High throughput screening of ionic liquids to enhanced catalytic performance of H_2SO_4-catalyzed C4 alkylation based on multi-scale simulations.

Weizhong Zheng[1*], Zhihong Ma[1], Weizhen Sun[1], and Ling Zhao[1]

1 State Key Laboratory of Chemical Engineering, School of Chemical Engineering, East China University of Science and Technology, Shanghai 200237, China

**Corresponding author: wzzheng@ecust.edu.cn*

Highlights

- Interfacial properties of alkylation with 11000 ILs as additives were predicted and screened
- Structure-activity relationship between ILs and interfacial properties was established.
- The targeted ILs were prepared and assessed based on complex kinetics model.
- The production capacity can be increased by about 30% with trace additives

1. Introduction

The alkylation between isobutane and C3~C5 olefins (C4 alkylation) under strong acidic condition is a very important industrial process to produce the alkylate. However, the H_2SO_4 catalyst has several fatal drawbacks, including serious equipment corrosion, huge spent acid and secondary pollution caused by disposal of spent acid. The introduction of additives as co-catalyst is a good way to enhance current H_2SO_4 alkylation process. Recently, ILs have attracted much attention as the promising additives for H_2SO_4 alkylation[1]. Given the numerous feasible cation-anion combinations of ILs (about 10^{14}), however, the large-scale screening and rational design of novel ILs using experimental methods is quite time-consuming and resource-intensive. It is extremely desirable to develop robust computational models that can establish mathematical relationships between structure of ILs additives and interfacial properties of H_2SO_4 alkylation for the large-scale screening and rational design of the efficient IL additives. Machine learning (ML) is a powerful approach for building quantitative structure-activity relationship (QSAR) models. Actually, ML has presented a distinct advantage to develop the QSAR models regarding various properties of ILs or gas solubility in ILs[2]. Therefore, in this work, the intensified interfacial properties of H_2SO_4 alkylation with 11000 ILs as additives were predicted, screened and assessed using multi-scale simulations inclduing MD simulations, semi-empirical DFT, machine learning and process simulation.

2. Methods

The interfacial properties of alkylation system were calculated using MD simulations and OPLS-AA force field was applied to treat the interaction between concentrated H_2SO_4, C4 hydrocarbons, and ILs. As for a typical MD simulation procedure, the simulated box was simulated for 8 ns under canonical (NVT) ensemble at 298.2 K with nose-hoover thermostat. Afterwards, the isothermal-isobaric (NPT) ensemble was conducted for 30 ns at 1 bar. The 3D structures individual cations and anions of ILs were were subjected to geometry optimization and force calculations based on semi-empirical PM6 Hamiltonian using MOPAC. The KRAKENX software to abstract various quantum chemical, charge partial surface area, density distribution-based eigenvalue, shape and geometry, and topographical molecular descriptors of the cations and anions. These ML models were established on the basis of molecular descriptors and interfacial properties of 1496 ILs, consisting of 44 cations and 34 anions, among which 25% of data were randomly selected from dataset as testing data, and the rest were used as the training set. $[N_{1,1,1,m}][C_nSO_4]$ (m=4, 8, 14; n=1,10,14) were prepared based two-step method, and the alkylation reaction were conducted in a 1 L batch reactor with strong stirring of 3000 rmp. The final alkylate products were analyzed using gas chromatography with Agilent GC7890A. Thus, the targeted ILs were screened, prepared and assessed for the enhancement of the quality of the alkylate. Finally, to further investigate the effect of the novel formyl functional $[N_{1,1,1.1}][C_{10}SO_4]$ additive, the process simulation of the C4 alkylation process was studied in detail with the embedded custom user model based on the complex kinetics using the Aspen plus simulation platform.

3. Results and discussion

For the interfacial properties, the extension in the alkyl chain length of either cations or anions contributes to the increasing σ_w and the reducing γ to a great extent. The structure features of ILs and interfacial thickness and tension can be well correlated by GMB and RF models. The built ML model can well predict for the interfacial thickness and tension of the 11000 ILs additive systems to a great extent, and there is a synergistic effect of both the cations and anions with longer alkyl chains on the interfacial thickness and tension. The novel N-trimethyl-N-alkylammonium alkylsulfate ILs with varying alkyl chain length ($[N_{111m}][C_nSO_4]$, m=4,8,14, and n=1,10,14) were developed as the additives for H_2SO_4 alkylation. The increase in the alkyl chain length of either cations or anions can contribute to the higher RON of the alkylate, which is ascribed to the much stronger intensification of the acid/hydrocarbons interfacial properties by the longer-alkyl-chain cations or anions. In addition, the process simulation can accurately predict the industrial alkylate composition. The introduction of $[N_{1,1,1,1}][C_{10}SO_4]$ additive (0.3 wt%) can remarkably improve the selectivity of targeted TMPs and the yield of alkylate with shorter space time and lower isoparaffin/olefin (I/O). At optimized conditions, the production capacity can be increased by about 30% with additives.

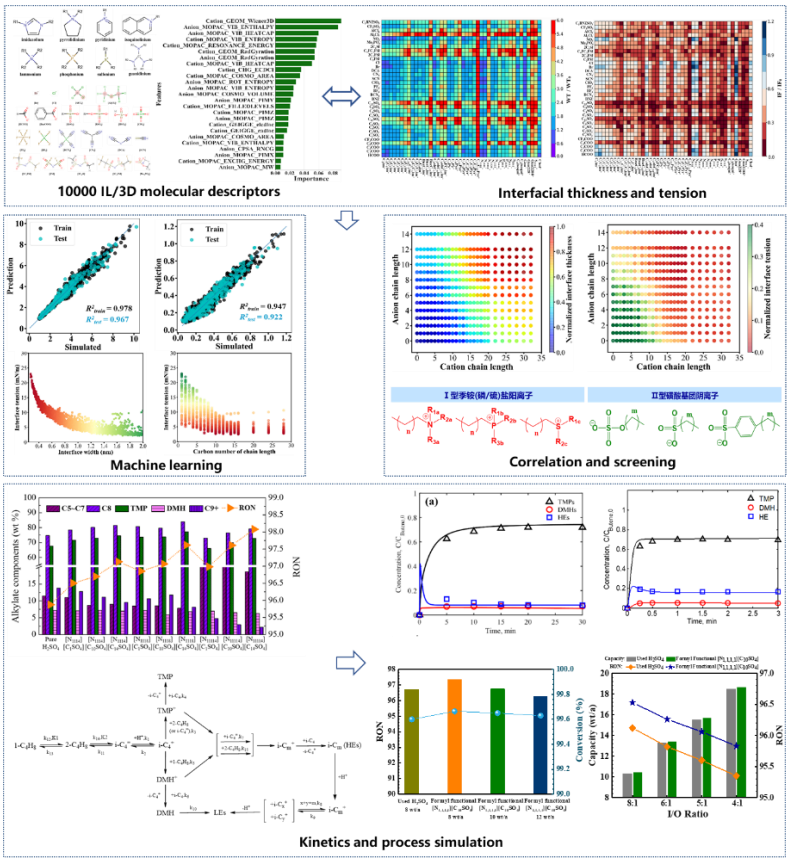

Figure 1. Correlation, screen, preparation and assessment of novel ILs to promote H_2SO_4 alkylation.

4. Conclusions

ILs additives with longer alkyl chain can significantly broaden interfacial thickness and decrease interfacial tension, and the cation- and anion-based descriptors play a synergistic prominent role, which present the ability to efficiently promote catalytic performance of H_2SO_4 at trace addition amount.

References

[1] Kore R, Scurto AM, Shiflett MB. Ind. Eng. Chem. Res.;59(2020):15811-15838.
[2] Beker W, Gajewska EP, Badowski T, Grzybowski BA. Angew. Chem. Int. Ed.;58(2019):4515-4519.

Keywords
H_2SO_4 alkylation; Ionic liquids; Interfacial properties; Multi-scale simulation.