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Development of a Novel Catalytic Distillation Process for Cyclohexanol Production: Mini Plant Experiments and Complementary Process Simulations

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ABSTRACT: A new, two-step process concept for the production of cyclohexanol by indirect hydration of cyclohexene using formic acid as a reactive entrainer is suggested, and its principle technical feasibility is demonstrated. The first step of this process is based on an ester formation reaction of cyclohexene with formic acid. This reaction was carried out in a mini plant stainless steel catalytic distillation column of 2.35 m height. The column was packed with noncatalytic structured packings (SULZER-DX) and catalytic structured packings (KATAPAK-S). The experiments were conducted under low-pressure conditions (<0.6 bar) to avoid formic acid decomposition. Concentration and temperature profiles were obtained under steady-state conditions. Up to 98.3% conversion of cyclohexene and 75.5 mol % ester concentration in the bottom product of the column was obtained. In a similar manner, the second step of the process, i.e. the hydrolysis of the cyclohexyl formate formed in the first step, was investigated experimentally in a continuous catalytic distillation column under low-pressure conditions (<0.4 bar). Important process design parameters such as the feed mole ratio of the reactants, the reboiler duty, the feed flow rate, and the column pressure were investigated with regard to their effect on the cyclohexene conversion and the purity of the bottom product. Furthermore, the experimental data were compared with results obtained from steady-state simulations of the catalytic distillation process.

1. INTRODUCTION: REVIEW OF PROCESS ROUTES AND CATALYSIS ASPECTS

Cyclohexanol is an important bulk chemical used in the chemical industries as an intermediate in the production of polymers such as Nylon 6,6 and Nylon 6.[1] Basically all industrially relevant production processes for cyclohexanol start from benzene. In current industrial practice, the most important synthesis route is the hydrogenation of benzene to cyclohexane and the subsequent liquid-phase oxidation of cyclohexane with air to form a mixture of cyclohexanol and cyclohexanone.[2,3] Several drawbacks of the oxidation process such as rather limited selectivities even at low conversions, large external recycle streams, and safety related issues with regard to the operation have stimulated both academic and industrial research to identify new process options. Nevertheless, the cyclohexane oxidation process still represents the state-of-the-art in cyclohexanol production.

Another route for cyclohexanol synthesis runs via phenol and its subsequent hydrogenation.[4,5] This route, however, has lost its dominating position in the past decades. Today, there are only a few phenol-based processes still running economically, especially at locations where phenol prices are attractive (e.g., in the United States). Otherwise, the liquid phase oxidation of cyclohexane is much more favorable.

In recent years, a new and promising alternative process has been developed to produce cyclohexanol, which consists of the selective hydrogenation of benzene to cyclohexene and subsequent hydration of cyclohexene to cyclohexanol. As advantages of this process, a reduction in the hydrogen demand by one-third, a safe operation, and the avoidance of side products can be mentioned. A challenge in this process concept is the strongly limited mutual solubility of the reactants, which leads to the formation of two liquid phases and results in a kinetic limitation of the reaction. Asahi Chemical Co. developed and commercialized a process[6] where cyclohexene is hydrated to cyclohexanol using a large amount of strong hydrophilic zeolite catalyst (H-ZSM 5, high Si/Al ratio) in a slurry reactor. The reaction products are separated in a decanter, and the catalyst is removed from the aqueous phase and recycled back to the reactor. The organic phase consists of cyclohexanol as the main reaction product and benzene and cyclohexane as volatile impurities from the upstream partial hydrogenation process step.

A main drawback of the aforementioned cyclohexene hydration process is the equilibrium limitation of the reaction which involves a relatively low conversion per pass. Considering this limitation, we suggest applying catalytic distillation as an innovative multifunctional reactor concept for the direct hydration of cyclohexene. Catalytic distillation is very attractive from a theoretical point of view because here the chemical equilibrium can be overcome, ideally allowing for complete conversion of cyclohexene. A prerequisite for the technical application of catalytic distillation with its simultaneous reaction and distillation is that the process operation windows of both reaction and separation match. For the reaction system under investigation in this study this requirement is fulfilled. As further advantages of the catalytic distillation process concept, the recycle streams are internalized, and the troublesome slurry handling is avoided. However, the low mutual solubility of cyclohexene and water still

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remains a challenge also in catalytic distillation, so that in order to obtain a significant conversion of cyclohexene, either measures to improve the mutual solubility of the reactants have to be taken or large amounts of catalyst and/or high residence times are required.

Peschel et al.[7] explored the possibility of simultaneous hydrogenation of benzene and hydration of cyclohexene in a catalytic distillation column. Benzene and water are fed continuously at the top of the catalytic section, and hydrogen is introduced at the bottom of the catalytic section. The bottom product of the column contains a mixture of cyclohexanol (29%), cyclohexane (61%), and water (10%). Simultaneous hydrogenation and hydration of cyclohexene in a single catalytic distillation column would be attractive, but the selectivity towards cyclohexanol is very low in this process.

In catalysis research, a few attempts have been made previously to enhance the reaction rate and to reduce side product formation using selective catalysts such as, e.g. ZSM-5, or by adding organic solvents. Panneman and Beenackers[8] used an ion-exchange resin in the presence of a solvent (sulfolane) to reduce the miscibility gap between cyclohexene and water. However, the addition of solvent will increase the complexity in the separation steps of the process.

Ishida[9] reviewed the characteristics of different types of zeolite catalysts for the liquid-phase hydration of cyclohexene to cyclohexanol. Zhang et al.[10] performed the direct hydration of cyclohexene with various solid catalysts (Amberlyst-15, ZSM-5, and Mordenite). A zeolite catalyst of ZSM-5 type with a SiO_2/Al_2O_3 ratio in the range of 30−50 was found to perform best with about 99% selectivity. Selective catalysts such as zeolites, however, are difficult to implement into catalytic distillation columns. If they are deposited as a thin film on a carrier, the amount of catalyst that can be installed in a column of reasonable size is very limited. On the other hand, it is not possible to use fine-grained zeolite catalyst particles since these cannot be fixed properly inside conventional structured packings.

The aforementioned drawbacks of the current process routes for cyclohexanol production along with the potential benefits of applying catalytic distillation in a multifunctional reactor unit were the motivation to develop and validate a new integrated process concept. The main idea of this novel process concept and the challenges that had to be solved are briefly described in the next section.

2. PROCESS CONCEPT: INDIRECT HYDRATION OF CYCLOHEXENE USING A REACTIVE ENTRAINER

As discussed before, the main challenge in cyclohexanol production from cyclohexene is to overcome the kinetic limitation of the direct hydration reaction by suitable means. Instead of using large amounts of catalyst we follow a different approach in our process concept, i.e. we modify the reaction route which results in an indirect hydration reaction scheme. The idea is to increase the overall reaction rate from cyclohexene to cyclohexanol by adding a suitable reactive component, which forms an intermediate product with cyclohexene. This intermediate product can further be converted to cyclohexanol, while the reactive component is recovered and recycled back to the initial feed stream. We refer to this reactive component as a reactive entrainer.

It is well-known that olefins can form an ester with different organic acids in presence of acidic catalysts.[11−14] Among all these organic acids investigated, formic acid shows the highest reactivity for the ester formation reaction with cyclohexene in presence of an acid catalyst under low temperature and pressure conditions. Saha et al.[15] performed experimental feasibility studies for the ester formation reaction of cyclohexene with formic acid and acrylic acid respectively in a batch and a continuous catalytic distillation column.

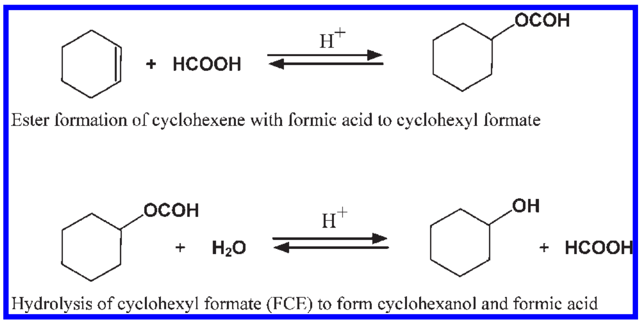

Figure 1. Reaction scheme for the production of cyclohexanol using formic acid as reactive entrainer.

On the basis of these previous experimental findings, i.e. in particular the relatively high reactivity of cyclohexene with formic acid, we investigated the corresponding reaction system in more detail with regard to thermodynamics and kinetics[16,17] and recently suggested a new approach for cyclohexanol production.[18] In this process concept, the ester formation reaction of cyclohexene with formic acid as a reactive entrainer is followed by the hydrolysis of the ester to produce cyclohexanol while recovering the formic acid. The advantage of this reaction scheme of the novel process (see Figure 1) is that the reaction of cyclohexene with formic acid to cyclohexyl formate proceeds at much higher reaction rates compared to the direct hydration of cyclohexene in presence of acid catalysts.[17] Side reactions that may take place in the presence of acid catalysts are the decomposition of formic acid[19−21] and the dimerization of cyclohexene, respectively. However, these side reactions can be minimized by maintaining low temperature and pressure conditions during the course of the reaction.

The reaction kinetics for the indirect hydration of cyclohexene using formic acid as a reactive entrainer were studied in detail in our previous work.[17] An extensive number of experimental data were collected for batch and continuous mode of a stirred tank reactor for both noncatalyzed and heterogeneously catalyzed (Amberlyst-15) reactions to cover the entire composition range. On the basis of the kinetic measurements, a Langmuir−Hinshelwood (LHHW) model was adopted to formally describe the kinetics of the reaction system.

As for the direct hydration, the reaction system based on the indirect hydration of cyclohexene involves the combination of polar and nonpolar components which leads to complexities in the phase behavior in the form of nonidealities between the liquid and the vapor phases along with liquid−liquid phase splitting. Hence, in order to describe the proper thermodynamics of the system, exact information is needed on vapor−liquid and liquid−liquid equilibrium of the system. Therefore, in our group detailed studies on vapor−liquid and liquid−liquid equilibrium were performed, and from the experimental data, the thermodynamic parameters for the NRTL model were obtained.[16]

On the basis of this previous work, we recently proposed a new process scheme with two coupled catalytic distillation columns for the indirect hydration of cyclohexene to cyclohexanol using formic acid as a reactive entrainer and carried out simulations that prove the principle feasibility of the process concept.[18] The complete process flowsheet is shown in Figure 2. In the first

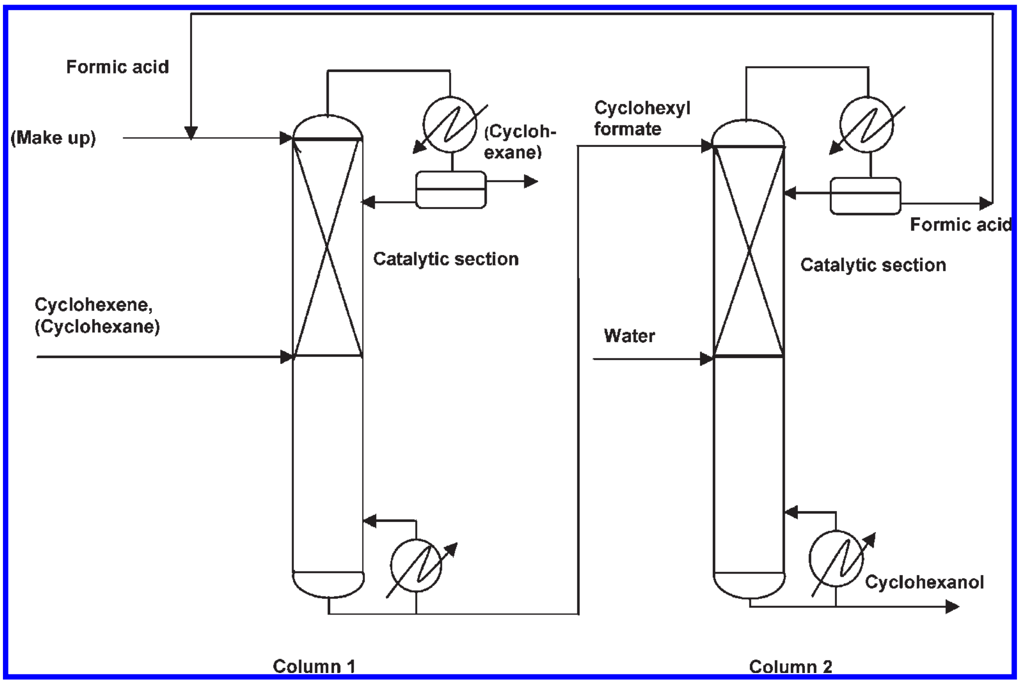

Figure 2. Process flowsheet for the indirect hydration of cyclohexene to cyclohexanol.

column, the ester formation reaction of cyclohexene with formic acid is carried out, followed by the hydrolysis of the ester in a second catalytic distillation column.

A reactive residue curve map analysis for the ester formation column indicates that the binary heterogeneous azeotrope of cyclohexene and formic acid is minimum boiling and will become a feasible top product of the first column.[18] The bottom product consists of a ternary reactive azeotrope of cyclohexene, formic acid and cyclohexyl formate. Hence, in order to obtain pure ester in the bottom of the catalytic distillation column, a noncatalytic section has to be provided in the lower part of the column.

For the hydrolysis step of the process in the second column, the residue curve map analysis[18] revealed that pure cyclohexanol can be obtained as a bottom product for a fully reactive column. However, our model based analysis[22] also indicates that a small noncatalytic section at the bottom of the column significantly improves the performance of the process. The unstable node in this diagram is pure formic acid, which can be recovered from the process as a top product of the column. This distillate product containing formic acid can be recycled back to the first step of the process.

As a further finding from the experiments relevant for the conceptual process design, the kinetic investigations[17] indicated that the formic acid decomposition rate is negligible if the temperature in the catalytic section is below 60 °C. Hence, the columns have to be operated below atmospheric pressure.

To sum up, in our previous work on the novel process concept for cyclohexanol production we have acquired a solid experimental data basis that enabled us to set up and parametrize the relevant model equations.[16,17] Using these model equations for simulation purposes, we have demonstrated the feasibility of the process by means of reactive residue curve map analysis.[18] In addition, we recently presented a more detailed simulation and an optimization of the process scheme based on rigorous column simulations.[22]

The aim of the present paper is to validate the conceptual process development by demonstrating the technical feasibility of the proposed catalytic distillation process scheme via experiments in a mini plant. For this, the continuous production of cyclohexanol from cyclohexene is investigated experimentally in a vacuum catalytic distillation column at the mini plant scale. In order to reduce the complexity of the process, the experimental studies were performed for the two individual steps of the process in a sequential approach. In the first step, cyclohexene reacts with formic acid to produce cyclohexyl formate (ester) as a reaction product under low pressure and temperature conditions. The cyclohexyl formate is then hydrolyzed in a second catalytic distillation column, which is also operated under low pressure (<0.4 bar) and temperature conditions.

3. EXPERIMENTAL SECTION

3.1. Chemicals. Cyclohexene (99%w/w), cyclohexanol, and analytical grade 1,4-dioxane (99.5%w/w) were purchased from Sigma Aldrich (Germany). Formic acid (>99%w/w) was supplied by Merck (Germany). Cyclohexyl formate (>97%w/w) was prepared by us in the laboratory. The details about the cyclohexyl formate preparation are given in the Appendix. The acidic ion-exchange resin Amberlyst-15 (Sigma Aldrich) with an average particle size of 0.5 mm was used as a catalyst.

3.2. Analytical Method. The analysis of the samples taken from the column was performed using a gas chromatograph (Hewlett-Packerd HP 6890 GC series) equipped with FID and TCD as a combination of detectors. An INNOVAX column (30 m, 250 μm, 0.25 μm) with helium as carrier gas was used for the quantification of the components. The oven temperature was varied from 80 to 130 °C at a rate of 50 °C min^{-1}. The temperature of the injector and the detector was maintained at 250 °C. The GC was calibrated using 1,4-dioxane as an internal standard. In case of biphasic mixtures, the samples were centrifuged, and each phase was analyzed separately by GC.

3.3. Experimental Setup and Procedure. In the present study, the principle experimental design for both steps of the process was based on our previous simulation studies.[18,22] However, since the experimental investigation of both process

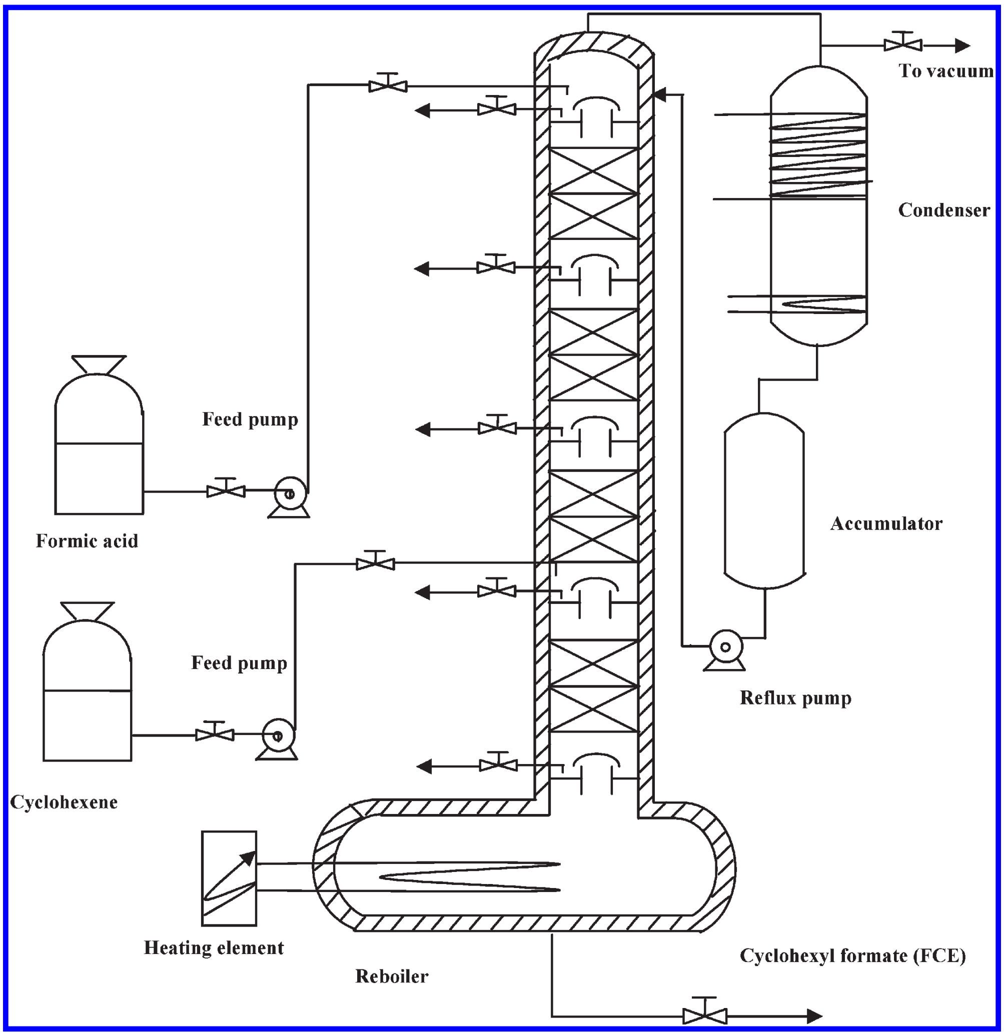

Figure 3. Experimental setup of the ester formation of cyclohexene with formic acid.

steps was performed in a multipurpose reactive distillation column, the design was not identical to the optimal column design obtained from the simulations. The ester formation from cyclohexene and formic acid was carried out in a continuous catalytic distillation column as shown in Figure 3. The experimental setup comprises the column, a condenser, an accumulator for refluxing the distillate product, a bottom product collector, and a vacuum unit. The column is made of stainless steel SS316l and features an inner diameter of 50 mm and a height of 2.35 m. The catalytic distillation column is divided into two different sections: a noncatalytic stripping section and a catalytic section (Figure 4). The catalytic section is packed with the structured packing KATAPAK-S filled with Amberlyst-15 cationic ion-exchange resin as acid catalyst as shown in the column assembly in Figure 5. The noncatalytic stripping section of the column is packed with structured Sulzer-DX packings. The specifications of the column design are given in Table 1.

For measuring the temperature profile, temperature sensors (Pt-100) were positioned at different sections in the column. To minimize the heat loss to the surrounding, the column wall was covered with insulating material. In addition, an external heating was provided at the column wall in order to compensate for the remaining heat loss that cannot be completely avoided. With these measures, the adiabatic operation of an industrial scale column can be imitated. The reboiler was equipped with an electrical heating power supply (2.8 kW).

A piston type rotary pump (Ismatec, Germany) and a diaphragm metering pump (KNF Flodos AG, Switzerland) which can be controlled via PC were used for feeding formic acid and cyclohexene into the column. An HPLC pump (HNP Mikrosysteme, Germany) was used for refluxing the distillate product. A condenser was attached to the top of the column to condensate the vapor stream. An accumulator was placed below the condenser for refluxing back the liquid to the top part of the column using the pump. A constant holdup inside the accumulator was maintained by a liquid level controller. The catalytic distillation mini plant unit was fully automated and controlled via the Siemens SIMATIC PCS7 control system.

In the first step of the process, the experiment was started with pure cyclohexene and formic acid in the reboiler, which was heated with the electric coil. Once the liquid started boiling and the vapor started being condensed and refluxed back to the column, formic acid and cyclohexene were fed with the desired flow rate from the top and the bottom part of the catalytic section, respectively. Both the feeds were preheated slightly below the boiling point of the reactants before feeding them into the column.

Since the experiments were performed with pure cyclohexene (no cyclohexane impurities) and pure formic acid, a purge stream

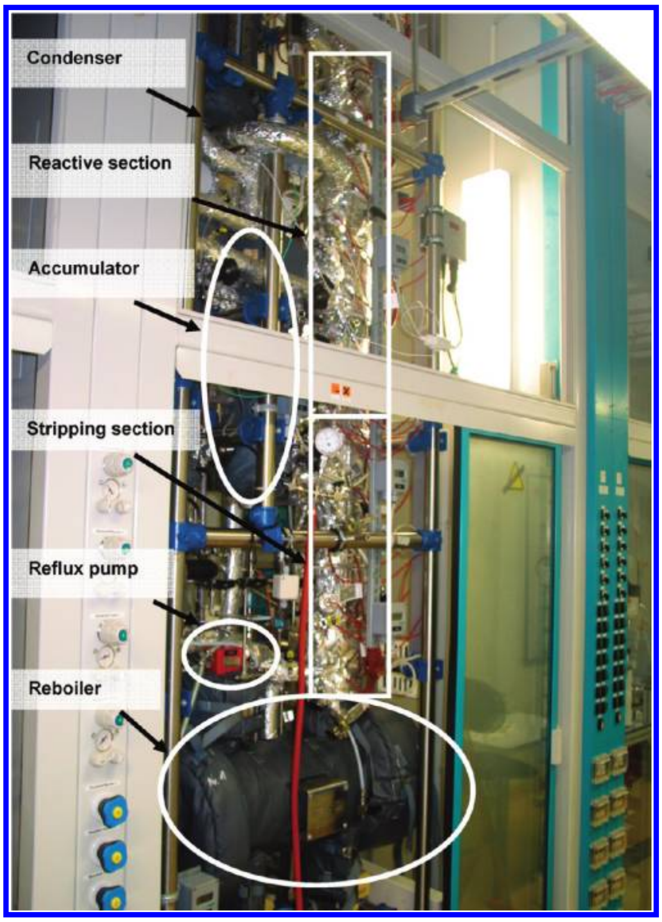

Figure 4. Mini plant catalytic distillation column setup.

was not necessary, and thus the overhead product of the column was condensed and totally refluxed to the top of the catalytic section of the column. The reboiler holdup was maintained constant by removing the bottom product continuously. In order to minimize the decomposition of formic acid which takes place at higher temperatures, the experiments were performed at low-pressure conditions (<0.6 bar). Samples were collected from different positions along the height of the column and analyzed by GC as described in section 3.2. At steady state, the flow rate of the bottom stream was measured and the overall material balance was verified.

In the second step of the process, some changes had to be made in the existing setup. The distillate product of the hydrolysis of cyclohexyl formate was collected in an accumulator and formed a biphasic mixture. The organic phase was refluxed back to the top of the column using the reflux pump. The polar phase was withdrawn continuously from the accumulator with the help of an additional distillate pump. Since cyclohexanol is in the solid state at room temperature, heating was provided to maintain the temperature at about 50 °C in the discharge line of the bottom product to the collecting tank in order to keep cyclohexanol in the liquid state.

In the following sections, the experimental results for the two columns are presented and discussed. In addition, a comparison of experimental and simulation results is performed for validation purposes.

4. PROCESS STEP 1: ESTER FORMATION FROM CYCLOHEXENE AND FORMIC ACID

The experimental investigation of the first step of the process was performed in continuous mode under total reflux conditions.

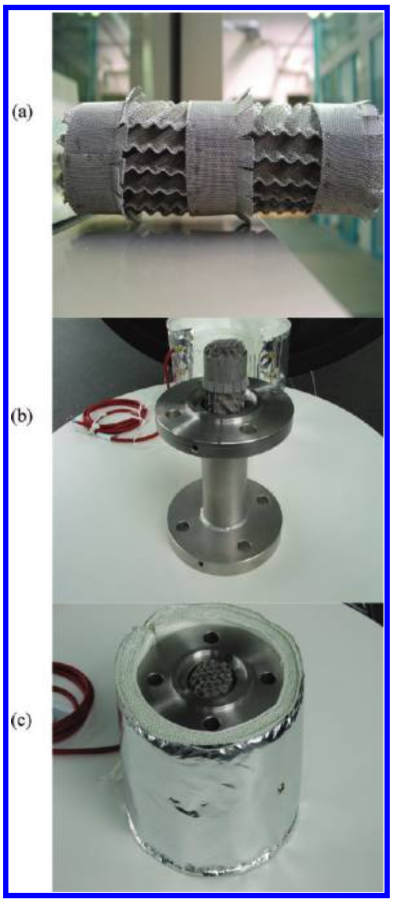

Figure 5. Catalytic distillation column tray assembly: (a) catalytic structured packing (Katapak-S), (b) catalytic tray assembly, (c) complete catalytic tray.

Table 1. Mini plant catalytic distillation column details

column parameters	values
height (m)	2.35
column holdup (L)	0.33
inner diameter (mm)	50
reboiler capacity (L)	26
noncatalytic section height (m)	0.66
type of packing	Sulzer-DX
catalytic section height (m)	1.69
type of packing	Sulzer Katapak-S
catalyst	Amberlyst-15

The column pressure was adjusted such that the temperature in the catalytic section was always below 60 °C. A steady-state column analysis was carried out on the basis of the composition of the biphasic or the single-phase mixture and the temperature profile obtained from measurements at different positions along the height of the column.

4.1. Results and Discussion. At the beginning, exploratory experiments were performed with the ester formation column to obtain steady-state conditions and reasonable limits for the operation parameter space. In the first experiment it took about 300 h to achieve steady state without any change in the parameters. In the following experiments, the effect of different operating parameters on the cyclohexene conversion and the cyclohexyl

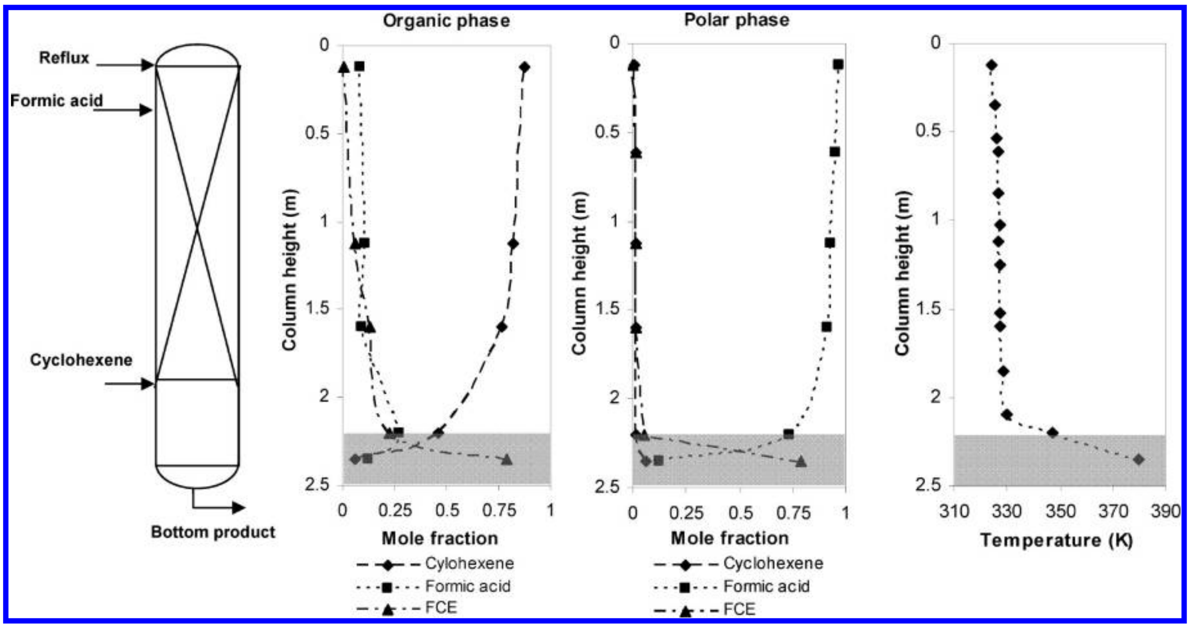

Figure 6. Composition and temperature profile of the column. Feed mole ratio (FA: cyclohexene = 1.06), reboiler duty = 280 W, pressure = 0.52 bar. Feed position: formic acid from top, cyclohexene from bottom of catalytic section. The shaded area represents the single-phase composition region.

formate (ester) concentration in the bottom product stream was systematically investigated in a parametric study. Steady state was achieved after the bottom product amount was equivalent to 4−5 times the volume of the liquid holdup inside the reboiler.

Representative results of the concentration and temperature profile of the column at steady-state conditions are shown in Figure 6. The shaded area in the figure represents the region of single-phase composition. In the catalytic section, cyclohexyl formate is produced by the reaction of cyclohexene and formic acid in the presence of the acidic catalyst (Amberlyst-15). The catalytic section of the column and the upper part of the stripping section contain a biphasic mixture. The organic phase contains mainly cyclohexene, while the polar phase comprises formic acid as a main component. The overhead product stream which contains unreacted cyclohexene and formic acid is recycled back to the column. In the lower section of the column, the liquid composition of both phases is dominated by the ester, which eventually leads to the formation of a single-phase composition in the lower part of the stripping section and the reboiler section. There is no significant change in the temperature of the catalytic section and the upper part of the stripping section of the column. However, in the lower part of the stripping section and the reboiler part of the column, there is a steep rise in the temperature caused by the separation of the high-boiling cyclohexyl formate.

With a nearly stoichiometric feed molar ratio of the reactants formic acid to cyclohexene of 1.02:1, 92.7% conversion of cyclohexene was achieved in the column. The bottom stream contains about 79.3 mol % cyclohexyl formate, 11 mol % formic acid, and the rest mainly contains unreacted cyclohexene (6.4 mol %). In the bottom stream of the column, small amounts of water and cyclohexanol were also detected. The presence of water in the column indicates a slight decomposition of formic acid in the catalytic section (2−3%). With the present column configuration, a maximum ester purity of 79.3% could be obtained in the bottom stream of the column. However, there is a possibility to further increase the ester purity by increasing the reactive section height or the catalyst amount per stage.

A summary of the experimental conditions and of the results obtained is outlined in Table 4. The reproducibility of the experimental data has also been checked by repeating the experiments under similar conditions. The cyclohexene conversion showed a deviation of 2.5%, the cyclohexyl formate concentration varied by 6% and the reboiler temperature by 0.34%. However, the feed conditions were not exactly the same in the mini plant column. Possible side product formation was investigated by analyzing the bottom stream product composition by GC−MS. In some experiments, small amounts of the cyclohexene dimer (cyclohexene, 1-cyclohexyl-) were detected, but the dimer concentration was always below 0.3 mol % and was therefore negligible.

The effect of different operating parameters such as the feed mole ratio of the reactants, the reboiler duty, the feed flow rate, and the column pressure on the column performance was studied. In order to evaluate the column performance, the cyclohexene conversion and the ester concentration in the bottom product of the column (i.e., the product purity) were selected as important criteria. The results of this parametric study are discussed in the following subsections.

4.1.1. Effect of the Feed Mole Ratio. Formic acid was fed in excess molar amount (1.027 to 1.25) from the top part of the catalytic section of the column to observe its influence on the column performance (Figures 7 and 8). With increasing molar amounts of formic acid, the cyclohexene conversion increases from 75.5% to 97.7%, and the ester purity increases from 65% to 75%. The reason is that at higher feed mole ratios of the reactants, the reaction rate of the ester formation increases, which leads to an increase in both the cyclohexene conversion and the ester purity in the bottom product of the column (Figure 8). A moderate increase of the formic acid concentration as realized in our experiments does not change the reaction stage temperature significantly; however, the reboiler temperature increases due to the increase in the ester concentration.

4.1.2. Effect of the Reboiler Duty. Figures 9 and 10 show the influence of the reboiler duty on cyclohexene conversion and ester purity in the bottom product of the column. The reboiler

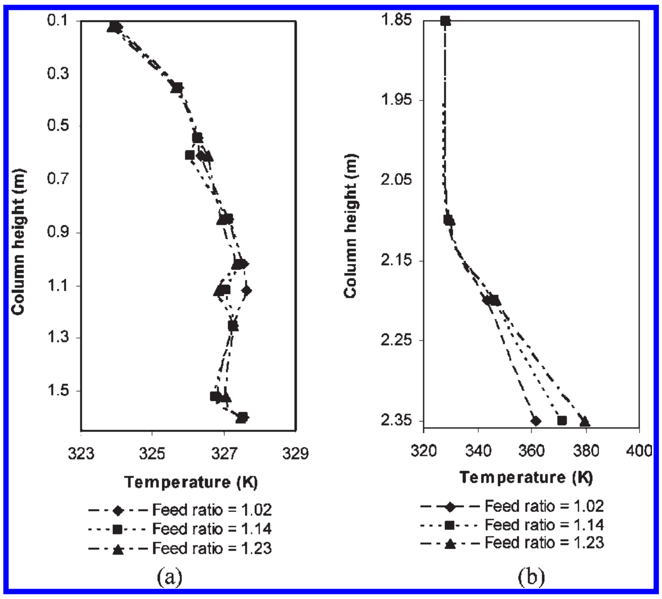

Figure 7. Temperature profile of the column for different feed mole ratios (FA: cyclohexene). (a) Catalytic section temperature profile, (b) stripping section temperature profile (Table 4: runs 2, 1, 5).

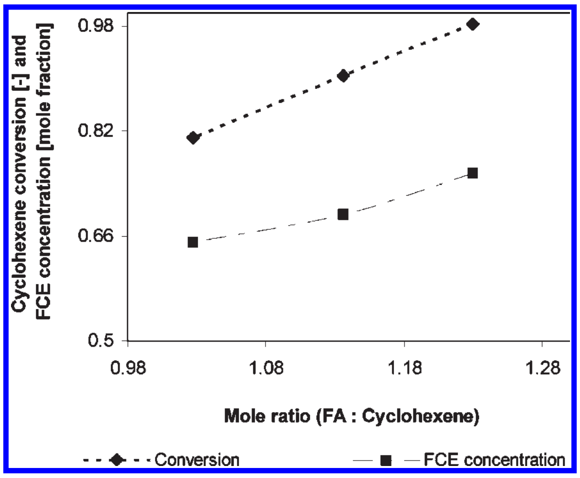

Figure 8. Cyclohexene conversion and ester purity in the bottom product at different feed mole ratios (Table 4: runs 2, 1, 5).

duty of the column was varied from 196 W up to 364 W. The temperature in the catalytic section decreases slightly at higher reboiler duties, which results in a decrease in the cyclohexene conversion and the ester purity in the bottom product of the column. The temperature in the noncatalytic section and in the reboiler does not change significantly despite the variation in the cyclohexyl formate concentration in the reboiler.

4.1.3. Effect of the Feed Rate. The total feed rate of cyclohexene and formic acid was varied between 3.0 mol/h and 1.7 mol/h, while keeping the other parameters constant. Figures 11 and 12 show the influence of the feed rate variation on the cyclohexene conversion, the ester purity in the bottom product, and the temperature along the height of the column. With decreasing feed flow rates, the residence time for each reactive stage of the column increases, which results in a higher cyclohexene conversion and higher ester purity in the bottom product stream. The temperature in the catalytic section increases slightly, while the temperature in the lower part of the noncatalytic section and the reboiler temperature increase abruptly with the increase in ester concentration at lower feed rates (Figure 11).

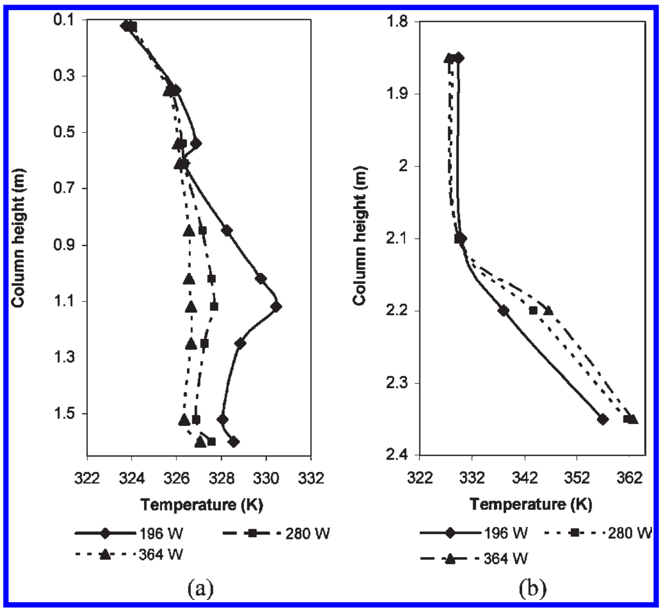

Figure 9. Temperature profile of column at different reboiler duties. (a) Catalytic section temperature profile, (b) stripping section temperature profile (Table 4: runs 3, 2, 4).

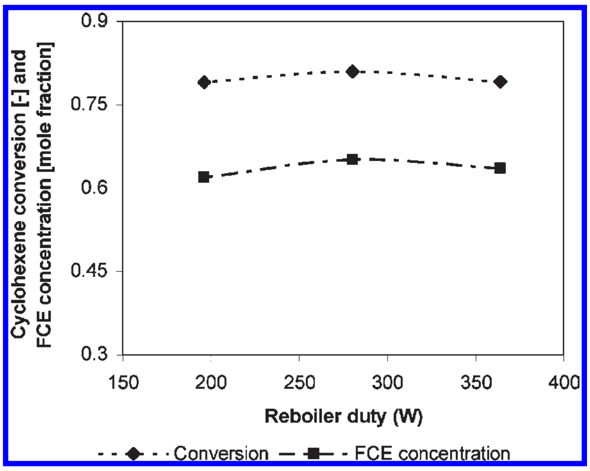

Figure 10. Cyclohexene conversion and FCE purity in the bottom product at different reboiler duties (Table 4: runs 3, 2, 4).

4.1.4. Effect of the Column Pressure. A change in the column pressure leads to a change in the temperature of the system and hence will also affect the reaction rate. The column pressure was changed in such a way that the temperature in the catalytic zone still remains below 60 °C in order to avoid the decomposition of formic acid. With the increase in pressure from 0.50 to 0.55 bar at constant reboiler duty, a slight decrease in conversion and ester purity was observed in the bottom product.

4.2. Comparison of Experimental and Simulation Results.

In addition to the experiments, complementary column simulations for the first process step were performed using an equilibrium stage model based on the MESH equations (mass balance, phase equilibrium, summation equation, and enthalpy balance).[23] The model was implemented in the DIVA simulation environment,[24] and the column parameters were chosen according to the mini plant setup for a comparison of the experimental data with

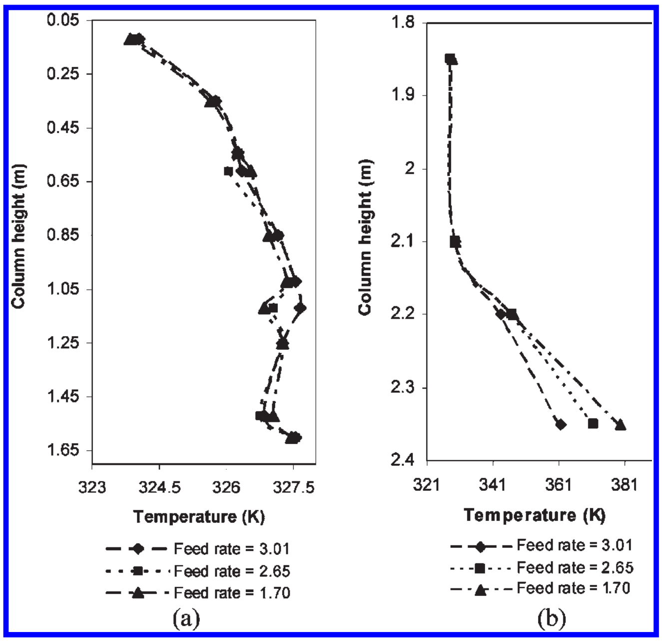

Figure 11. Temperature profile of the column at different feed rates. (a) Catalytic section temperature profile, (b) stripping section temperature profile. (Table 4: runs 2, 6, 7).

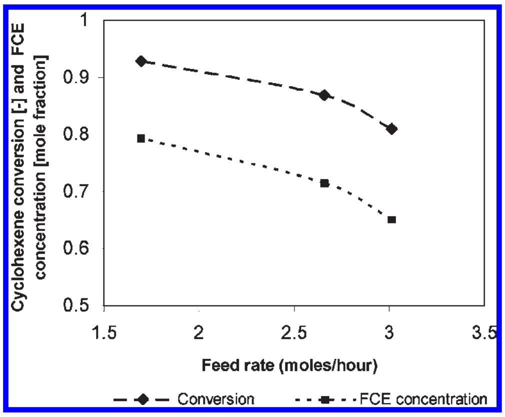

Figure 12. Cyclohexene conversion and FCE purity in the bottom stream at different feed rates (Table 4: runs 2, 6, 7).

simulation results. The equilibrium stage model assumes vapor—liquid and liquid—liquid equilibrium on each stage of the column. The NRTL model was used to describe the liquid-phase nonideality. The binary interaction parameters were determined on the basis of detailed experiments carried out previously in our group.[16] A Langmuir—Hinshelwood (LHHW)-based kinetic model[17] was used to calculate the reaction rate. In addition to our earlier work on the reaction kinetics, we carried out specific batch experiments in order to predict the reaction rate more precisely, especially in the higher temperature range (353—363K) relevant for the comparison in this work. The values for the kinetic parameters adapted on the basis of these additional experiments along with the thermodynamic data are given in Tables 2 and 3. The formic acid decomposition to CO and water was accounted for in the kinetic model.[21] The experimentally validated kinetic model was used in the simulations to predict the reaction rates of the system. More details about the column model for the simulation of the catalytic distillation process can be found in our recent publication.[22]

Table 2. Thermodynamic data used for the computation of the chemical equilibrium constant[17]

	H_f [J/mol]	S_0 [J/mol/K]	C_p [J/mol/K]
cyclohexene	−37820	216.3	148.8
formic acid	−425379	129.0	99.8
cyclohexyl formate	−487129	275.5	219.5
water	−285830	69.9	75.4
cyclohexanol	−351831	203.8	213.6

Table 3. Modified reaction kinetic parameters (adopted from ref 17)

	$k_{f0,hom}$ (1/s)	$E_{f0,hom}$ (J/mol)	$k_{f0,het}$ (mol/kg/s)	$E_{f0,het}$ (J/mol)
cyclohexene hydration	–	–	$3.829708 \times 10^{+11}$	88587
ester from cyclohexene	$1.8830 \times 10^{+07}$	85568	$6.234200 \times 10^{+18}$	85208
ester hydrolysis	$4.6362 \times 10^{+07}$	79111	$7.778133 \times 10^{+10}$	85244

The column conditions for the simulations such as feed flow rate, pressure of the column, heat duty, and other parameter values were chosen according to the conditions in the mini plant experiments. A comparison of experimental and simulation results for the organic phase, the polar phase, and the temperature along the height of the column is shown in Figure 13. The continuous line represents the simulation results, dotted points represent the experimental data, and the shaded area indicates the region of single-phase composition. The steady-state simulation results give a similar trend for the concentration and temperature profile as observed in the experiments. A quantitative comparison of experimental and simulation results of further runs are given in Table 4 in terms of cyclohexene conversion, reboiler composition and reboiler temperature. The experimental data are in good agreement with the simulation results for all the runs, which proves the reliability of our column simulation model and the predictions for the attainable process performance reported in our recent publication.[22]

5. PROCESS STEP 2: HYDROLYSIS OF CYCLOHEXYL FORMATE

In the second process step, the hydrolysis of cyclohexyl formate is carried out in the presence of an acid catalyst to yield cyclohexanol and formic acid, which results in a quaternary mixture in the column. The column configuration used is shown in Figure 14. As mentioned in section 2 regarding the column design for the ester hydrolysis in catalytic distillation, the catalytic zone was kept in the upper section of the column, and the noncatalytic zone was placed in the lower section of the column in order to obtain cyclohexanol as bottom product.

Continuous catalytic distillation experiments were performed with the ester (purity 92.5 mol %) produced in our lab to investigate the technical feasibility of the second step of the process. Cyclohexyl formate, which is a less volatile component, was fed continuously by a pump at the top part of the catalytic section. Water was fed by another pump continuously from the lower part of the catalytic section. The reaction rate of the ester hydrolysis is relatively low compared to the first step (i.e., the ester formation) of the process.[17] In order to achieve appropriate reaction rates in the column, an excess molar amount of water was used in the feed of the ester hydrolysis column. Cyclohexanol is formed in the catalytic section and flows towards the bottom of the column. The bottom product stream

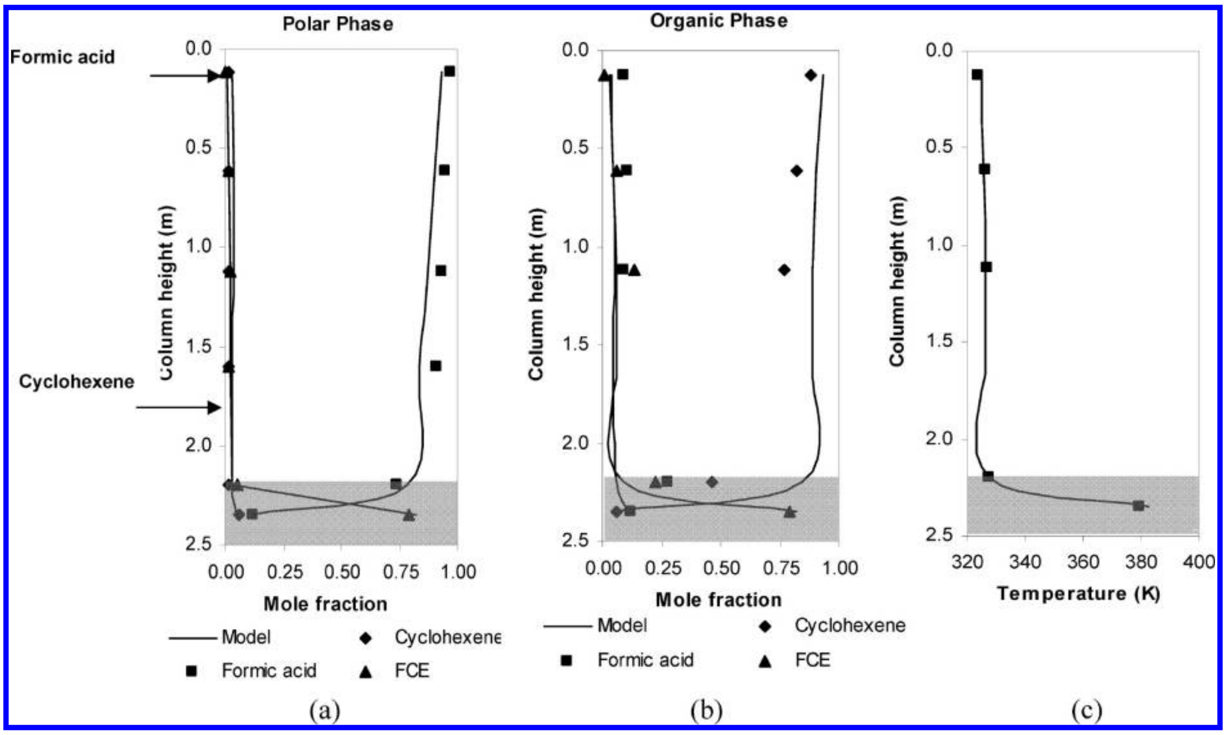

Figure 13. Comparison of experimental and simulation results for the ester formation column from cyclohexene and formic acid. (a) Polar-phase composition profile, (b) organic-phase composition profile, (c) temperature profile of column. The shaded area represents the single-phase composition region.

Table 4. Comparison of experimental and simulation results for different runs for the first process step

	run 1		run 2		run 3		run 4		run 5		run 6		run 7	
column parameters	exp.	model	exp.	model	exp.	model	exp.	model	exp.	model	exp.	model	exp.	model
cyclohexene feed rate (mol/h)	3.07	3.07	3.01	3.01	3.08	3.08	3.07	3.07	3.09	3.09	2.65	2.65	1.70	1.70
feed mole ratio (FA:Cyclohexene)	1.14	1.14	1.02	1.02	1.00	1.00	1.00	1.00	1.23	1.23	1.01	1.01	1.07	1.07
pressure (bar)	0.52	0.52	0.52	0.52	0.52	0.52	0.52	0.52	0.52	0.52	0.52	0.52	0.52	0.52
reboiler temperature (K)	370.5	371.8	361.6	361.1	362.7	363.0	356.9	356.1	382.0	380.5	371.5	371.7	379.7	379.5
conversion (%)	90.4	88.2	82.0	80.9	79.1	80.0	79.1	78.2	98.3	95.3	86.8	84.7	92.7	91.8
Bottom Stream Composition (Mole Fraction)														
cyclohexene	0.075	0.094	0.153	0.158	0.170	0.167	0.170	0.179	0.013	0.036	0.110	0.131	0.064	0.071
formic acid	0.198	0.194	0.175	0.163	0.175	0.157	0.185	0.167	0.210	0.212	0.151	0.135	0.110	0.123
FCE	0.693	0.694	0.650	0.659	0.635	0.657	0.620	0.635	0.755	0.740	0.714	0.710	0.793	0.769
water	0.008	0.007	0.007	0.006	0.007	0.007	0.007	0.005	0.009	0.005	0.008	0.012	0.001	0.024
cyclohexanol	0.025	0.010	0.012	0.013	0.012	0.012	0.018	0.014	0.014	0.006	0.014	0.011	0.013	0.012

containing cyclohexanol and unreacted cyclohexyl formate is removed continuously to maintain a constant holdup inside the reboiler. The distillate product containing a biphasic mixture of formic acid, water, and unreacted ester was collected in an accumulator. Initially both phases of the distillate were removed as top product. At this point, however, it has to be considered that the back splitting of the ester to cyclohexene and formic acid also takes place in the second column. This increases the complexity of this process step with regard to kinetics as well as thermodynamics. Since the removal of both phases from the distillate leads to a higher decomposition rate of cyclohexyl formate in the column, only the polar phase of the distillate was removed as top product by the pump while the organic phase was recycled back to the column. That way, the decomposition rate of the ester could be minimized and the conversion of the ester for cyclohexanol production could be improved. Under steady-state conditions, samples were collected at different positions along the column and analyzed by GC.

5.1. Results and Discussion. Steady-state composition profiles of the organic phase, the polar phase and the temperature are shown in Figure 15. Experimental details about the column are given in Table 5. Due to the presence of excess amount of water in the column, a biphasic composition is obtained in the catalytic section and in the upper part of the noncatalytic section of the column. As the concentration of water decreases in the lower section and in the reboiler part of the column, a single-phase composition is obtained. The shaded area in Figure 15 represents the single-phase composition region of the column. It can be seen from the organic composition profile (Figure 15a) that cyclohexyl formate is the major component in the catalytic section of the column as it is fed from the top part of the column. The cyclohexyl formate concentration decreases towards the bottom part of the catalytic section due to its reaction with water in the presence of Amberlyst-15 catalyst. In the noncatalytic section of the column, the ester concentration increases because the lower-boiling components formic acid and water are gradually stripped out. As mentioned before, the back splitting of cyclohexyl formate into cyclohexene and formic acid is also a competitive reaction in the second step of the process. This back splitting of the ester was observed in the catalytic section of the column from analysis of the column experiments. In the polar-phase profile, the water concentration decreases in the catalytic section while the concentration of formic acid, being produced by the back splitting reaction, increases. In the noncatalytic section, the large boiling point difference of water and formic acid from cyclohexyl formate and cyclohexanol leads to a sharp separation of the components; hence, the concentration of water and formic acid decreases drastically in the stripping zone, while the concentration of cyclohexanol and cyclohexyl formate increases. It can be seen from Figure 15 that there is a slight deviation in the trends of the temperature and the composition profile of the stripping section. This was because only a limited number of samples were taken from the stripping section. The actual representation of the stripping section profile may slightly differ depending on the number of samples that are taken from this section. The temperature in the lower part of the noncatalytic section and in the reboiler of the column increases due to an increase in the concentration of high-boiling components (cyclohexyl formate and cyclohexanol).

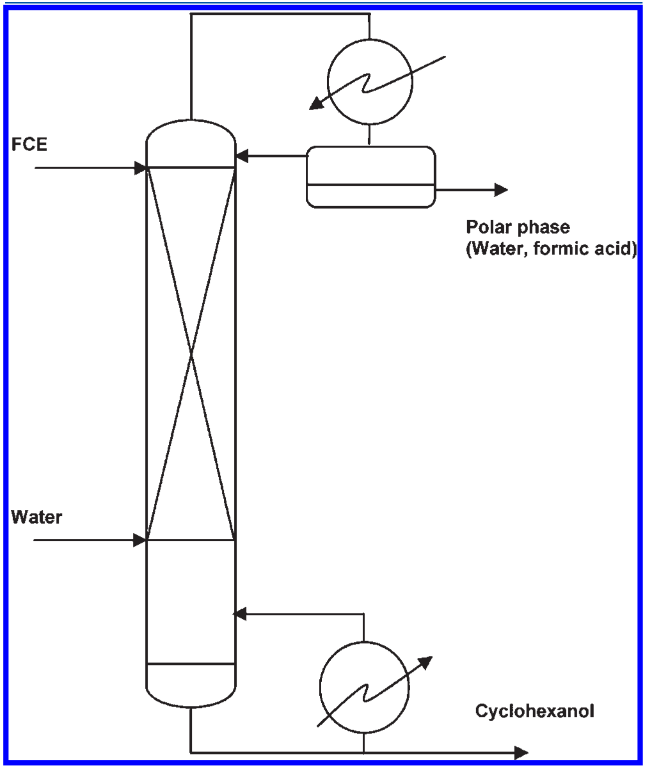

Figure 14. Column configuration for the hydrolysis of cyclohexyl formate (FCE).

Under steady-state conditions, 51% conversion of cyclohexyl formate and about 50% purity of cyclohexanol in the bottom stream could be achieved. At this point it should be noted that the column setup used in the experiments is part of a multipurpose mini plant that is not optimized for this particular process step. Although design considerations from the feasibility simulation studies[18] with regard to the placement of the catalytic section

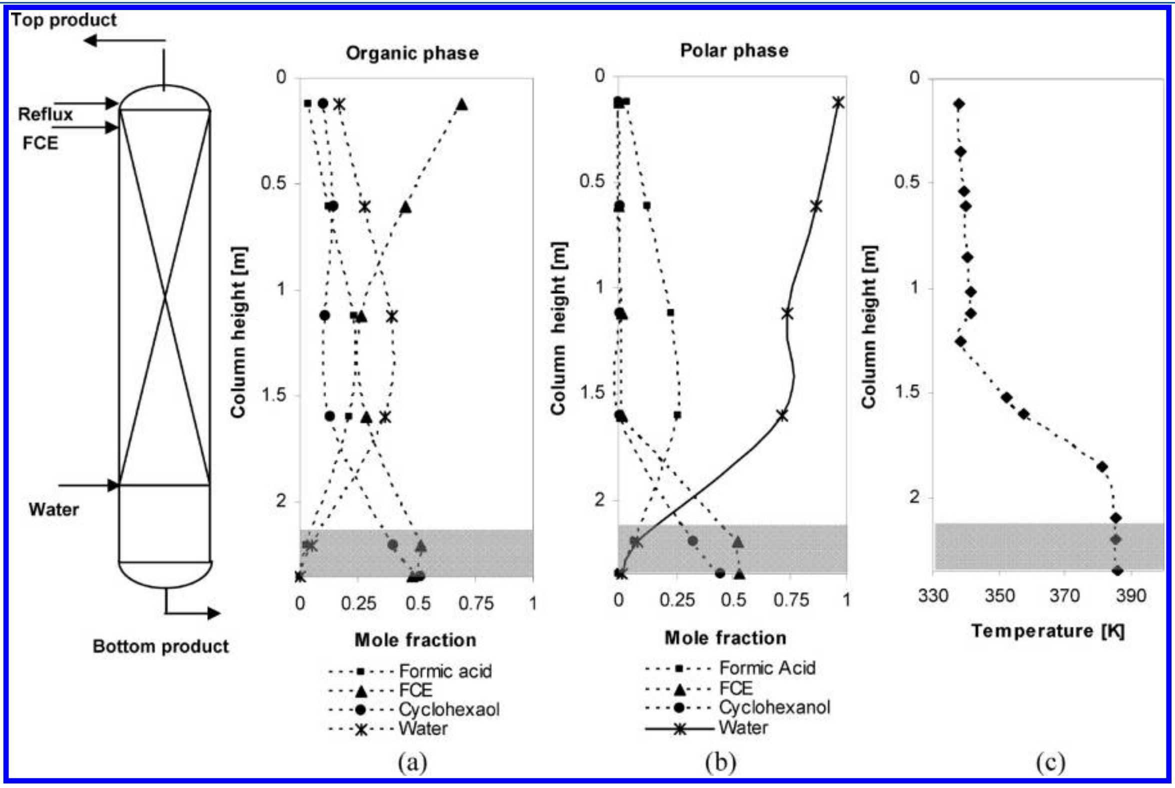

Figure 15. Steady-state composition and temperature profiles of the column for the hydrolysis of the ester (FCE). (a) Organic-phase composition profile, (b) polar-phase composition profile, (c) temperature profile. The shaded area represents the single-phase composition region.

Table 5. Experimental details for the hydrolysis of the ester (FCE)

column parameters	run 1	run 2
cyclohexyl formate (FCE) feed rate (g/h)	105.0	105.8
water feed rate (g/h)	124.0	129.5
FCE feed composition (mole fraction)		
cyclohexene	0.001	0.001
formic acid	0.001	0.001
cyclohexyl formate (FCE)	0.925	0.925
water	0.035	0.035
cyclohexanol	0.035	0.035
reboiler duty (W)	700.0	700.0
pressure (bar)	0.25	0.30
feed temperature (K)		
water	303.0	303.0
cyclohexyl formate (FCE)	313.0	313.0
bottom stream flow rate (g/h)	99.0	100.3
bottom product composition (mole fraction)		
cyclohexene	0.000	0.000
formic acid	0.000	0.000
cyclohexyl formate (FCE)	0.533	0.485
water	0.018	0.000
cyclohexanol	0.448	0.515
distillate product composition (mole fraction)		
cyclohexene	0.008	0.000
formic acid	0.040	0.033
cyclohexyl formate (FCE)	0.001	0.001
water	0.959	0.966
cyclohexanol	0.000	0.000
cyclohexyl formate conversion (%)	45.4	50.5
reboiler temperature (K)	386.1	391.4

have been taken into account, the column configuration is by far not optimized (e.g., owing to the limited amount of space available for the catalytic section). This is the reason for the relatively low values for the conversion of the ester and the cyclohexanol purity in the bottom product in the experiments. Nevertheless, the results of the experiments are sufficient for the intended purpose of demonstrating the technical feasibility of the individual steps of the novel process scheme. The optimization of the process can preferably be performed by simulations rather than by experiments. The results of our simulation studies[22] revealed that under optimal conditions nearly full conversion of cyclohexene to cyclohexanol with a purity of >99 mol % in the bottom stream of the second column can be achieved.

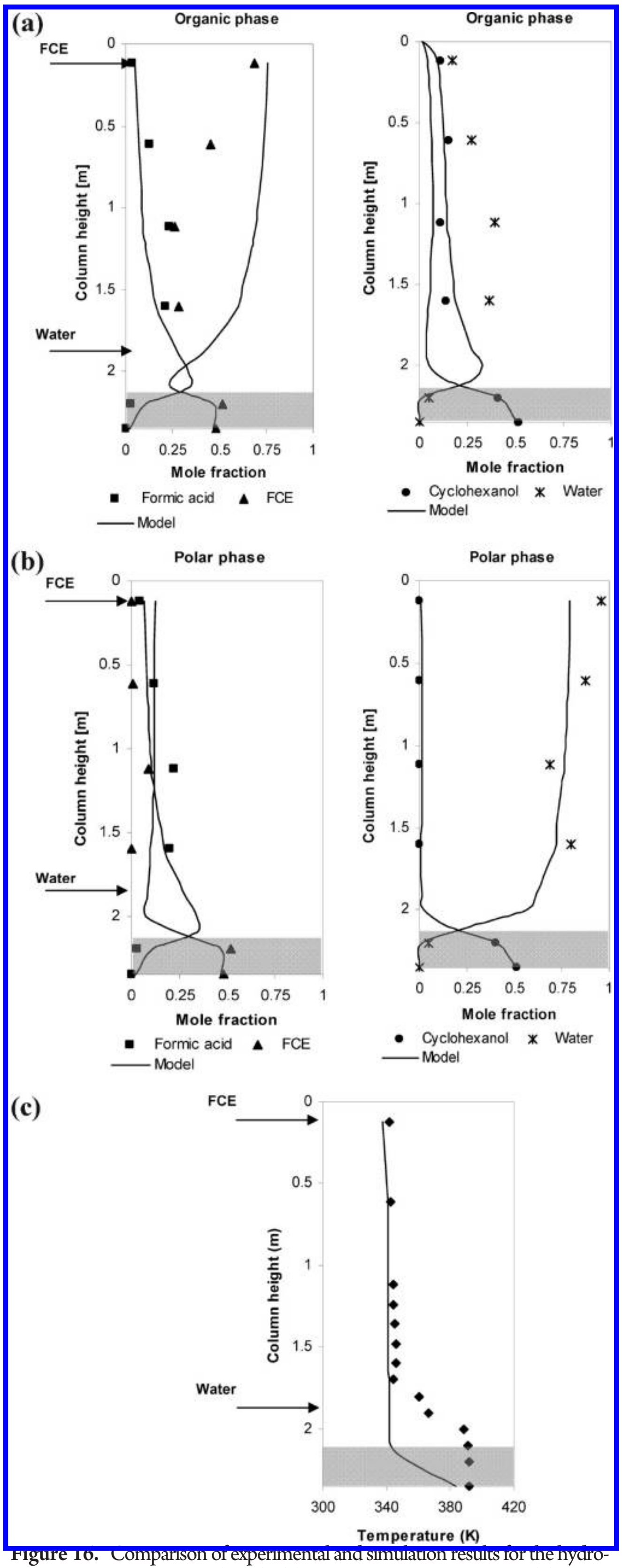

Figure 16. Comparison of experimental and simulation results for the hydrolysis of cyclohexyl formate (FCE). (a) Organic-phase composition. (b) Polar-phase composition. (c) Temperature profile. The shaded area represents the single-phase composition region.

The polar phase of the distillate product contains about 96 mol % water and 4 mol % formic acid. The column pressure was increased from 0.52 to 0.55 bar to investigate its effect on the ester conversion and cyclohexanol purity. The other operating parameters such as feed flow rate, heat duty and distillate rate were kept constant during the run. Under steady-state conditions with an increase in the column pressure, the temperature in the catalytic section increases. This results in an increase in the conversion of cyclohexyl formate and in the cyclohexanol purity in the bottom stream of the column. The effect of the column pressure was not investigated further because an additional increase in the column pressure (>0.55 bar) would lead to an increase in the reaction temperature beyond the desired operation limits of the system. The activity of the Amberlyst-15 catalyst packed into the catalytic structured column packings was checked after the whole measure-

Table A1. Experimental details for the synthesis of FCE from cyclohexanol

column parameters	values
cyclohexanol feed flow rate (g/h)	292.0
formic acid feed flow rate (g/h)	290.1
feed mole ratio (FA:cyclohexanol)	2.92
reboiler duty (W)	728
pressure (bar)	0.31
feed temperature (K)	
cyclohexanol	323.0
formic acid	313.0
reflux temperature	318.0
bottom stream composition (mole fraction)	
cyclohexene	0.000
formic acid	0.000
cyclohexyl formate (FCE)	0.960
water	0.000
cyclohexanol	0.032
distillate composition (mole fraction)	
cyclohexene	0.007
formic acid	0.584
cyclohexyl formate (FCE)	0.068
water	0.330
cyclohexanol	0.006
distillate flow rate (g/h)	291.0
reboiler temperature (K)	394.4
distillate temperature (K)	341.9

ment campaign has been accomplished. Compared to the initial value, a decrease in activity by 18−20% could be observed by ex-situ analysis via titration.

5.2. Comparison of Experimental and Simulation Results.

The comparison of the concentration and temperature profile of the ester hydrolysis column obtained from experimental data and simulation results is based on the same column model as described in section 4.2. In the mini plant experiments it was observed that the back splitting reactions of cyclohexanol to cyclohexene and water and of cyclohexyl formate to cyclohexene and formic acid was negligible in presence of water. Due to the low value of the rate constant for the back splitting reaction of cyclohexanol and of cyclohexyl formate, respectively, these reactions were neglected in the kinetic model used in the simulations. In the column simulations, the catalyst deactivation that was observed (see section 5.1) was taken into account for the comparison with the experimental results. The composition profile of the organic phase, the polar phase, and the temperature profile of the column are shown in Figure 16. The polar-phase concentration profiles of experimental and simulation results are in relatively good agreement. The organic-phase composition profile of the simulation results gives a similar trend compared to the experimental results; however, a significant deviation exists in the top part of the column and also for the temperature in the bottom part of the column. Due to the presence of polar and nonpolar components and multiple reactions in the second column of the process, it is difficult to predict the exact concentration profile in the individual phases of the column using an equilibrium stage model. Actual mass transfer between the vapor- and the liquid phase under liquid−liquid phase-splitting conditions differ from the assumptions in the equilibrium stage model, which is the reason for the deviation. Since the system in the second process step is in reality a six-component system and thus much more complex with regard to thermodynamics and kinetics compared to the first process step, the deviations of the simulations from the experiments are larger. Nevertheless, the experimental results for the second process step also prove the principle technical feasibility of the individual steps of the novel process scheme.

6. CONCLUSIONS

As a promising alternative to the conventional processes for cyclohexanol production, a two-step catalytic distillation process for the indirect hydration of cyclohexene to cyclohexanol is proposed. With this process scheme, the overall reaction rate for the cyclohexanol production can be improved by orders of magnitude when compared to the process based on the direct hydration of cyclohexene. In our previous work,[18] we have already proven the principle feasibility of the process concept by means of simulation studies. With this present work, we experimentally validate our simulation studies and demonstrate the technical feasibility of both steps of the novel process concept for the first time at the mini plant scale.

For the first step of the process (i.e., the ester formation from cyclohexene and formic acid), the effect of suitable operating parameters such as the feed mole ratio of the reactants, the reboiler duty, the feed rate, and the column pressure on the column performance are investigated. Furthermore, a comparison of the column concentration profiles and the temperature profile obtained from experiments with that obtained from the simulations is performed and reveals a good agreement. In a similar manner, experiments were carried out in the second catalytic distillation column where the hydrolysis of the ester to cyclohexanol and formic acid takes place. That way, the technical feasibility was also demonstrated for the second step of the process. The simulation results for the second process step gave similar trends when compared to the steady-state experimental data.

To sum up, the present contribution is an important step in our work on the development of a novel catalytic distillation process for the production of cyclohexanol, since it confirms our previous feasibility simulation studies by demonstrating also the principle technical feasibility of the individual process steps via experiments. In addition, since the experiments were carried out at the mini plant scale, the work bridges between the simulation studies and lab-scale experiments on the one hand and the industrially relevant production scale on the other hand. The full potential of this novel process concept, i.e. high conversion in combination with high selectivity, has been reported in our recent publication.[22] It still has to be investigated in more detail whether the optimal results from these simulation studies can be realized experimentally. For demonstrating the technical feasibility of the process concept, experiments with the coupled column process scheme under industrial conditions including all recycle streams would have to be carried out. On the basis of our process simulations[22] with the column model now being validated experimentally, it should be possible to obtain nearly 100% conversion of cyclohexene and more than 99 mol % purity of cyclohexanol with the new coupled catalytic distillation process scheme.

■ APPENDIX: CYCLOHEXYL FORMATE SYNTHESIS FROM CYCLOHEXANOL

Cyclohexyl formate had to be prepared in the lab because it is not commercially available. It was synthesized in a continuous catalytic distillation column by reacting cyclohexanol with formic acid in the presence of an acidic catalyst. A detailed description of the equipment is given in section 3.3. Since cyclohexanol is in the solid state at room temperature, it was preheated to 50°C to maintain it in the liquid state. The column feed lines were externally heated in order to prevent a blockage inside the line. Preheated cyclohexanol (50°C) was fed continuously by pumps to the top part of the catalytic section. Formic acid was fed continuously in slight excess molar amount from the bottom part of the catalytic section. Cyclohexyl formate was produced in the catalytic section of the column in the presence of the acidic ion-exchange resin Amberlyst-15. The bottom product that contains mostly cyclohexyl formate was removed continuously. The distillate product contains mostly water and formic acid and was pumped out. The experiments were performed under low pressure and temperature conditions to avoid formic acid decomposition as well as the formation of side products (e.g., dicyclohexyl ether). The column conditions and the results under steady-state conditions are given in Table A1. About 96 mol % purity of the ester was obtained in the bottom product stream. The experiments were continued under steady-state conditions for a long time (>4 weeks) to obtain the required amount of ester.

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NOMENCLATURE

C_p = molar heat capacity (J/mol/K)
$E_{f0,het}$ = activation energy of heterogeneous reaction (J/mol)
$E_{f0,hom}$ = activation energy of homogeneous reaction (J/mol)
FCE = cyclohexyl formate (ester)
FA = formic acid
H_f = standard enthalpy of formation (J/mol)
$k_{f0,het}$ = kinetic forward reaction rate constant for heterogeneous reaction (mol/kg/s)
$k_{f0,hom}$ = kinetic forward reaction rate constant for homogeneous reaction (1/s)
S_0 = standard entropy of formation (J/mol/K)

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