

Assessing industrial-scale H₂SO₄-catalyzed C₄ Alkylation enhanced by novel [N_{1,1,1,1}][C₁₀SO₄] additives based on a complex kinetic model

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Highlights

- The catalytic performance and reaction kinetics of C₄ alkylation catalyzed by used H₂SO₄ without and with novel additive was investigated.
- Custom user model with embedded complex kinetics was integrated with Aspen Plus.
- The production capacity of alkylate with [N_{1,1,1,1}][C₁₀SO₄] additives can be increased by about 30%.

1. Introduction

The alkylation of isobutane with butenes (C₄ alkylation) is a significant industrial process to produce environmental-friendly gasoline. The concentrated H₂SO₄ has been widely used as the preferred commercial alkylation catalyst due to its high stability and excellent catalytic performance. To further enhance the quality of alkylate and reduce acid consumption in C₄ alkylation catalyzed by H₂SO₄ on the industrial scale, various strategies have been investigated, including reactor redesign, feed-stream purification, optimization of operating conditions tailored to different olefins, regulation of the iso-paraffin/olefin (I/O) ratio, and reduction of reaction temperature¹. These strategies aim to enhance liquid-liquid dispersion and reduce the reaction temperature, thereby obtaining a better quality of alkylate. However, the redesign of the alkylation reactor requires high costs and cannot be directly implemented in an existing operational process. An alternative approach is the introduction of additives, which plays an important role in enhancing interfacial mass transfer on C₄ alkylation with several advantages, such as low additive dosage, reduced formation of byproducts, and the feasibility of direct cofeeding with H₂SO₄². However, there are still no efficient and cheap additives that can meet the requirements for industrial applications for H₂SO₄-catalyzed C₄ alkylation. Moreover, the industrial application of novel additives remains challenging because it is difficult to predict their promoting effect on the large-scale alkylation process. To address these challenges, the novel formyl functional [N_{1,1,1,1}][C₁₀SO₄] additive were prepared and the catalytic performance were systematically investigated through experimental and multi-scale simulation methods including batch and continuous experimental process, kinetic modeling, and process simulation.

2. Methods

The novel formyl functional [N_{1,1,1,1}][C₁₀SO₄] additive was synthesized using one-step method, and a continuous experimental process was established in a 1 L batch reactor with strong stirring of 3000 rpm. The final alkylate products were analyzed using gas chromatography with Agilent GC7890A. To further investigate the effect of the novel formyl functional [N_{1,1,1,1}][C₁₀SO₄] additive on the industrial scale, the whole process simulation of C₄ alkylation 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

In this work, the optimal mass ratio for formyl functional [N_{1,1,1,1}][C₁₀SO₄] additive to the used H₂SO₄ is about 0.3 wt%. The [N_{1,1,1,1}][C₁₀SO₄] additive with addition of 0.3 wt% exhibits an outstanding ability to improve the RON of the alkylate with shorter reaction time and relatively high reaction temperature. The concentration changes about trimethylpentanes (TMPs), dimethylhexanes (DMHs), and heavy ends (HEs) of C₄ alkylation catalyzed by the used H₂SO₄ with and without formyl functional [N_{1,1,1,1}][C₁₀SO₄] additive along time at the temperature range of 277.15 to 289.15 K were well

predicated based on the batch experiments. Compared with the used H_2SO_4 -catalyzed alkylation, the reducing activation energies reveal that the $[\text{N}_{1,1,1,1}][\text{C}_{10}\text{SO}_4]$ additive plays a major role in the increase of reaction rate and the reduction of reaction time. And the prediction of the complex kinetic model can agree well with the continuous experimental alkylate distribution, including TMPs, DMHs, LEs, and HEs. For the process simulation, the introduction of 0.3 wt % $[\text{N}_{1,1,1,1}][\text{C}_{10}\text{SO}_4]$ additive can remarkably improve the selectivity of targeted TMPs and the yield of alkylate, even at the space time down to 20 min from typical 30 min in the pure used H_2SO_4 system and at lower I/O ratio from 8:1 to 6:1. Specifically, the RON of alkylate can be maintained above 96.00, even with 40.72% decrease in space time as well as 33.3% decrease in the I/O ratio. Under optimized conditions, the production capacity of alkylate with $[\text{N}_{1,1,1,1}][\text{C}_{10}\text{SO}_4]$ additives can be increased by about 30% up to 134.01 kt/a from typical 103.13 kt/a in the pure used H_2SO_4 system.

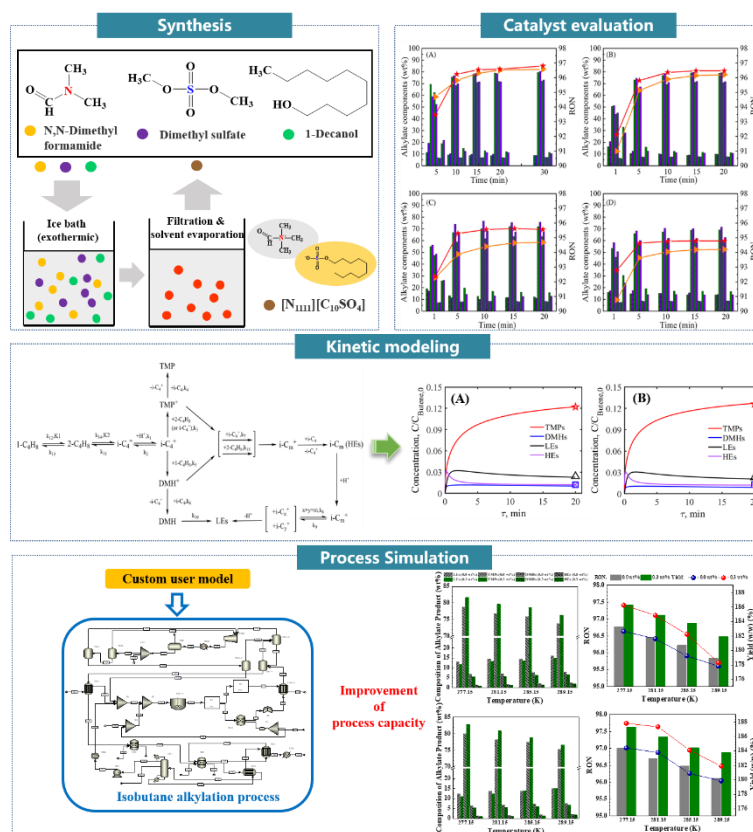


Figure 1. Synthesis, evaluation, kinetics and process simulation of novel $[\text{N}_{1,1,1,1}][\text{C}_{10}\text{SO}_4]$ additives to enhance H_2SO_4 alkylation.

4. Conclusions

The formyl functional $[\text{N}_{1,1,1,1}][\text{C}_{10}\text{SO}_4]$ has a better effect on the conversion of C_8 components and improves the RON compared with the used H_2SO_4 -catalyzed alkylation. To increase the process capacity while maintaining the quality of alkylate above 96.00, two approaches can be taken. The first approach is to keep the molar ratio of I/O unchanged at 10:1, while increasing the mass flow of feedstock. The second approach is to keep the feedstock quantity unchanged while decreasing the molar ratio of I/O.

References

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Keywords

H_2SO_4 alkylation; Additives; Kinetics; Process simulation.