Production Process for Diesel Fuel Components Polyoxymethylene Dimethyl Ethers from Methanol and Formaldehyde Solution

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Abstract: Polyoxymethylene dimethyl ethers (PODE_n) as clean diesel additive can improve the combustion efficiency and quality of diesel fuel and alleviate the problem of atmospheric pollution. Considering synthetic routes, PODE production from methanol and formaldehyde is regarded as the most economical and promising synthetic route. However, methanol used for synthesizing PODE can produce water, which causes the loss of active center of catalyst and hydrolysis of PODE_n in the production process. Macroporous strong acidic cation exchange resin catalyst was prepared, which has comparative advantages over other common solid acid catalysts in terms of stability and catalytic efficiency for synthesizing PODE. Catalytic reactions were carried out under 353 K, 1 MPa and 3mL·g_{cat}⁻¹·h⁻¹ in a fixed bed reactor. Methanol conversion and PODE₃₋₆ selectivity reached 49.91% and 23.43%, respectively. Catalyst lifetime evaluation showed that resin catalyst retained its catalytic activity for 20 days without significant changes and catalytic activity of completely deactivated resin catalyst can basically return to previous level by simple acid regeneration. The acid exchange capacities of original and deactivated catalyst were 2.5191 and 0.0979 mmol·g⁻¹, respectively, while regenerated catalyst reached 2.0430 mmol·g⁻¹, indicating that the main reason for resin catalyst deactivation is that Brønsted acid sites of original resin catalyst were temporarily replaced by non-hydrogen ion cations. A separation process consisting of extraction and distillation for PODE₃₋₆ product was designed for separation of water and unreacted formaldehyde from reactive mixture and purification of PODE₃₋₆, respectively. The concentration of PODE₃₋₆ in final product can reach up to 97%. These results indicate that the scale-up production of PODE₃₋₆ from methanol and formaldehyde solution is feasible.

Keywords: inactivation, polyoxymethylene dimethyl ethers, separation process, sulfonic cation exchange resin

Conference Title: ICCET 2018: International Conference on Chemical Engineering and Technology

Conference Location : New York, United States

Conference Dates: October 08-09, 2018