A continuous reactive distillation process for the production of cyclohexanol from cyclohexene

Rakesh Kumar[1,*], Amit Katariya[1], Hannsjoerg Freund[1], Kai Sundmacher[1,2]
[1]Max Planck Institute for Dynamics of Complex Technical Systems, Magdeburg, Germany
[2] Process Systems Engineering, Otto von Guericke University, Magdeburg, Germany
Email: kumar@mpi-magdeburg.mpg.de

1 Introduction

Cyclohexanol is one of the important bulk chemicals used widely in the chemical industries as an intermediate for the production of polymers (Nylon 6,6 and Nylon 6). Conventionally, cyclohexanol is produced by the hydrogenation of benzene to cyclohexane and its subsequent oxidation by air to cyclohexanol/cyclohexanone. This process has a high energy demand; a further disadvantage is the risk associated with the operation of the process. In recent years, a promising alternative process has been developed that includes hydrogenation of benzene to cyclohexene and further hydration of cyclohexene to cyclohexanol. Cyclohexanol production by direct hydration of cyclohexene is a challenging task due to its low solubility with water. Asahi Chemical Co. made an attempt in this direction to improve the reaction rate using a zeolite catalyst of HZSM5 type[1]. However, still a large amount of catalyst is required to obtain significant reaction rates of cyclohexene hydration.

We propose a novel process scheme for the indirect hydration of cyclohexene to cyclohexanol in a reactive distillation column using formic acid as a reactive entrainer. The proposed process includes the continuous esterification of cyclohexene with formic acid in a reactive distillation column followed by hydrolysis of cyclohexyl formate in a second reactive distillation column to produce pure cyclohexanol[1]. Previously, our group performed thermodynamic, kinetic and process feasibility studied regarding this system [2,3,4]. In the present study, the feasibility of the first step of this process scheme (i.e. the esterification of cyclohexene with formic acid) is investigated experimentally in a vacuum reactive distillation column.

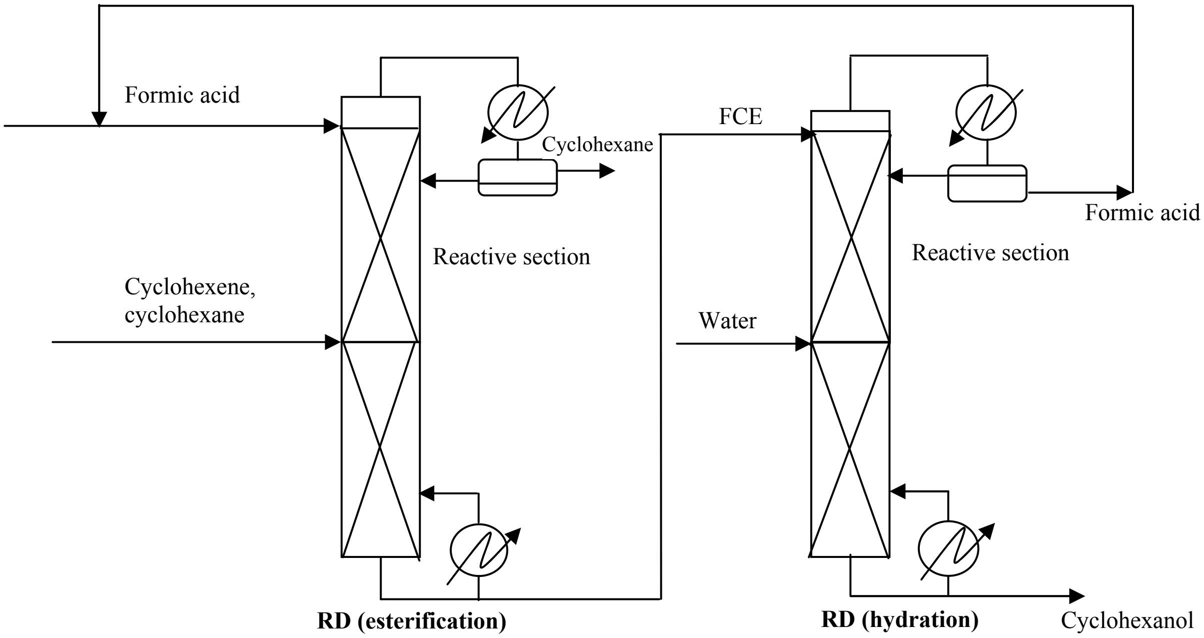


Figure 1: Process flowsheet for the indirect hydration of cyclohexene to cyclohexanol

2. Experimental

2.1 Chemicals:

Cyclohexene (99%) and 1,4 dioxane (99.5%) was obtained from Sigma Aldrich. Formic acid was supplied by Merck (Germany).Cyclohexyl formate (>97%w/w) was prepared in the laboratory. Detail of the method can be found elsewhere[3].

2.2 Analytical method

Analysis of samples obtained from the different position of column was performed on a Gas chromatograph equipped with FID and TCD as a combination of detectors. INNOVAX column (30m, 250μm, 0.25μm) was used for the quantification of the component. GC was calibrated using 1,4 dioxane as an internal standard. In case of biphasic mixture, samples were centrifuged before analysis on GC.

2.3 Experimental Setup and procedure

Esterification of cyclohexene with formic acid was conducted in a continuous reactive distillation column as shown in Figure 2. The reactive distillation column consists of two different sections: non reactive stripping section and reactive section. Reactive section is packed with the structured packing Sulzer-KATAPAK filled with Amberlyst-15 cationic ion exchange resin as acid catalyst. Non reactive stripping section of the column is packed with Sulzer-BX packing. The temperature sensors were (Pt-100) provided at different sections in the column. To prevent the heat loss from surrounding, the column wall was covered with the insulating materials and external heating was provided to column. Reboiler was equipped with electrical heating power supply (2.8 kW). Low volatile component (Formic acid) was fed from the top of the column and cyclohexene from the middle of stripping section. Since experiments were performed with pure cyclohexene, overhead product of the column was condensed and total refluxed

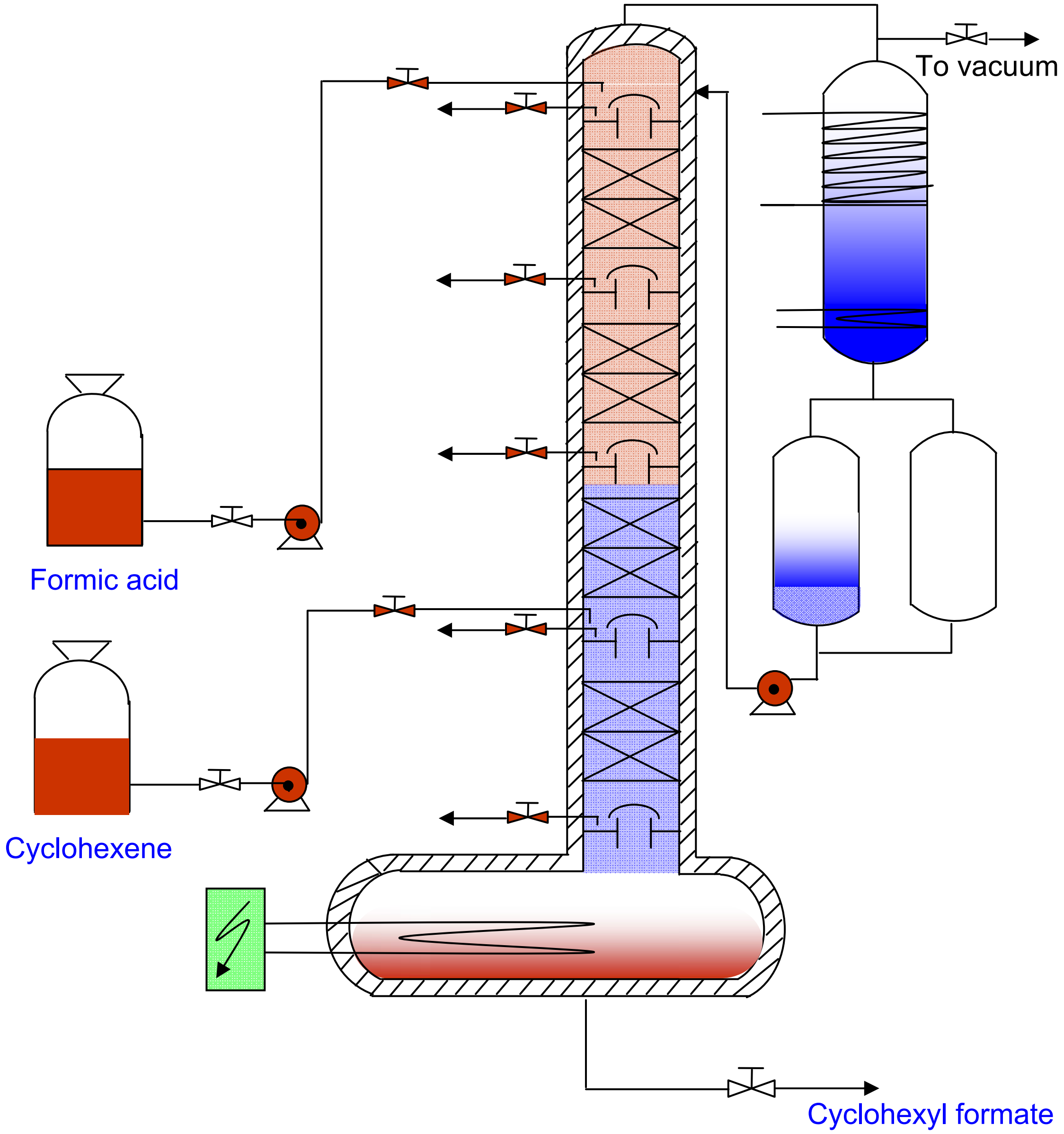


Figure 2: Experimental setup for the esterification of cyclohexene with formic acid

to reactive section of the column. Reboiler holdup was maintained constant by removing of bottom product continuously. In order to minimize the decomposition of formic acid, experiments were performed at low pressure conditions (<0.7 bar). Samples were collected from different position along the height of column and analyzed on GC. At steady state, flow rates of the bottom stream were measured and overall material balance was verified. Effect of feed mole ratio was studied to see the effect on column performance

3. Results and discussion

Initially, experiments were performed to obtain the steady state compositions and temperature profile of column. It took more than 72 hrs to get steady because of large hold up of liquid inside the reboiler. Representative results of concentration and temperature profile obtained under steady state condition are shown in Figure 3. Liquid-Liquid phase splitting take place in whole column except top of reactive section and reboiler part of column. Due to the presence of high concentration of the formic acid in top part of reactive section, it leads to an increase in reaction temperature. Towards the bottom of reactive section and in stripping section, temperature in the column decreases because of increase in concentration of cyclohexene. In bottom part of stripping section and reboiler part of column, there is a steep rise in temperature with increase in concentration of cyclohexyl formate. With 2.19:1 feed molar ratio of the reactants (Formic acid: cyclohexene), 90% conversion of cyclohxene was observed in column. Bottom stream contains about 58 %w/w cyclohexyl formate, 37 %w/w formic acid and unreacted cyclohexene. In the bottom streams of column, presence of water and cyclohexanol was also detected because of the decomposition of formic acid in presence of catalyst in the reactive section.

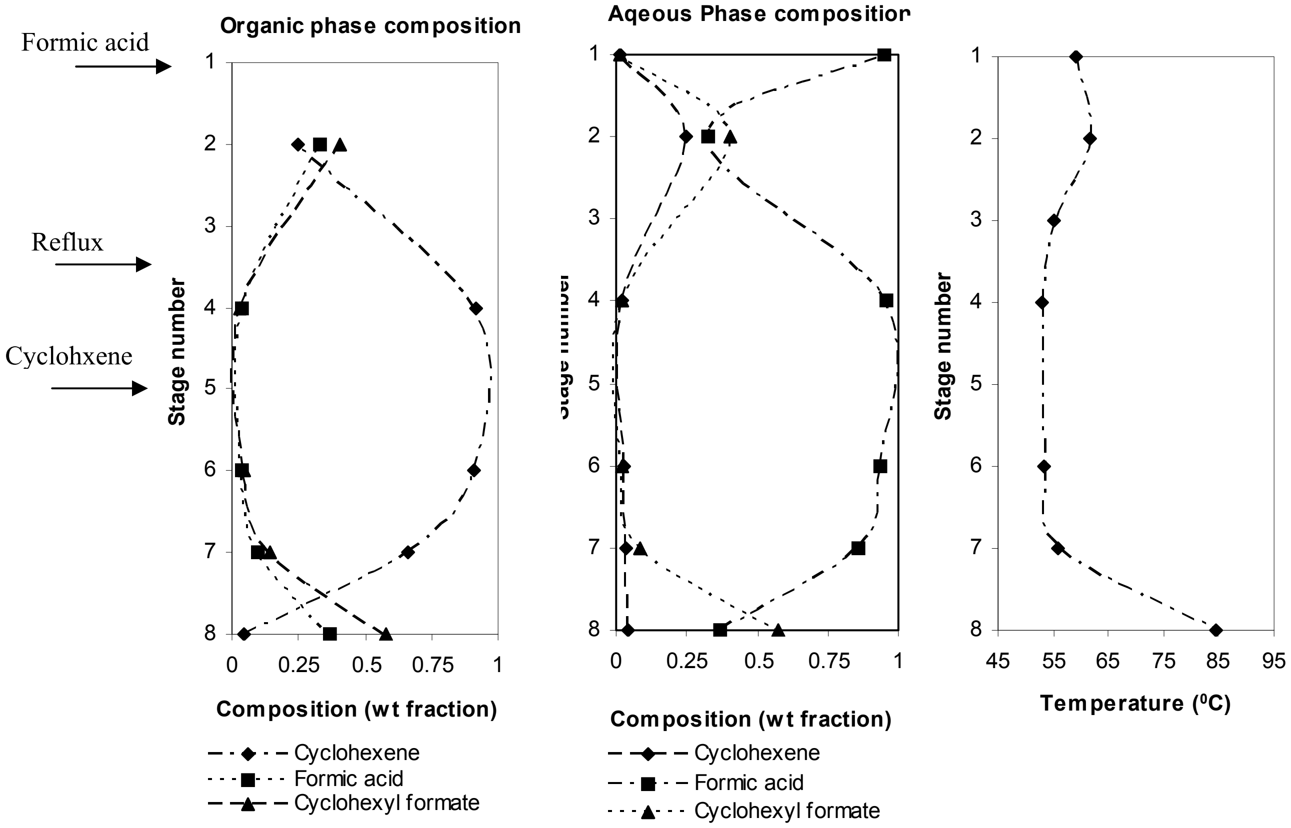
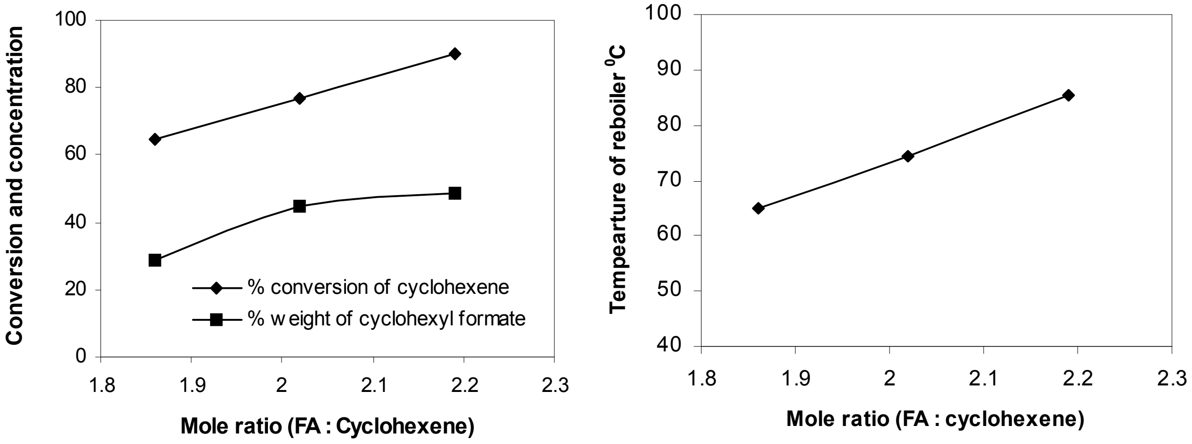


Figure 3: Composition and temperature profile of column. Feed mole ratio (FA: Cyclohexene =2.19), Reboiler duty =700 W, Pressure = 0.544 bar, Feed position: Formic acid from top, Cyclohexene from middle of stripping section

3.1 Effect of feed mole ratio

Feed flow rate of cyclohexene was changed to observe its effect on the column performance by keeping other parameter constant. At high feed mole ratio of the reactants (formic acid: cyclohexene), reaction rate of cyclohexene esterification increases that lead to increase in the conversion. However, excess amount of formic acid in column, reduces the concentration of cyclohexyl formate in the bottom product (Figure

4a). Temperature in the reboiler part of column increases because of the increase in formic acid and cyclohexyl formate concentration (Figure 4b).



(a) (b)

Figure 4: Effect of feed mole ratio of the reactants

4 Conclusions

Esterification of cyclohexene was studied in a continuous reactive distillation column using the formic acid as a reactive entrainer. Experiments were conducted in a pilot scale column using amberlyst-15 as a catalyst in KATAPAK structured packing. About 90% conversion of cyclohxene was obtained with 2:19 mole ratio of the reactants (Formic acid: cyclohexene) under steady state conditions. Effect of feed mole ratio was investigated to evaluate the column performance.

References

[1] O. Mitsui, Y. Fukuoka, Process for producing cyclic alcohol, *United state patent* 4588846 (1986).

[2] F. Steyer and K. Sundamcher, Cyclohexanol production via esterification of cyclohexene with formic acid and subsequent hydration of the ester- reaction kinetics, *Ind. Eng Chem. Res.,* 46 (2007) 1099-1104.

[3] F. Steyer, K. Sundamcher, VLE and LLE data set for the system Cyclohexane + Cyclohexene + Water + Cyclohexanol + Formic acid + Formic Acid Cyclohexyl Ester *J. Chem Eng. Data,* 50 (2005) 1272-1282.

[4] F. Steyer, H. Freund and K. Sundamcher, A novel reactive distillation process for the indirect hydration of cyclohexene using a reactive entrainer, *Ind. Eng. Chem. Res.,* (Submitted)