

Application of catalytic distillation in a novel process concept for the production of cyclohexanol

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Cyclohexanol is a bulk chemical that is primarily used as intermediate in the production of nylon. In industrial practice, the most important synthesis route to cyclohexanol is currently the oxidation of cyclohexane. Several drawbacks of the oxidation process, such as rather limited selectivities even at low conversions and large external recycle streams, have motivated academic and industrial research activities in identifying a new process.

A promising alternative route is the liquid-phase synthesis of cyclohexanol by hydration of cyclohexene using acidic catalysts. Due to the strongly limited mutual solubility of the reactants, two liquid phases occur, leading to a kinetic limitation of the reaction. Thus, high reaction rates can only be obtained when the mutual solubility of the reactants is improved and/or the wettability of the heterogeneous catalyst with both the organic and the aqueous phase can be adjusted individually. The process of Asahi Chemical Co. [1], using a zeolite catalyst of the HZSM5-type, is a step in this direction. However, since the reaction rates of the direct hydration of cyclohexene to cyclohexanol are fairly low, a large amount of catalyst is required in the slurry reactor. In addition, the above-mentioned drawback of large external recycle streams is still not eliminated in this alternative process.

In our work, we therefore suggest a catalytic distillation process that offers a couple of potential advantages. Here the recycle streams are internalized, slurry handling is avoided and the chemical equilibrium limitation can be overcome, theoretically allowing for complete conversion of cyclohexene. On the other hand, for fluid dynamical reasons the catalyst loading of the column is limited and an appropriate fixing of the catalyst has to be ensured. Instead of using the fine-grained zeolite catalyst from the Asahi process, we apply the typical catalytic distillation catalyst Amberlyst15 that is embedded in a structured packing. Due to the comparatively low amount of catalyst that can be installed in a column of reasonable size, the direct hydration would only proceed at very low reaction rates. We therefore suggest a new reaction path where an appropriate reactive entrainer (e.g. formic acid) first reacts with cyclohexene to the respective cyclohexyl ester (see Fig. 1). Then, in a second step, the ester is hydrolyzed. In addition to the product cyclohexanol, the reactive entrainer is also recovered in this reaction and can be recycled and re-used in the first process step. An extensive study on the reaction kinetics of the reactions has been performed and confirmed the fundamental feasibility of such a two-step reaction system of the indirect hydration of cyclohexene to cyclohexanol [2].

Fig. 2 shows the flow scheme of such a process, consisting of two coupled catalytic distillation columns. Based on experimentally approved thermodynamic and kinetic data, we present a conceptual process design for this new cyclohexanol production process. Steady-state and dynamic column simulations have been performed with a Vapor-Liquid-Liquid-Equilibrium model that accounts for the potential liquid-phase splitting [3] in the columns. Currently we are working on complementary experiments in a pilot scale plant that will be used for validation of the simulations.

References

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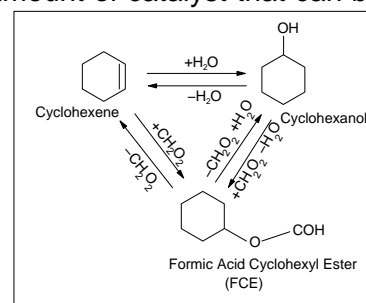


Fig. 1: Reaction network

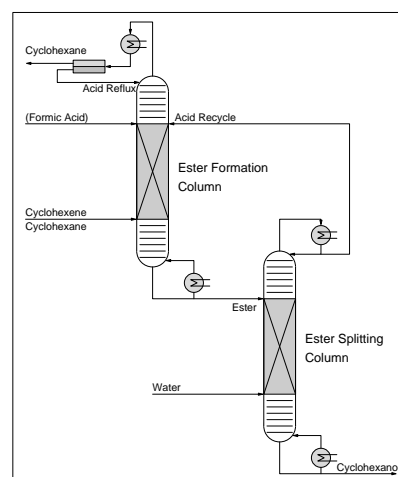


Fig. 2: Process scheme