRODUCTION & AIM

**Background (Why DESs?):** Lignocellulosic biomass deconstruction remains a key challenge in the transition toward a sustainable bioeconomy. Deep eutectic solvents (DESs) have emerged as green alternatives to conventional ionic liquids for biomass pretreatment due to their tunable hydrogen-bonding networks, low toxicity, and biodegradability.

**Research Gap (Why TEAC?)** While choline chloride (ChCl)-based DESs have been widely studied, Triethylammonium chloride (TEAC) offers a less explored yet promising hydrogen bond acceptor (HBA) framework with distinct ionic and steric characteristics.

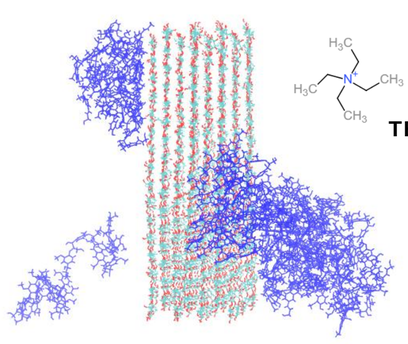
**Focus Systems** This study employs all-atom molecular dynamics (MD) simulations to elucidate the molecular mechanisms underlying lignin-cellulose disruption in two binary TEAC-based DESs:

1. **TEAC:Urea (1:2)**
2. **TEAC:Lactic acid (1:2)**

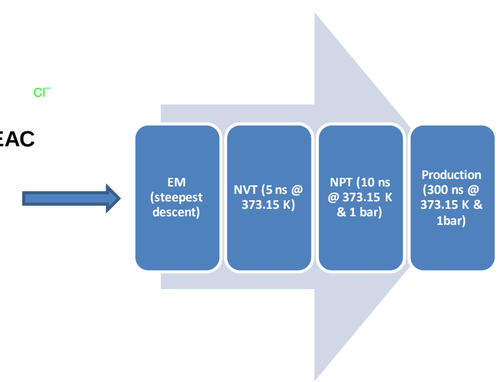
## METHOD

### Model Systems and Simulation Details

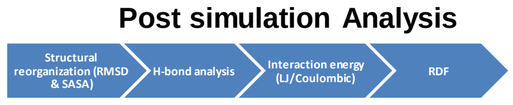
**Lignin-Cellulose-DES system**




**MD simulation details**

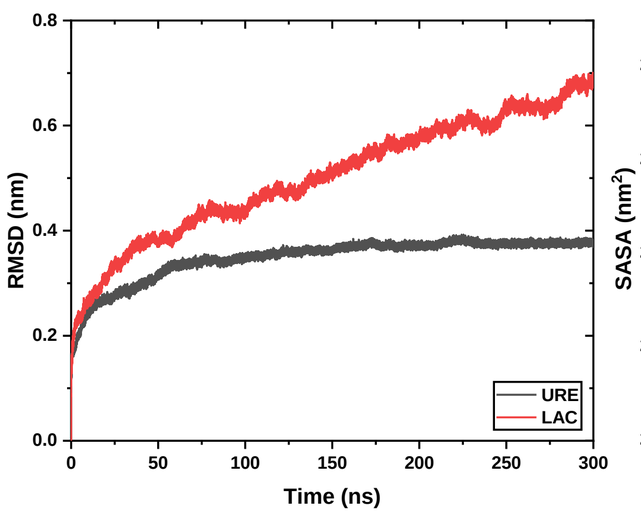


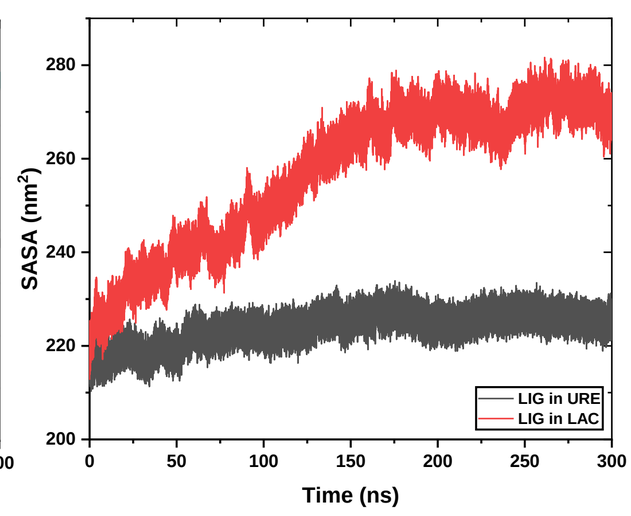

**Post simulation Analysis**




## RESULTS & DISCUSSION

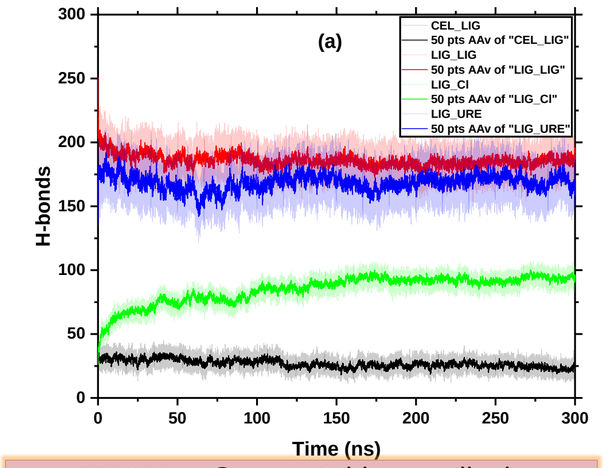
### Structural Stability & Delignification



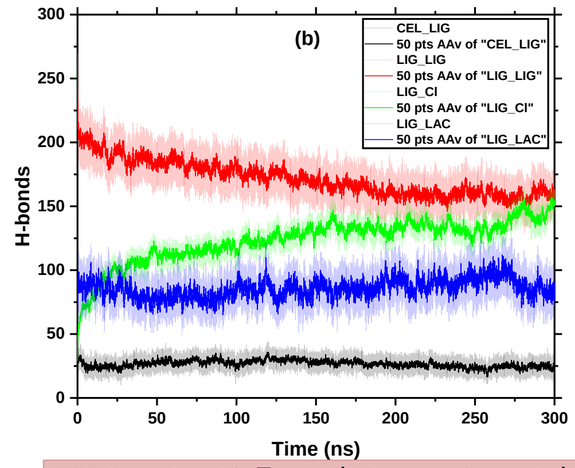




Both systems preserved cellulose crystallinity. TEAC:Lactic acid showed higher lignin RMSD and SASA values, indicating enhanced delignification.

### Hydrogen Bonding Networks




**TEAC:Urea:** Strong, stable urea–lignin interactions (150–200 H-bonds) form a **rigid solvation shell**, resulting in limited lignin disaggregation.




**TEAC:Lactic acid:** Fewer but more **dynamic** lactic acid–lignin bonds (60–120 H-bonds), continuously breaking and reforming, enable **progressive lignin release.**

Although urea-based systems exhibit higher HBD-lignin bond counts (urea: ~180) than lactic acid systems (lactic acid: 60–120), delignification efficiency follows the order:

TEAC:Urea < TEAC:Lactic acid

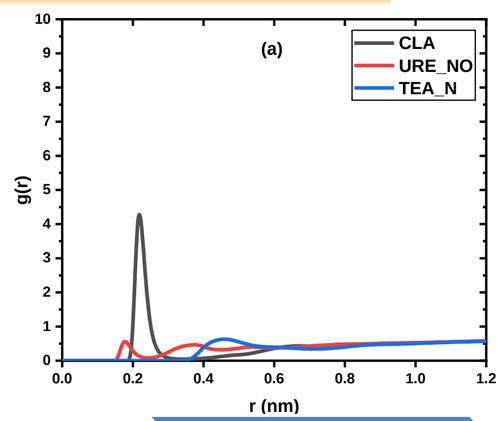
### Interaction Energies

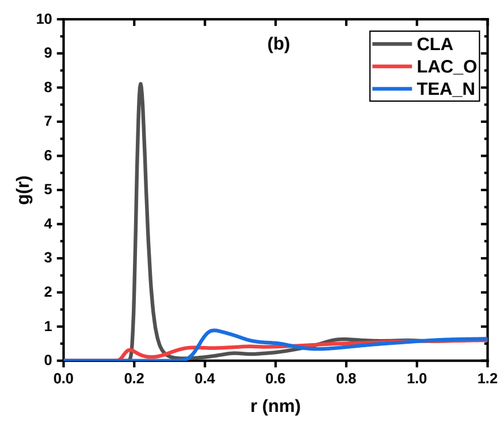
| Interaction (kJ mol⁻¹) | TEAC:Urea (1:2) | TEAC:Lactic acid (1:2) |
|---|---|---|
| CEL–LIG (LJ / Coulombic) | −1279 / −869 | −1096 / −840 |
| CEL–TEA | −3373 / −4400 | −3136 / −4998 |
| CEL–Cl⁻ | +515 / −9996 | +767 / −11,686 |
| CEL–HBD | **Urea:** −2620 / −5557 | **Lactic acid:** −2973 / −2763 |
| LIG–TEA | −3739 / −23 | −3458 / +526 |
| LIG–Cl⁻ | +303 / −9167 | +632 / −11,207 |
| LIG–HBD | **Urea:** −2790 / −3236 | **Lactic acid:** −3988 / −1891 |

**Cellulose–Lignin:** TEAC:Urea > TEAC:Lactic acid, confirming stronger residual binding in the urea system.

**Lignin–DES:** TEAC:Lactic acid exhibited **stronger Lignin–HBD and Lignin–Cl- interactions**, explaining its superior delignification performance.

### Radial Distribution Function




Overall, the RDF data highlight a hierarchy of interactions:

$Cl^- \gg$ HBD (LAC_O / URE_NO) $\gg$ TEA_N

## CONCLUSION

**TEAC:Lactic acid** definitively **outperforms TEAC:Urea** in disrupting lignin–cellulose interactions.

Chloride ions synergize with lactic acid to **penetrate and weaken** the lignin–cellulose interface.

**Impact of this study:**
Findings highlight the potential of **non-choline chloride DESs** in lignin valorization and sustainable biomass pretreatment.

## FUTURE WORK / REFERENCES

**Future work:**
Extend the MD study to ternary TEAC-based DES systems and explore the effect of temperature and water content on deconstruction efficiency.

References:

Haldar D, Purkait MK. A review on the environment-friendly emerging techniques for pretreatment of lignocellulosic biomass: Mechanistic insight and advancements. Chemosphere. 2021 Feb 1;264:128523.

Giummarella N, Pu Y, Ragauskas AJ, Lawoko M. A critical review on the analysis of lignin carbohydrate bonds. Green Chem. 2019 Apr 1;21(7):1573–95.

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