

## Hydration of Cyclohexene to Cyclohexanol in a Hybrid Reactive Distillation with a Side Decanter

Ivan Marchante<sup>a</sup>, Alexandra Elena Bonet Ruiz<sup>a,\*</sup>, Valentin Plesu<sup>b</sup>, Jordi Bonet-Ruiz<sup>a</sup>, Petrica Iancu<sup>b</sup>, Joan Llorens<sup>a</sup>

<sup>a</sup>University of Barcelona, Department of Chemical Engineering, 1, Martí i Franquès Street, E-08028 Barcelona, Spain

<sup>b</sup>University POLITEHNICA of Bucharest, Centre for Technology Transfer in Process Industries (CTTPI), 1, Gh. Polizu Street, RO-011061 Bucharest, Romania  
 abonetrui@ub.edu

Nowadays, more than 1 Mt of cyclohexanol is produced each year by the direct hydration of cyclohexene according to the patented Asahi process proposed in 1990. The Asahi process involves a reactor and a separation system to recover the reactants back to the reactor and collect the pure product. The non-reacted water is recovered in a decanter and the non-reacted cyclohexene in a distillation column. Nowadays, many processes have been successfully intensified, combining several unit operations into a single unit providing savings in units, piping and often also in energy due to the synergies generated. Examples of these synergies are: the continuous removal of products push forward the reaction to total conversion overcoming the chemical equilibrium limitations; the catalyst placed in the rectifying section of the column becomes protected from heavy compounds that could poison or deactivate the catalyst; the enthalpy of reaction is directly used in the separation; the boiling point of the mixture avoids hot spots that could damage the catalyst, etc. Although its advantages, it is not widely used in the industry and further study on intensification providing further successful examples are required.

The present study shows by rigorous simulation with Aspen Plus V9.0 that the Asahi process is a good candidate to be intensified in a single unit. The rigorous simulation results show that cyclohexanol is collected with a molar fraction purity of 0.9999 at the bottoms of a hybrid reactive distillation column with 11 equilibrium stages operated at total reflux, i.e. total conversion of reactants. The water is fed at the top to stage 1 and the cyclohexene on stage 3, both in equimolar flow rate. The catalyst is only placed in these three stages at the column top. A side stream from stage 6 is fed to a side decanter, where the aqueous phase is recycled to the column top (stage 1) and the organic phase to the next bottom stage, i.e. stage 7. As in the Asahi process, a great excess of water is present to push the reaction equilibrium forward. Hence, the molar ratio of water recycled vs feed to the system is of 125. The reboiler duty is 197 kJ/mol of cyclohexene, and the condenser duty is 564 kJ/mol cyclohexene due to the exothermic reaction. Therefore, a novel intensified process scheme for cyclohexene hydration is proposed.

### 1. Introduction

In 1990, Asahi patented and commercialized a process to produce cyclohexanol with a 100 t/y plant in Japan, and it is still the process used nowadays in the industry. The process involves three primary steps: the selective hydrogenation of benzene; the separation of the cyclohexene from the unconverted benzene and the over-hydrogenation product cyclohexane; and the hydration of the cyclohexene. The hydrogenation is carried out with a specially prepared heterogeneous nickel catalyst. The reaction is run to about 50 % conversion, at which point the product consists of about 35 % cyclohexene, 15 % cyclohexane, and 50 % unconverted benzene. The mixture of cyclohexane, cyclohexene and benzene cannot be distilled but must go through two successive extractive distillations. The hydration of cyclohexene is also performed with a heterogeneous catalyst in a slurry reactor. The extent of hydration is limited by the equilibrium constant to about 14 %. The use of several additives to increase the conversion of cyclohexanol has also been patented. The yield of this process from benzene to

cyclohexanol is extremely high, probably greater than 95 %. The present study focuses on the last step: the direct hydration of cyclohexene.

The Asahi process (Figure 1) is composed of a reactor, a decanter and a distillation column. According to the stoichiometry, an equimolar amount of cyclohexene (b.p. 83 °C) and water (b.p. 100 °C) are feed to the process and in a reactor are converted to cyclohexanol (b.p. 162 °C). Taking advantage of the phase immiscibility of the reactor output stream, an aqueous phase is split in a decanter and recirculated to the reactor where an excess of water reactant is present. The organic phase is distilled collecting cyclohexanol at the bottoms and the non-reacted cyclohexene in the distillate that is also recirculated to the reactor. Although the distillation is not complicated due to the high difference in their volatilities, a very high flow rate stream is recirculated due to the low conversion in the reactor, consequence of chemical equilibrium.

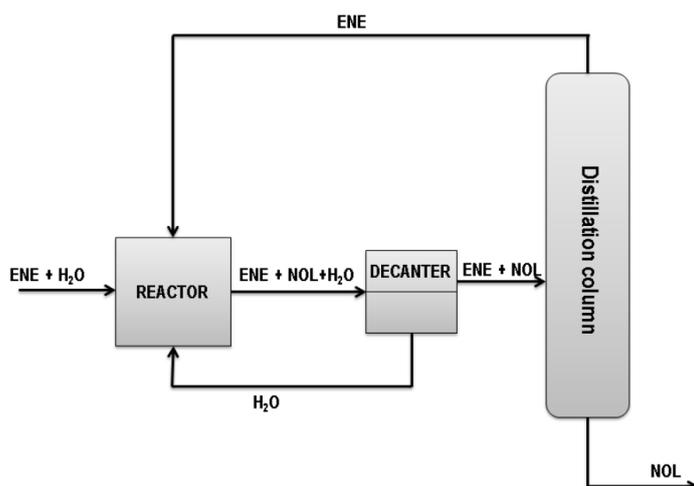


Figure 1: Asahi process scheme to cyclohexene hydration to cyclohexanol

Reactive distillation where reaction and distillation are performed in a single reactive distillation unit seems a suitable choice because the continuous separation product by distillation shifts the reaction to a total conversion. It is an exothermal reaction, and the energy liberated helps to evaporate the liquid phase and the product is less volatile than the reagents and is expected to be collected at the bottom. Steyer et al. (2008) proposed reactive distillation using formic acid as a reactive entrainer. Other authors also tried to increase the conversion using different solvents for reactive distillation, e.g. 1,4-dioxane (Qiu et al., 2013), or adding a side reactor to the reactive distillation column (Ye et al., 2014). Chen et al. (2014) also used reactive distillation and concluded that it is necessary to use an excess of water and to take advantage of the phase split using decanters at the reactive distillation output streams. Zhen et al. (2017) proposed a process scheme that includes a reactive distillation column using isophorone as an extractive agent. The process also includes two decanters and two distillation columns and therefore is more complex than the Asahi process scheme. The effect of the pressure on the separation has also been considered (Tian et al., 2018). The aim of the present study is to study the intensification of the cyclohexanol production process by reactive distillation in a single distillation unit.

## 2. Residue curve map

The residue curve map (RCM) provides an insight into the thermodynamic behaviour of the mixture. RCM is a useful tool to identify feasible process schemes. The RCM of the mixture cyclohexene (ENE), water and cyclohexanol (NOL) presents two distillation regions divided by a boundary line between the binary azeotrope water-ENE and the binary azeotrope water-NOL (Figure 2). The binary azeotrope water-ENE is the common unstable node for both regions what means that when this composition is collected by the distillate, then the bottoms is feasible anywhere in the map according to the  $\infty/\infty$  analysis (obviously the mass balances must also be fulfilled). NOL is the stable node of the wider distillation region, and a large immiscibility region is generated between water (aqueous phase) and ENE (organic phase).

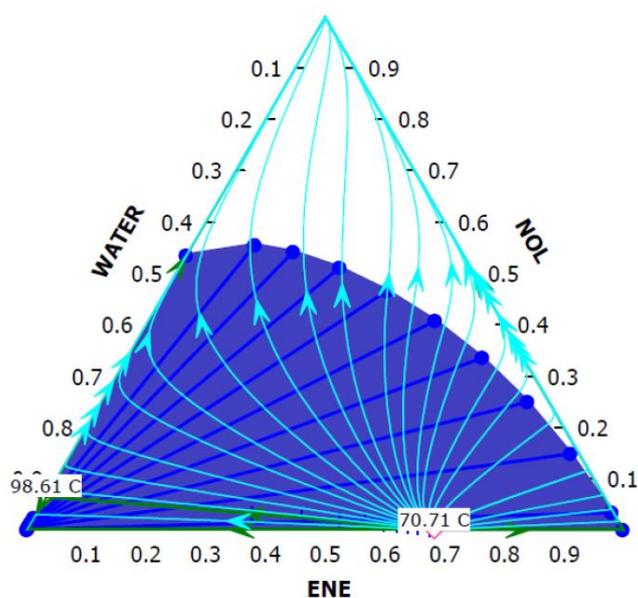


Figure 2: Residue curve map of the system water, cyclohexene (ENE) and cyclohexanol (NOL) (1), molar parts

### 3. Methodology

The selected chemical process is rigorously simulated using Aspen Plus® v9.0 with the thermodynamic model NRTL (Table 1) assuming that the chemical reaction reaches the chemical equilibrium (minimizing the Gibbs energy).

Table 1: NRTL parameters used in the simulation

Component i	Component j	$A_{ij}$	$A_{ji}$	$B_{ij}$ (K)	$B_{ji}$ (K)	Alpha
ENE	H <sub>2</sub> O	0	0	1,705	2,609.45	0.267
NOL	H <sub>2</sub> O	0	0	160.78	1,318.19	0.360
ENE	NOL	0	0	429.31	0.1158	0.803

### 4. Results

A novel and simple process scheme of a reactive distillation column operated at total reflux with a side decanter at the middle of the column is proposed. A side decanter allows to separate an organic phase, that is returned again to the column to the plate under the decanter feed, and an aqueous phase stream that is fed at the upper stage of the reactive distillation column. The column has three sections: the upper section rich in reactants is where the reaction takes place, the section between the crude feed and the decanter is used to return the non-reacted cyclohexene to the reactive zone, and the lower part under the decanter is where the cyclohexanol is purified. Cyclohexanol is collected pure at the bottoms. Figure 3 shows the optimized process scheme results, whose molar flows and molar fraction composition in each stream are provided in Table 2.

The column has 11 stages but only requires three reactive stages at the upper section. The side decanter is placed in the middle of the column, i.e. connection to stage 6. The streams table shows that although the crude feed of the column is equimolar (streams 1 and 2), there is a very large amount of water being recirculated inside the column, i.e. stream 4. The molar ratio of water recycled vs feed to the system is of 125. The water is the reagent in excess because it is the cheapest and safest and also in the Asahi process, water is in excess. The reactants have a counter-current flow: the water is heavier and has a descendant flow from the stage 1 to stage 6, and the cyclohexene is lighter and has an ascendant flow to the top stages where the complete reaction takes place. The organic phase from the decanter, i.e. stream 5, is mainly composed of more than the half by cyclohexene, a little part of water and the rest of cyclohexanol. The cyclohexanol pure collected at the column bottoms has a molar fraction higher than 0.9999. The reboiler duty is 197 kJ/mol, and the condenser duty is 564 kJ/mol due to the exothermal reaction. The reboiler duty represents only 10 % of the energy requirements of the process proposed by Zhen et al. (2017). There is a great synergy between reaction and distillation: the

distillation allows the reaction to overcome the chemical equilibrium and allows good control of the reaction temperature due to the evaporation. Also, the exothermal reaction allows energy saving for the distillation operation as the enthalpy of reaction is directly used by the distillation. Consequently, the condenser duty is much larger than the reboiler duty. Another advantage is related to the catalyst lifetime. If the cyclohexene contains some heavy organic compounds that could poison the catalyst, as the catalyst is located above this feed stream, then these compounds do not reach so easily the catalyst and then its lifetime becomes extended.

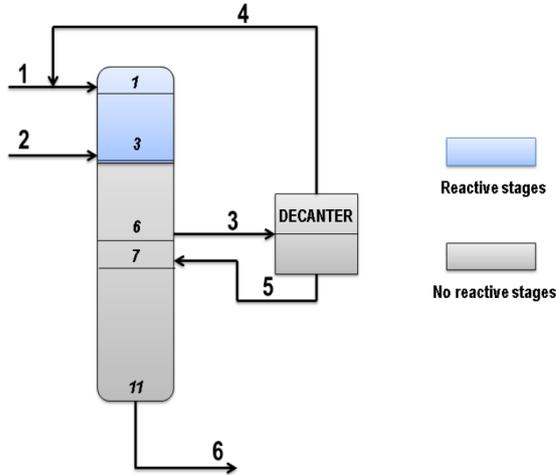


Figure 3: Novel process scheme to hydrate cyclohexene (ENE) to cyclohexanol (NOL)

Table 2: Molar flows and molar fraction composition in each stream of the novel process scheme

Streams	$W_{ENE}$ (kmol/h)	$W_{WATER}$ (kmol/h)	$W_{NOL}$ (kmol/h)	$X_{ENE}$ (1)	$X_{WATER}$ (1)	$X_{NOL}$ (1)	T (°C)
1	0	5.00	0	0	1.00	0	99.65
2	5.00	0	0	1.00	0	0	82.44
3	10.90	624.4	8.88	0.0169	0.9693	0.0138	11.51
4	0.022	622.2	1.58	$3.5 \cdot 10^{-5}$	0.9974	0.0025	13.70
5	10.87	2.16	7.30	0.5350	0.1060	0.359	13.70
6	$0.29 \cdot 10^{-4}$	$5.2 \cdot 10^{-7}$	5.00	$5.790 \cdot 10^{-5}$	$1.05 \cdot 10^{-7}$	0.99994	160.38

Figure 4 shows that the temperature is not increasing monotonically from the bottom to the distillate along the column. This is a consequence of the changes of composition due to feeds (stages 1, 3 and 7), side streams (stage 6) and reaction that produces compositions fluctuations whose boiling points do not increase monotonically.

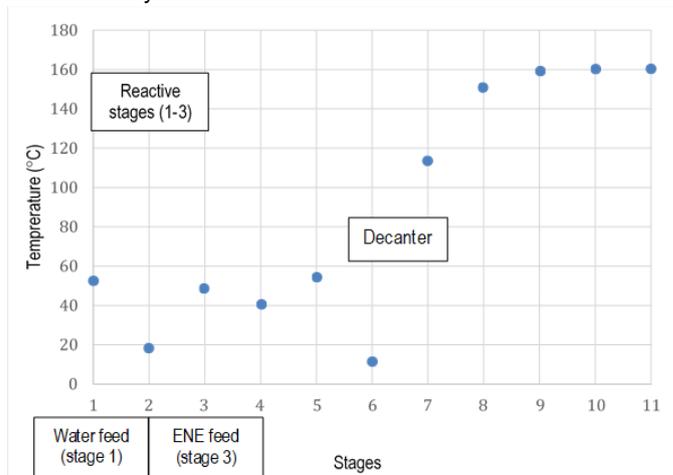


Figure 4: Novel process scheme distillation temperature profile

Figure 5 shows a clear tendency at the lower section to increase the cyclohexanol (NOL) purity and a low amount of water that has been eliminated in the decanter. The mole fractions of NOL in the other distillation column sections are very low, although it is generated by the reaction in the three first stages. Water is the main compound in the two upper sections in the liquid phase, as mentioned previously in the last paragraph, and the fluctuations of the cyclohexene concentrations, that affect the temperature profile, are clearly observed. Cyclohexene (ENE) is the main compound in the two upper sections in the vapour phase, as it is the lightest compound (Figure 6).

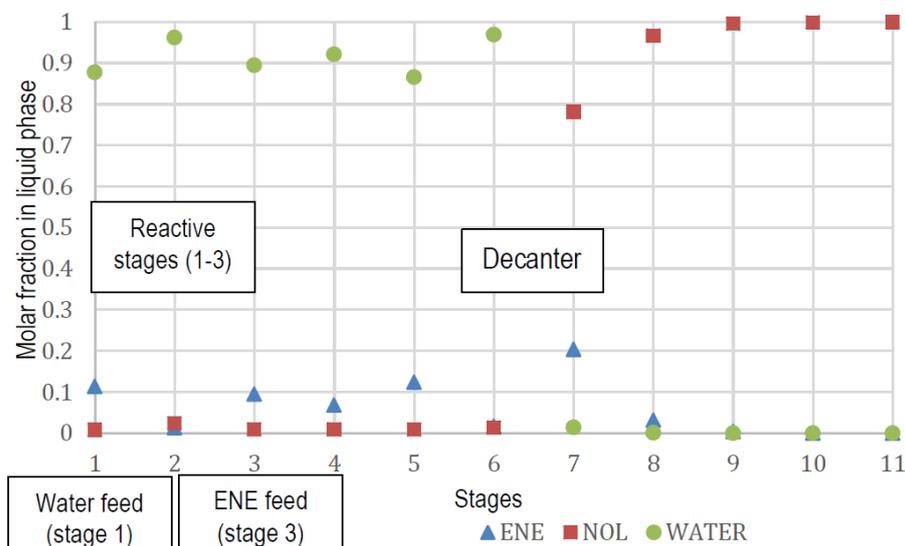


Figure 5: Novel process scheme distillation liquid composition profile

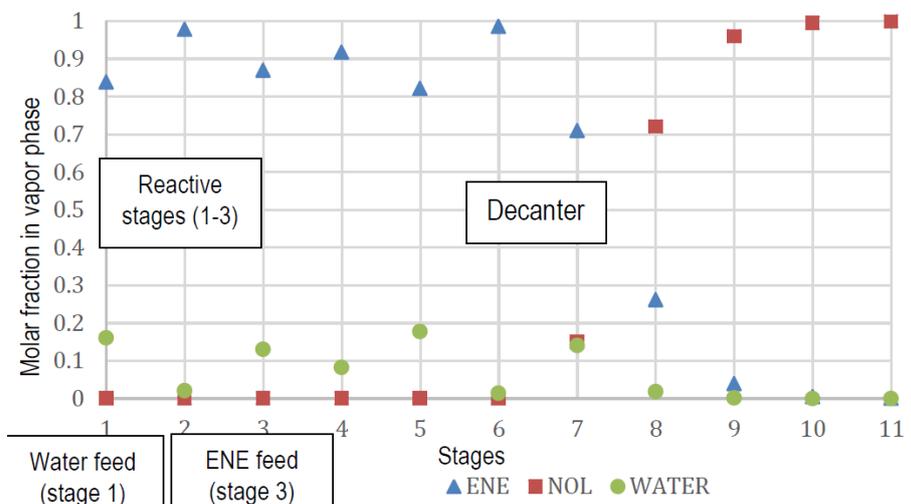


Figure 6: Novel process scheme distillation vapour composition profile

Comparing the column profiles compositions (Figure 5) with the residue curve map (Figure 2), it is observed that the upper stages compositions rich in water are in the distillation region whose stable node is the water meanwhile the lower stages composition are in the distillation region whose stable node is the cyclohexanol. The change from one distillation region to another takes place between the stages 6 and 7, i.e. where the decanter is located.

According to the feasibility analysis of distillation, the boundary lines cannot be crossed. However, in this example, Figure 2 illustrates that stages 6 and 7 are located in different distillation regions, meaning that the boundary line has been crossed. In this case, this situation is possible as the side decanter configuration allows to perform this separation. Otherwise, without taking advantage of the phase split region and the decanter, when

collecting a mixture rich in cyclohexanol in the bottoms of the distillation column, only a mixture with a composition close to the azeotrope cyclohexene-water can be collected in the distillate, not close to mixtures where the water is the main compound. The decanter removes a large amount of water and the mixture composition moves to the other distillation region.

## 5. Conclusions

Nowadays, the Asahi process is used for the direct hydration of cyclohexene to produce cyclohexanol. Although this process has a lot of characteristics like the reaction is an equilibrium and the reagents have bigger relative volatilities than the desired product and can be separated easier, the use of a reactive distillate column improves the conventional design. The results obtained in the rigorous simulation of the new design show less energetic requirements than the Asahi and the isophorone process. The Asahi design consumes more energy due to the necessity of unreacted reagents recycle. More recent process schemes using reactive distillation such as the isophorone design require several distillation columns, and all the cyclohexanol produced has to leave the system by the top of the last column as distillate. In opposition to these processes, the new design consists of only has one reactive distillation column, constant recycle of unreacted reagents to a previous reactor is not necessary and all the cyclohexanol formed is collected at the bottom stream of the distillation column.

## Acknowledgements

The authors would like to thank the financial support of the project CTM2016-76275-R (Ministry of Economy, Industry and Competitiveness –Spanish Government) who provided the opportunity to complete this research. Two authors (VP and PI) are grateful for the financial support received in the framework of structural project POC P\_37\_449 contract 155/25.11.2016, code MySMIS 107714.

## References

- Chen B.-C., Yu B.-Y., Lin Y.-L., Huang H.-P., Chien I.-L., 2014. Reactive-distillation process for direct hydration of cyclohexene to produce cyclohexanol, *Industrial and Engineering Chemistry Research*, 53(17), 7079-7086.
- Qiu T., Kuang C.-H., Li C.-G., Zhang X.-W., Wang X.-D., 2013. Study on feasibility of reactive distillation process for the direct hydration of cyclohexene to cyclohexanol using a cosolvent. *Industrial and Engineering Chemistry Research*, 52(24), 8139-8148.
- Steyer F., Freund H., Sundmacher K., 2008. A novel reactive distillation process for the indirect hydration of cyclohexene to cyclohexanol using a reactive entrainer. *Industrial and Engineering Chemistry Research*, 47(23), 9581-9587.
- Tian H., Sun J., Du Y., Xu W., 2018. Vapor-Liquid Phase Equilibrium of a Cyclohexene + Water + Cyclohexanol + Isophorone Quaternary System at 500 kPa. *Journal of Chemical and Engineering Data*, 63(11), 4020-4023.
- Ye J., Li J., Sha Y., Lin H., Zhou D., 2014. Evaluation of reactive distillation and side reactor configuration for direct hydration of cyclohexene to cyclohexanol, *Industrial and Engineering Chemistry Research*, 53(4), 1461-1469.
- Zheng H., Lin M., Qiu T., Shen Y., Tian H., Zhao S., 2017. Simulation study of direct hydration of cyclohexene to isophorone as cosolvent. *Chemical Engineering Research and Design*, 117, 346-354.