

SEPARATION OF OLEFIN ISOMERS WITH REACTIVE EXTRACTIVE DISTILLATION

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ABSTRACT

Reactive extractive distillation has been investigated to separate α -olefins from other olefin isomers. The extractive agent is enriched with metal ions capable of reversibly complexing olefins enhancing the solvent selectivity. Experiments with 1-hexene/2-methyl-1-pentene showed that the addition of silver nitrate to ethylene glycol increases the solvent selectivity from 0.9 to 1.8. Normal extractive distillation would require a minimum of 250 trays for this separation. Reactive extractive distillation can reduce this to below 100 actual theoretical trays. A low pressure is beneficial for the separation due to the larger solvent selectivity. More trays or a higher solvent-to-feed and reflux ratio also facilitate the separation. However, too high reflux ratio's decrease the internal solvent-to-feed ratio frustrating the separation.

INTRODUCTION

A substantial part of the capital and variable costs of an olefin production unit is concentrated in the separation section. Especially difficult in this field is the recovery of higher ($>C_4$) α -olefins from other olefin isomers because of the low relative volatility's encountered [1]. For these applications conventional technologies such as normal and extractive distillation usually fall short. They need to be combined with an additional reaction step for the selective conversion of one of the isomers to make separation feasible. Application of selective (π -) complexation by (transition) metal ions may be a promising alternative that could significantly reduce the capital and variable costs by enhancing the selectivity [2]. Although already investigated in liquid membranes [1, 3] and liquid-liquid extraction [4], such reactive solvent systems have not been considered so far for application in extractive distillation: Reactive Extractive Distillation (RED).

In this paper the benefits of reactive extractive distillation over normal extractive distillation are investigated for the recovery of 1-hexene (1H) from a mixture of n-hexane (NH), 2-methyl-1-pentene (2M1P) and 1-methylcyclopentene (1MCP).

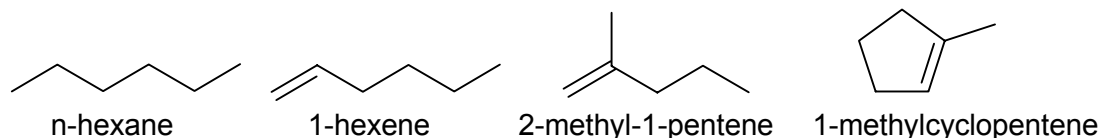


Figure 1: Investigated hydrocarbons.

A simple solvent is used, silver nitrate dissolved in ethylene glycol. For this system equilibrium constants for the involved olefin isomers are available from literature [5]. This system was modelled in Aspen to determine some basic parameters like number of trays and reflux ratio. Important design variables, like column pressure and solvent-to-feed ratio were varied to investigate their influence on the basic column design and 1-hexene purity.

SELECTIVE COMPLEXATION

The complexation of olefins by transition metal ions is described by the Dewarr-Chat-Duncanson or π -complex model. A π -complex is composed out of two bonds, a σ and π -bond. The σ -bond is formed between the vacant s-orbital of the metal ion and the π -molecular orbital of the olefin as illustrated in Figure 1 [2]. The empty s-orbital of the metal ion acts as a Lewis acid by accepting an electron from the olefin. The metal ion also acts as a Lewis base by back-donating electrons from its full d-orbital in the empty π^* -orbital of the olefin [2]. In principle all transition metal ions may be used, but copper(I) and silver(I) exhibit a strong yet reversible complexation reaction.

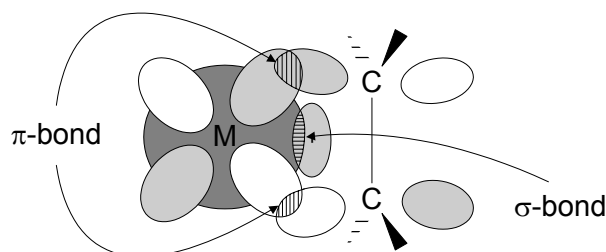


Figure 2: π -Complex formation between silver(I) or copper(I) ion (M) and olefin [2].

All olefin isomers are capable to complex with the metal ion, but steric hindrance from the side groups located around the double bond influences the equilibrium constant [5]. Based on this difference in equilibrium constant it is possible to separate close boiling olefin isomers. Table 1 presents the equilibrium constants (K_r) for the three olefins under investigation [5]. The equilibrium constant of 1-hexene is about twice the value of the other two olefins.

Olefin Solubility in Reactive Solvents

In Figure 3 a schematic representation of the olefin solubility in the (reactive) solvent system is given.

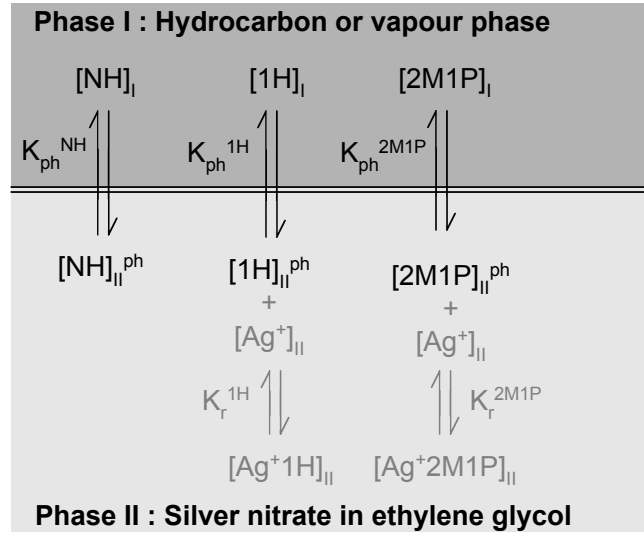


Figure 3: Olefin solubility in silver nitrate dissolved in ethylene glycol.

Modelling solvent selectivity in reactive solvents

The solvent selectivity is defined by the concentration ratio of 1-hexene and 2-methyl-1-pentene over the two phases:

$$\alpha_{1H/2M1P} = \frac{[1H]_{II}^T / [1H]_I}{[2M1P]_{II}^T / [2M1P]_I} \quad (1)$$

The total solubility in the solvent phase (phase II) of e.g. 1-hexene ($[1H]_{II}^T$) is the sum of the physical solubility ($[1H]_{II}^{ph}$) and the chemically complexed olefin ($[Ag^+1H]_{II}$). Two parameters are used to describe the total solubility: the physical solubility constant K_{ph} and the chemical equilibrium constant K_r . The silver ion and olefin are assumed to react at an equimolar ratio. The following equilibrium equations can be derived in case only 1-hexene and 2-methyl-1-pentene are present in phase I:

$$[1H]_{II}^T = K_{ph}^{1H} [1H]_I (1 + K_r^{1H} [Ag^+]) \quad (2)$$

$$[2M1P]_{II}^T = K_{ph}^{2M1P} [2M1P]_I (1 + K_r^{2M1P} [Ag^+]) \quad (3)$$

A total silver balance yields:

$$[Ag^+] = \frac{[Ag^+]^T}{1 + K_r^{1H} K_{ph}^{1H} [1H]_I + K_r^{2M1P} K_{ph}^{2M1P} [2M1P]_I} \quad (4)$$

Table 1 presents the equilibrium constants and physical solubility constants used in the model. These parameters were determined by Muhs and Weiss using gas chromatography at a temperature of 313 K [5].

Table 1: Equilibrium constants for complexation reaction ($T=313$ K) [5].

isomer	K_{ph} [-]	K_r [M^{-1}]	B [K]
1-hexene	3.5	4.3	456
2-methyl-1-pentene	3.7	2.1	232
1-methylcyclopentene	9.0	2.1	232

Because the equilibrium constant (K_r) is only known at a single temperature, the temperature dependence is approximated by classical thermodynamics:

$$\ln(K_r) = \frac{-\Delta G_r}{RT} \Rightarrow \ln(K_r) = \frac{B}{T} \text{ with } B = \frac{-\Delta G_r}{R} \quad (5)$$

The influence of temperature on the physical solubility constant is neglected. The physical solubility constant of 1-hexene and 2-methyl-1-pentene will change in a similar way with temperature, i.e. the selectivity will not change. To confirm the model assumptions, liquid-liquid extraction experiments are conducted. The separation factor β is determined in these experiments and compared to the model prediction.

EXPERIMENTAL RESULTS

Experimental Procedure

Silver nitrate is dissolved at the appropriate concentration in ethylene glycol. The ethylene glycol solution was contacted with the olefin solution, which was diluted, if required, with n-hexane. The ethylene glycol and olefin solution are contacted at a 1:1 weight ratio, left overnight in a thermostated shaking water bath to ensure sufficient time for equilibration. An experiment was conducted to determine the equilibrium time, which was determined to be around 300 min, well below the time used. After settling, samples from both phases were analysed with a Varian CP3800 gas chromatograph with ethanol as internal standard. Dark glass bottles were used to prevent degradation of silver by sunlight.

Interpretation experimental data

In the experiments the separation factor, β , is determined. The separation factor from these experiments can be correlated to the solvent selectivity α . The separation factor is based on total mol fractions, so including free and complexed olefin:

$$\beta = \left(\frac{x_{II}(1 + K_r^{1H} [Ag^+]_{II})}{x_I} \right)_{1H} / \left(\frac{x_{II}(1 + K_r^{2M1P} [Ag^+]_{II})}{x_I} \right)_{2M1P} \quad (6)$$

The vapour fraction of component i (y_i^i), at equilibrium is related with the fraction in the liquid (hydrocarbon phase) (x_i^i) by equation (7) (assuming an ideal liquid).

$$y_i^i = \frac{P_i^*}{P} x_i^i \quad (7)$$

In a vapour-liquid equilibrium, the solvent selectivity, α is defined as:

$$\alpha = \frac{(x_{II}(1 + K_r [Ag^+]) / y_i)_{1H}}{(x_{II}(1 + K_r [Ag^+]) / y_i)_{2M1P}} = \frac{(x_{II}(1 + K_r [Ag^+]) / (P_{1H}^* x_i))_{1H}}{(x_{II}(1 + K_r [Ag^+]) / (P_{2M1P}^* x_i))_{2M1P}} \quad (8)$$

Thus the solvent selectivity factor can now be calculated from the experimentally determined separation factor β :

$$\alpha = \frac{(x_{II}(1 + K_r [Ag^+]) / x_i)_{1H}}{(x_{II}(1 + K_r [Ag^+]) / x_i)_{2M1P}} \frac{P_{2M1P}^*}{P_{1H}^*} = \beta \frac{P_{2M1P}^*}{P_{1H}^*} \quad (9)$$

Physical and Chemical Solubility

In Figure 4 the total 1-hexene and 2-methyl-1-pentene solubility's in ethylene glycol are presented as a function of its weight percentage in the hydrocarbon phase. The addition of silver to the ethylene glycol phase increases both the 1-hexene and 2-methyl-1-pentene solubility. The difference, however, is that, the 2-methyl-1-pentene solubility is, roughly, only a half of 1-hexene, due to it's lower equilibrium constant.

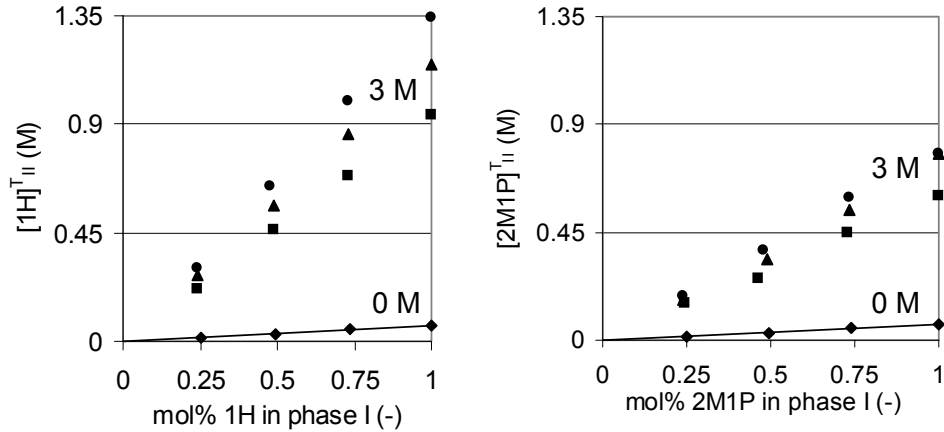


Figure 4: 1H and 2M1P solubility in 3M AgNO₃/ethylene glycol, (●) 300, (▲) 308, (■) 323 K.

The total 1-hexene or 2-methyl-1-pentene solubility decreases with increasing temperature because of a decreasing equilibrium constant.

Selectivity

In figure 5 the solvent selectivity is plotted as a function of the temperature. The addition of silver nitrate to ethylene glycol enhances the solvent selectivity from 0.9 to approximately 1.8. The experimental data and model correlate well. The approximation of the equilibrium constant can be used to make a design.

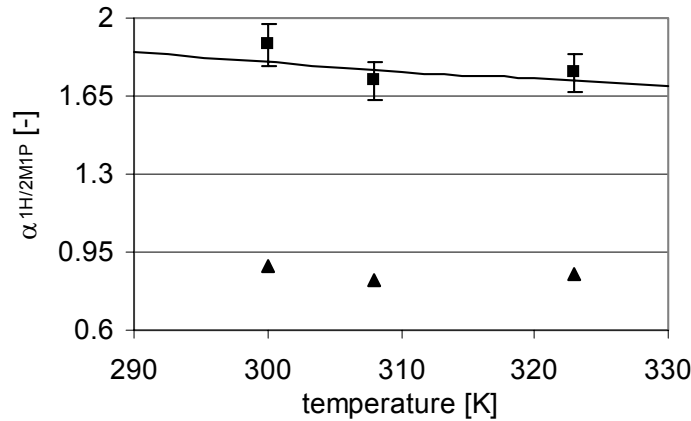


Figure 5: Solvent selectivity of 1-hexene over 2-methyl-1-pentene as function of temperature (50/50 wt% in vapour, 1 bar). Symbols: experiments (▲) 0 M, (■) 3 M AgNO₃. Line: model.

DESIGN

Reactive Extractive Distillation

In Figure 6 a reactive extractive distillation system is presented. The feed, an α -olefin mixed with close-boiling olefin isomers, is supplied to the complexation column. A solvent enters this column at the top, similar to normal extractive distillation. The difference is that the solvent contains a metal ion that can complex with the α -olefin. However, other olefin isomers will also complex with this metal ion, but do this with a lower reaction equilibrium constant [5]. The difference in the value of the equilibrium constants is the basis for separating these components. The α -olefin is preferentially

absorbed relative to the other olefins by the solvent due to its higher equilibrium constant. It leaves the column with the solvent at the bottom. The other olefin isomers go over the top and may be directed elsewhere.

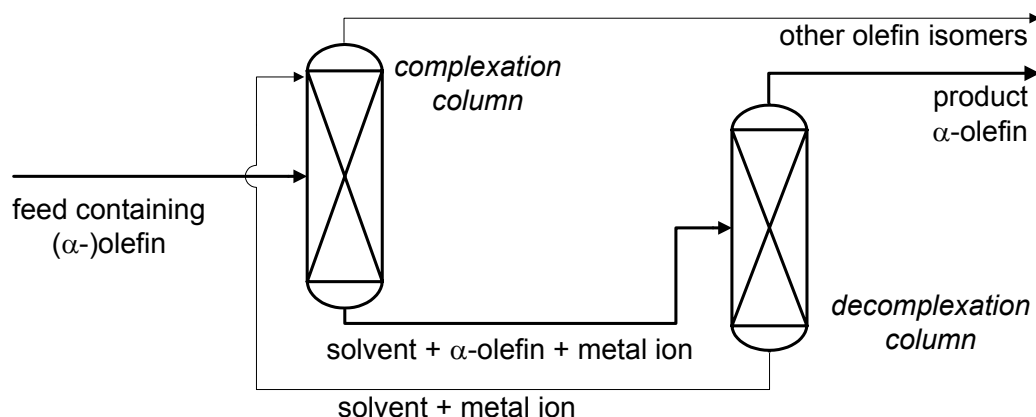


Figure 6: Reactive extractive distillation scheme.

The complexed α -olefin and solvent go to the second, decomplexation column. In this column the α -olefin is decomplexed from the metal-ion by applying a higher temperature or lower pressure. The metal ion loaded solvent exits at the bottom and is recycled to the first column. Pure α -olefins leave this column at the top.

Design Approach

The equilibrium-based column is modelled in Aspen using the Radfrac-method. Radfrac offers the possibility to model complicated equilibrium based columns. The solvent, silver nitrate dissolved in ethylene glycol, should be modelled as an electrolyte. Calculations involving electrolytes are complicated and may be faulty. It was decided to define both the silver(I)-ion and the reaction products as pseudo-components. In this way the electrolyte calculations can be circumvented. The reactions were defined in a reaction bloc that is linked with the Radfrac column. In this reaction block both the reaction stoichiometry and equilibrium constants of the individual reactions are defined.

SIMULATION RESULTS

In Table 2 the feed and product specifications are given. Product purity and recovery are set at 99.5 mol% and 99.8% respectively, which is industrially realistic. The solvent is a solution of 3.36 M silver nitrate in ethylene glycol. In this case the silver concentration is equal to the highest concentration encountered in literature [7]. It is expected that the selectivity and capacity are the highest at this concentration.

Table 2: Feed and product specifications.

component	feed wt%	product mol%
1H	59	99.5
2M1P	25	0.5
NH	11	
1MCP	5	

The effect of column pressure, number of trays and reflux ratio on the 1-hexene purity are determined and used to establish an operating window assuming realistic

column parameters to produce 1-hexene from the specified feed at the required purity. The calculations are focussed on the complexation column, because in this column the required 1-hexene purity has to be achieved. In the decomplexation column, the 1-hexene is only decomplexed and separated from the solvent, which is a relatively simple operation.

Base Case

To show the beneficial effect of silver, a base case scenario is first presented. This reference case is a normal, non-reactive extractive distillation system. The solvent selectivity based on the literature data for 1-hexene and 2-methyl-1-pentene would be around 0.95 (with 1-hexene the more volatile component) [5]. The minimum number of trays would be around 250 as determined by the Fenske-Underwood equations [8]. Using the same method, the minimum reflux ratio would be around 28.

Influence of Pressure and Solvent-to-Feed ratio on 1-Hexene Purity

In Figure 7 the 1-hexene purity is plotted as a function of the pressure in the complexation column for different solvent-to-feed ratio's. The 1-hexene purity increases if the pressure decreases. It is believed that this is due to a reduced physical solubility which enhances the 1-hexene/2-methyl-1-pentene selectivity. Also the lower average temperature in the column positively influences the solvent selectivity via the higher equilibrium constant. Higher solvent to feed ratio's also improve the product purity, as in normal extractive distillation.

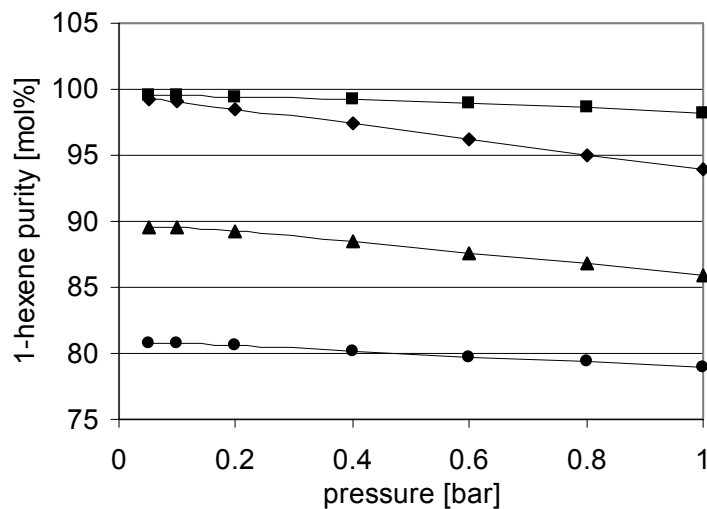


Figure 7: Effect of pressure and solvent-to-feed ratio on the 1-hexene purity. Column: 100 trays, reflux ratio 4; (-●-) S/F = 2, (-▲-) S/F = 4, (-◆-) S/F = 7 and (-■-) S/F = 10.

Effect Number of Trays on 1-Hexene Purity

In Figure 8 the product purity is plotted as a function of the number of trays. It is observed that at a higher column pressure the product purity decreases. This effect is especially significant with a lower number of trays, or high reflux ratio's.

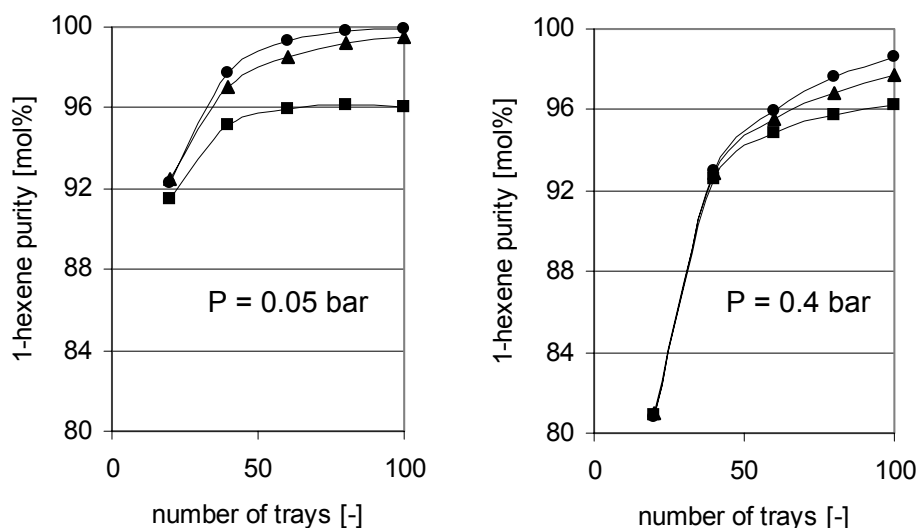


Figure 8: Effect of number of trays and pressure on 1-hexene purity at three reflux ratio's. Solvent-to-feed ratio 7. (-■-) RR = 2, (-▲-) RR = 4, (-●-) RR = 8.

This result shows that a column operated at 0.05 bar can yield the required purity within 100 trays. However, at 0.4 bar the purity requirements can not be obtained with 100 trays, independent of the value of the reflux ratio. The positive influence of a pressure reduction is the result of two effects. A lower pressure decreases the column temperature, increases the equilibrium constant and consequently the solvent selectivity. Also the physical solubility is reduced at a lower pressure.

Relation Between Reflux Ratio and Number of Trays

In simulations it was found that a higher reflux ratio not always resulted in a better 1-hexene purity at a fixed number of trays. Initially an increase of the reflux ratio positively influences the purity, reaching a maximum. With any further increase the 1-hexene purity decreases, as is shown in Figure 9. However, similar to normal extractive distillation, at high reflux ratio's the internal solvent-to-feed ratio is decreased, frustrating the separation.

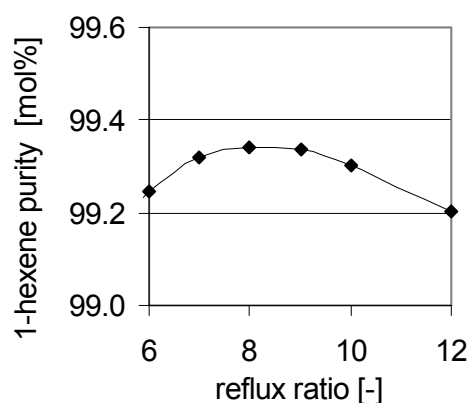


Figure 9: 1-Hexene purity (mol%) as function of molar reflux-ratio (S/F=7, 60 trays, 0.05 bar).

The maximum purity as observed in Figure 9 can be above or below the specifications from Table 2 depending on the reflux ratio and number of trays. Using these specifications (purity 99.5 mol%, recovery 99.8 %) it is possible to find combinations of number of trays and reflux ratio that have a maximum just touching these specifications. The results are shown in Figure 10.

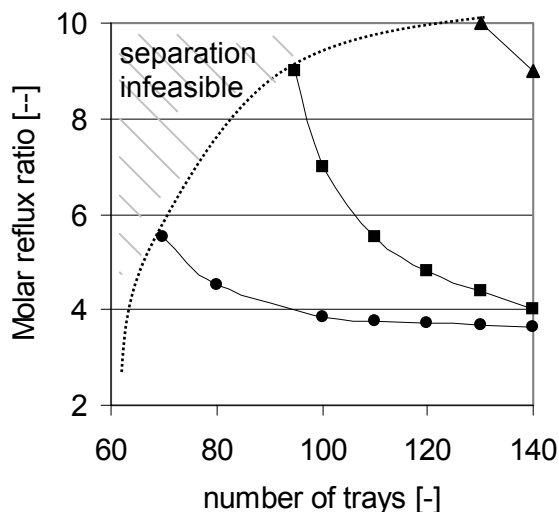


Figure 10: Relation between number of trays and reflux-ratio to obtain a purity of 99.5 mol% and recovery of 99.8%. Pressure (-●-) 0.05, (-■-) 0.2, (-▲-) 0.4 bar.

At a column pressure of 0.05 bar, the approximate minimum number of trays is 70 at a reflux ratio of 5.5 to reach the required 1-hexene purity. A higher reflux ratio would only decrease the product purity for reasons just explained. If the number of trays increases the required reflux ratio, subsequently decreases. With an increasing number of trays this effect becomes progressively smaller. The same correlation's hold at higher column pressures, only the absolute values for the reflux ratio and number of trays are higher.

CONCLUSIONS

A conceptual column design using Aspen demonstrated that it appears to be possible to separate close-boiling olefin isomers via Reactive Extractive Distillation. Although all olefin isomers are able to complex with silver ions, it is possible to separate these because of their different chemical equilibrium constant.

A simple model was used to correlate the solvent selectivity with the physical distribution coefficient and equilibrium constant. Experiments showed that the model predictions are in good agreement. The measured liquid selectivity is 1.8 (at 3 M) for 1-hexene versus 2-methyl-1-pentene. With a non-reactive system this would be around 0.9, illustrating the beneficial effect of the addition of silver. The solvent selectivity increases because of a difference in the equilibrium constant.

The simulations show that the trends in product purity and column size can be explained and are similar to normal extractive distillation. In Reactive Extractive Distillation a lower pressure reduces the number of trays because of a lower column temperature, increasing equilibrium constant and lower physical solubility. Higher solvent-to-feed ratio's also reduce the column size. However, higher reflux ratios do not always result in a higher purity. At high ratio's the actual solvent-to-feed ratio within the column is decreased.

In normal extractive distillation the minimum number of trays is around 250 to separate 1-hexene from the feed, with a minimum reflux of around 28. These numbers decrease dramatically when applying reactive extractive distillation. A column operated at 0.05 bar can already recover 1-hexene in 70 trays and a reflux

ratio of only 5.5. This clearly illustrates the beneficial effect of selective complexation, integrated within a novel process operation: Reactive Extractive Distillation.

ACKNOWLEDGEMENTS

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NOMENCLATURE

symbol	explanation	unit
K_r^i	chemical equilibrium constant	l/mol
$[Ag^+]$	silver concentration	mol/l
$[..]$	concentration (general)	mol/l
R	gas constant	J/(mol K)
T	temperature	K
ΔG	Gibbs free energy	J/mol
B	parameter for K_r temperature dependence	K
α	solvent selectivity	-
β	separation factor	-
x	mol fraction in solvent phase (only physical)	-
y	mol fraction in vapour or hydrocarbon phase	-
P	total system pressure	bar
P^*	saturated vapour pressure	bar

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