ENTRAINER-ENHANCED REACTIVE DISTILLATION

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ABSTRACT

The paper presents the use of a Mass Separation Agent (entrainer) in reactive distillation processes. This can help to overcome limitations due to distillation boundaries, and in the same time increase the degrees of freedom in design. The catalytic esterification of fatty acids with light alcohols C2-C4 is studied as application example. Because the alcohol and water distillate in top simultaneously, another separation is needed to recover and recycle the alcohol. The problem can be solved elegantly by means of an entrainer that can form a minimum boiling ternary heterogeneous azeotrope. Water can be removed quantitatively by decanting, or by an additional simple stripping column. The use of entrainer has beneficial effect on the reaction rate, by increasing the amount of alcohol recycled to the reaction space. The paper discusses in more detail the design of a process for the esterification of the lauric acid with 1-propanol. The following aspects are investigated: chemical and phase equilibrium, entrainer selection, kinetic design, and optimisation. Minimum and maximum solvent ratio has been identified. A significant reduction of the amount of catalyst can be obtained compared with the situation without entrainer.

INTRODUCTION

Reactive Distillation (RD) is considered a promising technique for innovative processes, because the reaction and separation could be brought together in the same equipment, with significant saving in equipment and operation costs. However, ensuring compatibility between reaction and separation conditions is problematic. The manufacture of fatty acid esterification is an interesting potential application. Presently, these are produced in batch processes with homogeneous acid catalyst. Large excess of alcohol used in the batch recipe has to be recovered by batch distillation. The catalyst is destroyed by neutralisation. This operation creates chemical pollution problems. Bock et al. [1] described a continuous process for fatty esters produced by the reaction of myristic acid with iso-propanol in two-columns using homogeneous acid catalysis. The catalyst is lost with the product. Because alcohol and water distillate together, a secondary recovery column is needed, which recycles in fact the azeotrope water/iso-propanol.

Omota, Dimian and Bliek [2] investigated the feasibility of a continuous process for fatty acid esterification based on reactive distillation by using a solid acid catalyst based on sulphated zirconia. As substrates they considered lauric acid (C12), as well as 2-ethyl-hexanol (C8) and methanol (C1), the highest and the lowest boilers in the series C1-C8 alcohols. They found that both fatty esters could be produced in the same RD column, but with different operation policies: alcohol reflux for high-boiling alcohol (C8), and acid reflux for low-boiling alcohol (C1). The last strategy could be in principle applied for intermediate alcohols, as C2-C4, but problems might arise because of high sensitivity of purity with the reflux ratio. In fact, these alcohols give homogeneous azeotropes with water, from which the alcohol should be recovered and recycled in additional separation steps.

To overcome this problem, the present research proposes an original solution, the use of a Mass Separation Agent, called here entrainer. This can enhance simultaneously the water removal and the internal recycle of the alcohol. A second unit for alcohol recovery is no longer necessary, or can be reduced to a simple stripper. An important feature is that the same flowsheet configuration may be preserved for different substrates acids and alcohols. The design of a multi-purpose continuous process can be envisaged, which is in itself an element of novelty.

Literature search showed that the use of an entrainer in reactive distillation processes has been not reported so far. Therefore, the presented work has in some extent an exploratory character.

PROBLEM DEFINITION

The fatty acid esters are produced by the reversible reaction:

$$R_1\text{-COOH} + R_2\text{-OH} \quad \leftrightarrow \quad R_1\text{-COO-}R_2 \quad + \quad H_2O \tag{1}$$
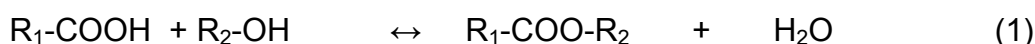
An undesired secondary reaction is the etherification of alcohol:

$$R_2\text{-OH} \quad + \quad HO\text{-}R_2 \quad \leftrightarrow \quad R_2\text{-O-}R_2 \quad + \quad H_2O \tag{2}$$
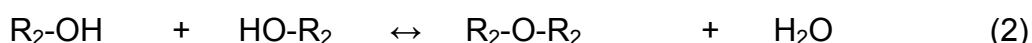
Further impurities might be produced by alkene dimerisation at higher temperatures. In this work we consider as reactants lauric (dodecanoic) acid and 1-propanol. Homogeneous organic reaction phase and high degree of water removal from the reaction medium are key requirements, necessary both to shift the equilibrium reaction to completion, and to protect the catalyst against deactivation by free-water.

Table 1 displays some important thermodynamic properties of the reactive mixture. The components form azeotropes with each other. The ester is the highest boiler, followed by the acid, and at large distance by water and 1-propanol. Because the high boiling point of the ester the RD column should operate under vacuum, even by diluting the product with some alcohol, which can be recycled after product conditioning. Without further treatment, the top distillate would be the azeotrope 1-propanol/water. Thus, a solution should be found for the separation of water product and alcohol recycle.

Table 1 Key thermodynamic properties of the reactive mixture

Normal boiling points	Dodecanoic acid	1-propyl dodecanoate	1-propanol	Water
T, K	571.75	574.95	370.35	373.15
Azeotrope	Acid(1)/Ester(2) Homogeneous	Acid(1)/Water(2) Heterogeneous	Ester(1)/Water(2) Heterogeneous	Alcohol(1)/Water(2) Homogeneous
T, K Composition	568.9 $y_{az,1}$=0.5784	373.15 $x_1(w)<0.0001$ $x_1(o)=0.7195$ $y_{az,1}=0.0001$	373.13 $x_1(w)<0.0001$ $x_1(o)=0.9254$ $y_{az,1}=0.0004$	360.86 $y_{az,1}$=0.4330

Note: w - water phase, o-organic phase.

METHODOLOGY

The methodology of the investigation consists in an evolutionary search of the feasible design space by a systematic combination of thermodynamic analysis, computer simulation and experimental research. The environment of constraints ensures a proper bounding of the feasible design space. The approach can be decomposed in the following steps:
1. Property generation and estimation when missing.
2. Simultaneous Chemical and Phase equilibria, and reduction of the design space.
3. Preliminary equilibrium-based design: solvent selection, feasibility by Residue Curve Map (RCM) analysis and finite reflux calculations, rigorous simulation, and analysis of data uncertainty by sensitivity analysis.
4. Thermodynamic experiments identified by simulation.
5. Reviewed equilibrium-based design.
6. Catalyst study and kinetic experiments.
7. Kinetic design and optimisation.

PRINCIPLE OF USING ENTRAINER IN REACTIVE DISTILLATION

Figure 1 illustrates conceptual alternatives of a RD process by the fatty acid esterification with light alcohols that may form homogeneous azeotropes. Three situations may be distinguished:

Case 1: Acid reflux (A_1), L-L separation with quantitative water removal (A_2), and acid recycle (A_R). The alcohol is completely converted in the reactive zone (Omota et al., 2001), such as no auxiliary column is needed for alcohol recovery.

Case 2: Alcohol/water top product (B_1), homogeneous azeotropic distillation for water removal (B_2) and azeotrope recycle (B_R). The process requires an additional distillation column for alcohol recovery as homogeneous azeotrope. Recycling the alcohol carries with a large amount of water in the reaction zone.

Case 3: Reactive distillation with excess of alcohol (C_1), heterogeneous azeotropic distillation (C_2), liquid decanting (C_3) and entrainer recycle (C_R). This case will be investigated in the present research.
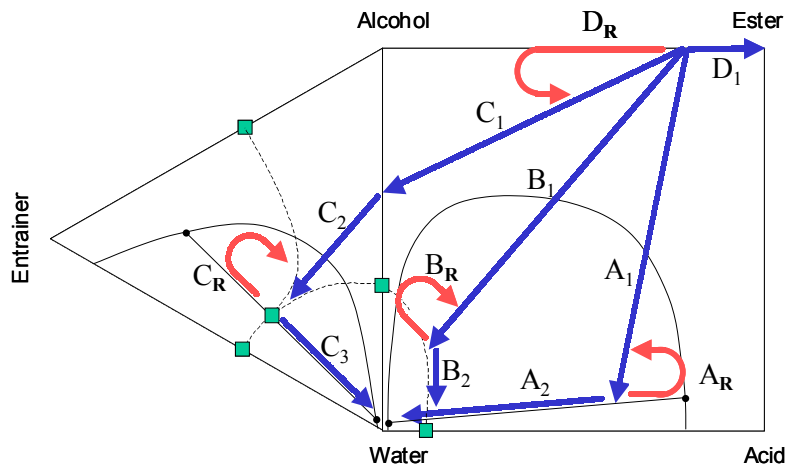

Figure 1 Three conceptual design alternatives for fatty acid esterification with light alcohols forming homogeneous azeotropes.

■ azeotrope; (.......) distillation boundary; (___) two-liquid phase splitting. Curved red lines means recycle (A_R- acid, B_R- azeotrope, C_R- entrainer) for different alternatives. D_R alcohol in bottom recovered and recycled is common to all.

ENTRAINER SELECTION

Rules for entrainer selection in azeotropic distillation has been studied a decade ago by Pham and Doherty [3], and updated recently in the books of Fair and Stichlmair [4] and Doherty and Malone [5]. Warter et al [6] reviewed practical rules for entrainer selection in both batch and rectification processes. They distinguished among one-step and two-steps rectification processes. For the special case of batch distillation a systematic investigation of the entrainer selection for separating azeotropic mixture by heterogeneous has been proposed recently by Rodriguez al. [7] on a basis of a topological analysis of possible RCM's.

In the case of the fatty acid esterification some peculiar physical properties can be used to restrict the entrainer selection. Fatty acid and its ester are high boilers that can be eliminated from the analysis. The light alcohols from the series C2-C4 give all minimum boiling azeotropes with water. By consequence, the following three conditions for the entrainer selection can be formulated:

1. Form minimum boiler ternary *heterogeneous* azeotrope with alcohol and water, or binary heterogeneous azeotrope with water in the most preferable case. Note that the heterogeneity condition implies necessarily the existence of a minimum boiler ternary azeotrope. Moreover, a topological analysis can show that the entrainer must form also a minimum binary azeotrope with the alcohol.
2. The L-L split of the heterogeneous azeotrope should give a water-rich phase with low solubility of entrainer and alcohol, and an organic phase relatively rich in alcohol but with limited content of water.
3. Give acceptable impurity in the final product.

Figure 2 displays a desired RCM for the entrainer selection. The ternary azeotrope should have such composition that gives a reduced amount of entrainer. The liquid resulting by the condensing of the top vapour from the RD column must be placed in the heterogeneous region. The second condition may be supplemented with the observation regarding the orientation of the tie lines the L-L domain, which should point to the vertex of water. By consequence, the water separated by decantation should be preferably free of entrainer and alcohol, or contains only limited amounts that could be easily recovered by simple stripping.
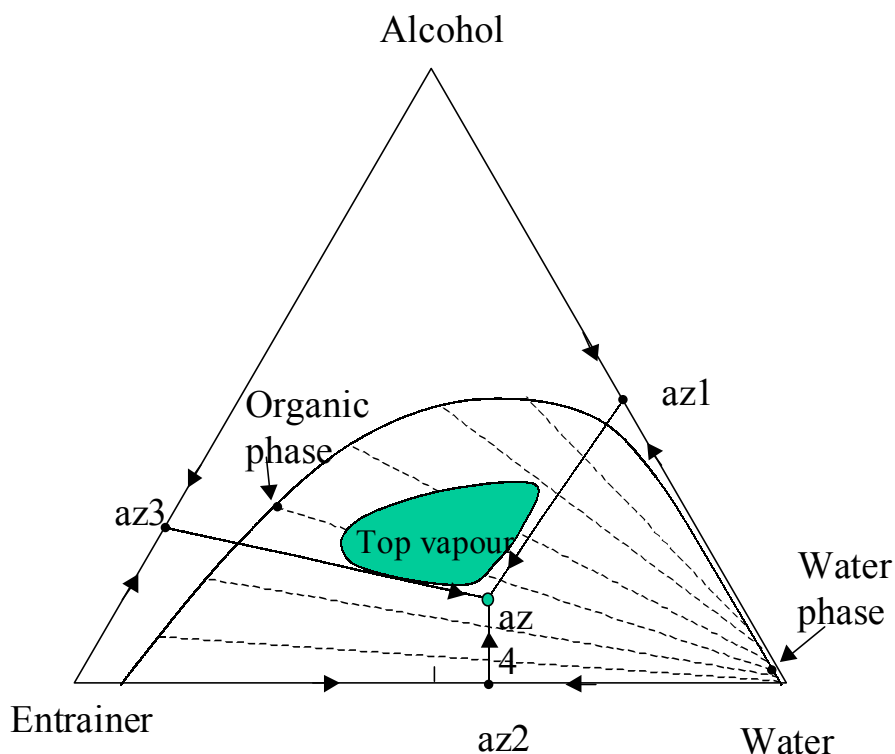

Figure 2 Conceptual Residue Curve Map for entrainer selection in fatty acid esterification with light alcohols

Suitable entrainers have been searched primarily in an extensive data book on azeotropes [8]. Table 2 presents data for candidates that have been found ordered by chemical classes as following: alkanes, iso-alkanes, n-alchenes, iso-alchenes, aromatics, oxygenated components, halogenated components. Beside experimental values for the boiling point and composition of the ternary heterogeneous azeotrope, information about the L-L equilibrium after condensation is given. Fat characters highlight suitable entrainers.

Some representative RCM's calculated with Aspen Split[TM] 10.2 [9] are presented in Fig. 3. UNIQUAC liquid activity model has been used in all cases, with interaction parameters from Aspen Plus[TM], and UNIFAC predictions when interaction parameters were missing. Note that VLLE rather than VLE data have been used to ensure the correctness of predictions.

The examination of the RCM's from Fig. 3 highlights the behaviour of different chemical classes, as follows:

1. Hydrocarbons are in principle suitable entrainers. Although the shape of the heterogeneous region is similar, the behaviour of each solvent is different. A lower molecular component, as hexane, gives low reciprocal solubility with water, and the orientation of tie lines is favourable. However, high solvent consumption can be anticipated, because minimum four moles of solvent are necessary to extract one mole of water. Heptane offers a convenient entrainer ratio, but the tie lines start to diverge slightly to the alcohol corner. This behaviour is even more critical for higher alkanes, as octane or iso-octane. Ring hydrocarbons, as cyclohexane, benzene and toluene, are also convenient, particularly the toluene.

2. Oxygenated components as esters, ethers, and ketones, display an interesting behaviour. RCM's are illustrated for n-propyl-acetate, 3-pentanone and dipropyl-ether. The water phase is practically solvent free, and contains only small amounts of alcohol. Note that the organic phase refluxed in the column could contain some water.

3. Halogeno-hydrocarbon, as 1-chloro-methyl- propane have suitable properties, giving RCM close to the oxygenated components.

Summing up, suitable entrainers from the above list are toluene, di-propyl-ether and n-propyl acetate. The first one may be suspended because potential undesired impurity. The di-propyl-ether is very interesting, being practically insoluble in water.. The reciprocal solubility of water in ether is also low, of order of 4%. Moreover, this is a by-product of the reaction! However, in the present study the decision was to select as entrainer the n-propyl-acetate. The shape of RCM is very convenient, although the organic phase shows somewhat higher content of water. This component is very convenient as impurity, sharing the same alcohol with the fatty ester.

Table 2 Entrainer classification for heterogeneous azeotropic distillation of 1-propanol/water mixture

Entrainer	Entrainer Nbp, ºC	Ternary heterogeneous azeotrope			Azeotrope Nbp, ºC	Water phase		Entrainer phase	
		water	alcohol	entrainer		water	entrainer	water	entrainer
N-Alkanes									
hexane	**68.73**	**0.19**	**0.094**	**0.716**	**59.23**	**0.99**	**0.01**	**0**	**0.95**
heptane	98.4	0.381	0.21	0.409	75.3	0.71	0.01	0.02	0.83
octane	125.69	0.485	0.291	0.224	81.4	0.65	0.01	0.02	0.82
nonane	150.66	0.5655	0.317	0.1175	85.4	0.64	0.01	0.04	0.8
Iso-alkanes									
2,2,4-trimethylpentane	109.8	0.44	0.208	0.352	73.89	0.65	0.01	0.01	0.92
1-Alkenes									
1-hexene	**63.35**	**0.057**	**0.153**	**0.79**	**57.07**	**0.97**	**0**	**0.01**	**0.92**
1-heptene	93.7	0.333	0.191	0.476	73.34	0.92	0	0.04	0.7
1-octene	121.23	0.461	0.288	0.251	81.57	0.64	0.02	0.07	0.76
Iso-alkenes									
4-octene (cis)	122.59	0.458	0.296	0.246	81.45	0.64	0.02	0.05	0.8
Dialkenes									
1.3-cyclohexadiene	**80.29**	**0.273**	**0.104**	**0.623**	**67.75**	**0.95**	**0**	**0.09**	**0.76**
Alkynes									
4-octyne	126.15	0.514	0.305	0.181	83.05	0.93	0	0.35	0.22
Cycloalkanes									
cyclohexane	80.78	0.2936	0.1036	0.6028	66.55	0.93	0	0.02	0.81
Cycloalkenes									
cyclohexene	82.88	0.289	0.115	0.596	68.5	0.91	0	0.02	0.79
N-Alkylbenzenes									
benzene	**80.13**	**0.2761**	**0.0907**	**0.6332**	**67.96**	**0.96**	**0**	**0.02**	**0.85**
methyl benzene	110.68	0.424	0.249	0.327	79.72	0.93	0	0.09	0.54
Esters									
Propyl-acetate	**101.44**	**0.5623**	**0.1566**	**0.2811**	**82.2**	**0.98**	**0.01**	**0.24**	**0.57**
Ketones									
3-pentanone	**101.75**	**0.5188**	**0.1556**	**0.3256**	**81.2**	**0.96**	**0.02**	**0.22**	**0.62**
Aliphatic ethers									
dipropyl ether	**89.95**	**0.393**	**0.2035**	**0.4035**	**74.8**	**0.97**	**0**	**0.09**	**0.75**
Polyfunctional C,H,O									
Dipropoxymethane	144.05	0.2871	0.482	0.2309	86.4				
Cl, Br, I compounds									
1-chloro-2methyl propane	**68.81**	**0.2055**	**0.0544**	**0.74**	**64.2**	**0.98**	**0.02**	**0.02**	**0.93**
1-bromo-butane	**102**	**0.402**	**0.184**	**0.414**	**76.58**	**0.95**	**0.00**	**0.06**	**0.65**
1-iodo-propane	102.46	0.4783	0.1326	0.3892	78.25	0.88	0.04	0.40	0.46

Hexane

Heptane

Octane

Nonane

Iso-octane

Cyclohexane

Benzene

Toluene

n-propyl-acetate
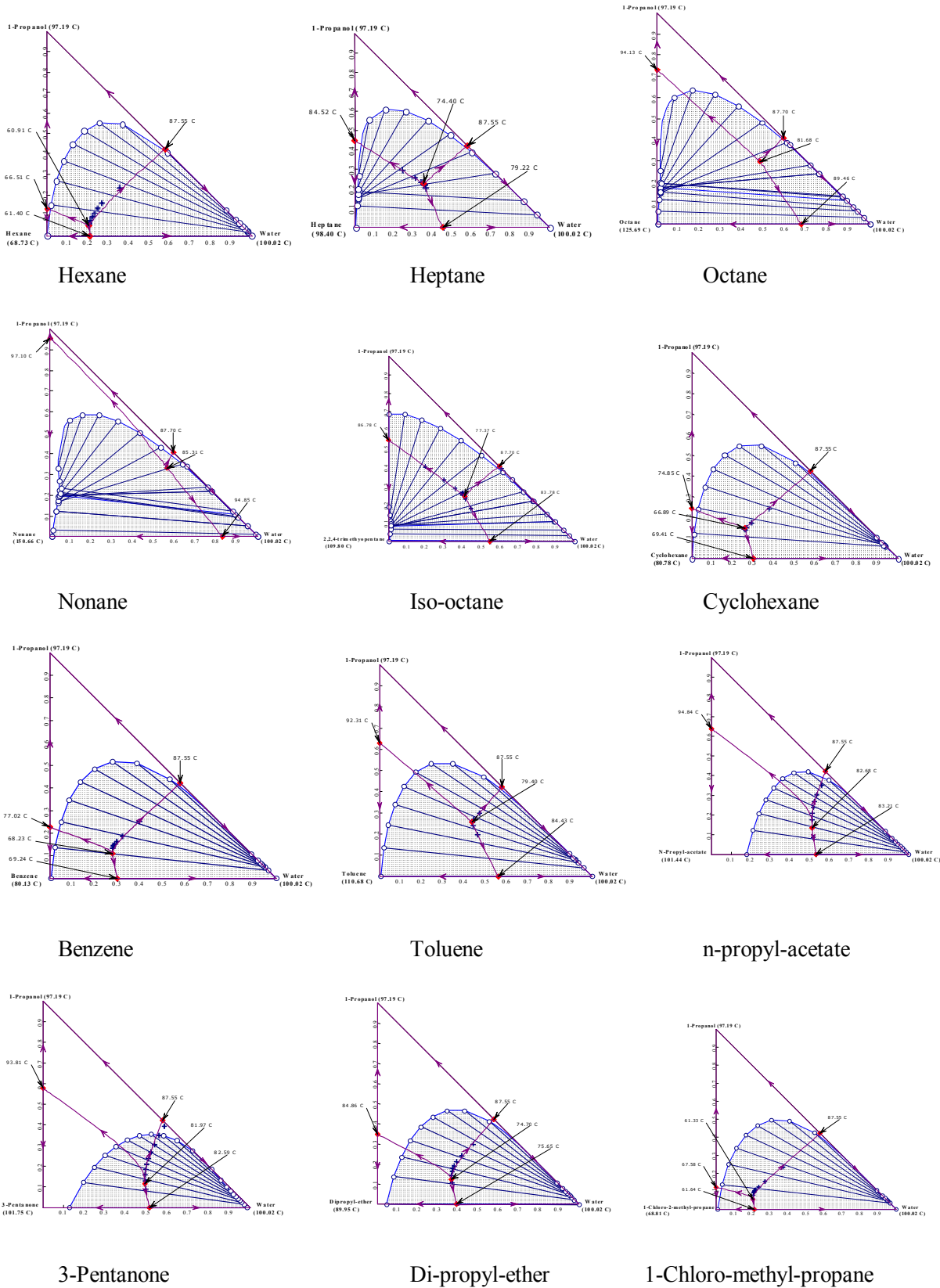
3-Pentanone

Di-propyl-ether

1-Chloro-methyl-propane

Figure 3 Selected RCM's for the entrainer selection of breaking the azeotrope 1-propanol/water

CHEMICAL AND PHASE EQUILIBRIUM

The thermodynamic equilibrium constant based on activities K_a has been calculated by Gibbs free energy minimisation [9]. The constant of activity coefficients has been determined by UNIQUAC K_γ. The equilibrium constant based on molar fraction K_x, can be calculated as $K_x = K_a / K_\gamma$. Thermo-chemical data and interaction parameters have been calibrated by means of experimental data, which finally verified the results predicted by simulation (Fig. 4a). Fig. 4b displays in transformed co-ordinates X_1 (acid +water), X_2 (acid+ ester) the simultaneous chemical and phase equilibrium diagram calculated by Gibbs free energy minimization. A temperature higher than 373 K is necessary to ensure that the reaction takes place only in homogeneous system.
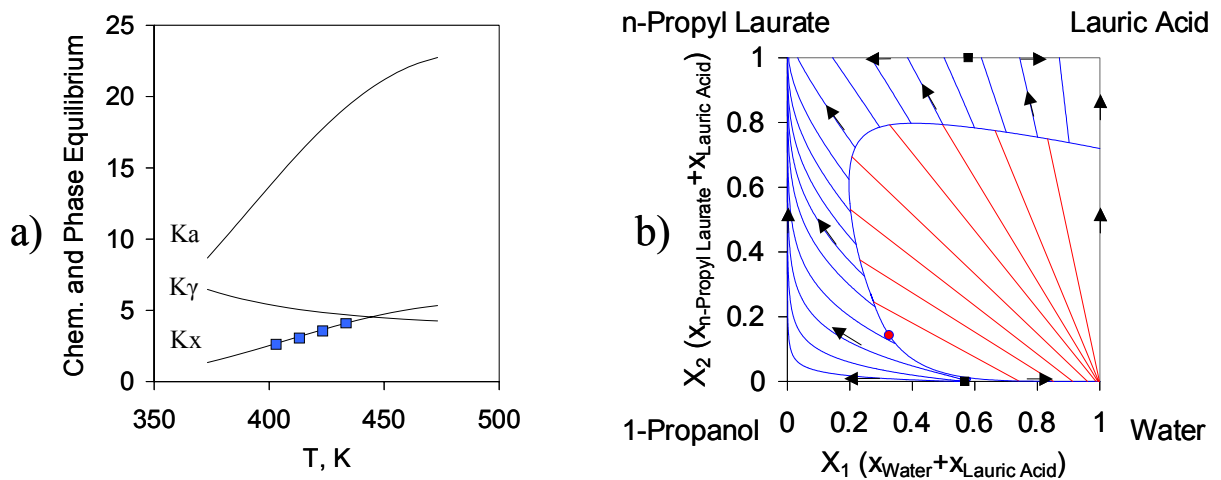
Figure 4 a) Chemical and phase equilibrium (■ experimental data), and b) RCM.

FLOWSHEET

Fig. 5 presents the flowsheet. Liquid acid and vapour alcohols are introduced at the top and at the bottom of the reaction zone at the temperatures of 453 K and 380 K, respectively. The bottom product containing 3% 1-propanol is sent to an evaporator, from which high purity fatty ester is obtained, while the alcohol is recycled. The vapour leaving the reaction zone enters a distillation section in counter-current with the entrainer-rich reflux. The top vapour is condensed. After decantation the water-phase is removed as by-product, or sent to a simple stripping device with few stages, from which water can be obtained in bottom. Note that the recovered alcohol with some water is recycled to the decanter and not to the RD column. This is a key difference with the homogeneous azeotropic set-up mentioned [1], where a substantial amount of water was recycled into the RD column.
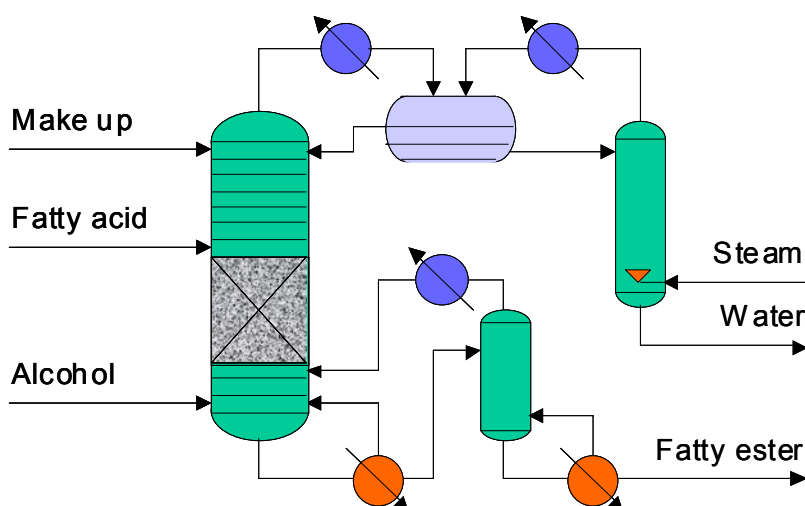
Figure 5 The flowsheet for the esterification of lauric acid with 1-propanol using entrainer.

KINETIC MODELLING

Profiles

The flowsheet from Fig. 5 has been model simulated with Aspen Plus[TM] 10.2. by considering a stage-equilibrium model with chemical reaction. Kinetic data has been introduced by analogy with the system lauric acid/1-ethyl-hexanol [10].

It has been found that the following column design is compatible with the above kinetic data: 15 reaction stages, 15 rectification stages, acid feed as liquid at 453 K, 1-propanol feed on the stage 30 as vapour, atmospheric pressure.

As general observation the entrainer enhances the water extraction from the reaction zone, and increases the amount of alcohol recycled. The top composition is placed in the heterogeneous ternary mixture of alcohol-water-entrainer. By liquid decantation at 353 K the mixture splits into an aqueous-phase containing 98 % water and a recycled organic phase.

The examination of profiles (Fig. 6) shows how the process works. In the reactor zone the acid concentration decreases sharply after the first 7 stages (Fig. 6a). The remaining 7 reactive stages are still required to achieve high purity. The temperatures of the reaction and distillation zones are quite different (Fig. 6b), corresponding to reaction and separation requirements. Therefore, at the junction of the two zones the insertion of a heater for reflux (not shown in the flowsheet) is necessary to compensate the enthalpy difference.
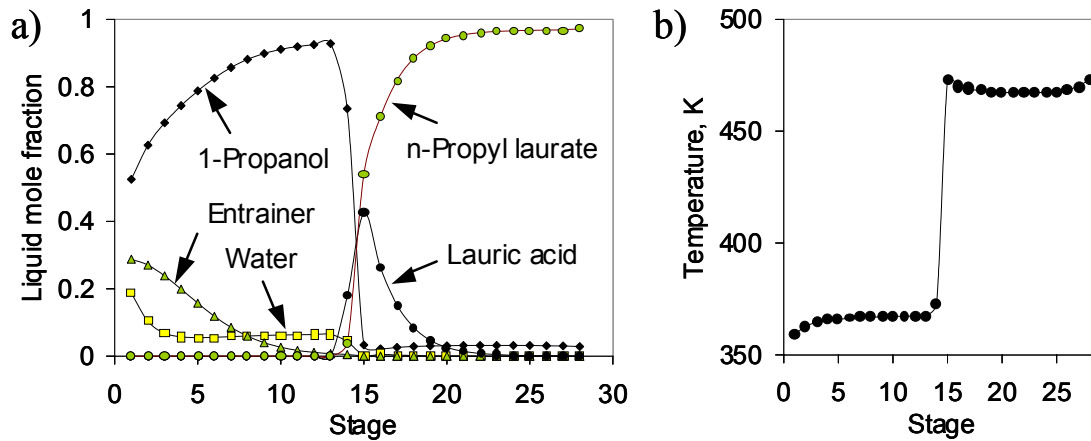
Figure 6 Concentration profiles in the RD column in ternary diagram alcohol-water-entrainer

Entrainer ratio

The effect of the entrainer/feed ratio is presented in Fig. 7, where both liquid and vapour concentration in the rectification zone is displayed in a treiangular diagram. A minimum amount of entrainer is necessary, corresponding to the azeotrope composition. Indeed the simulation shows clearly that the composition profile becomes stable above a ratio solvent of 0.914 (profile A). The entrainer acts only on the top stages. Increasing the ratio of entrainer pushes the alcohol back to the reaction zone, while the water is sent to the top and concentrated in the vapour phase (profiles B and C). Only the top vapour has the concentration in the heterogeneous region. Surprinsingly, at higher entrainer ratio, in this case 3.8, the profile crosses the distillation boundary set by the azeotrope alcohol/entrainer, and change the direction. Now the entrainer concentrates to the bottom of the rectification zone, while the alcohol migrates to the top together with water. Hence, a maximum entrainer ratio is detected.
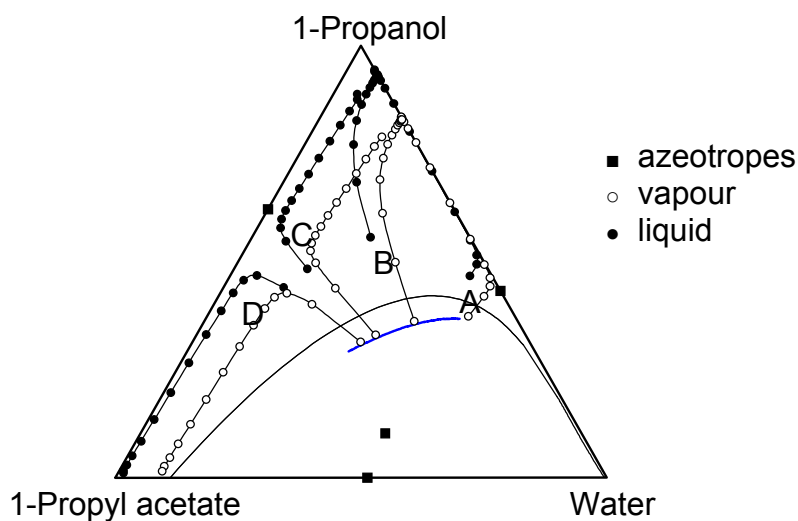

Figure 7 Profiles for component concentration in liquid (a) and vapour phase (b)
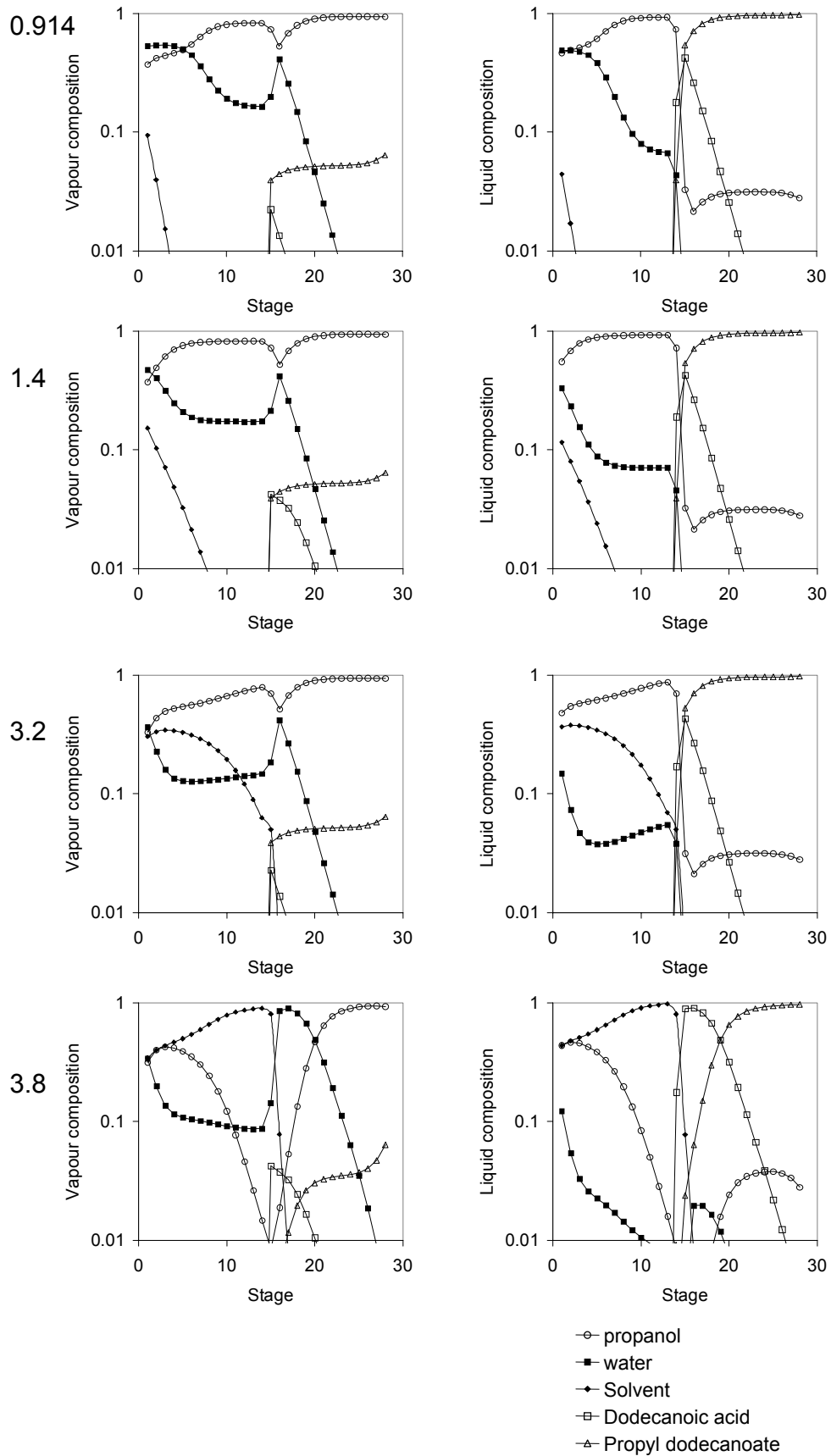
Figure 8 Liquid and vapour phase profiles for different solvent ratio

Fig. 8 displays in more detail the concentration profiles of vapour and liquid for four solvent ratios: 0.914, 1.4, 3.2 and 3.8. It may be observed the removal of water is effective even at minimum entrainer ratio. The molar fraction of water in liquid phase in the reaction zone is kept below 0.01, a good value for preserving catalyst activity. However, at a higher solvent ratio, in this case 3.8, the removal of water gets worse. Increased concentration of water at the top of reaction zone is recorded, where the reaction rate is at maximum. The explanation can be found in the inversion of the profiles of alcohol and entrainer, in the sense that the entrainer replaces the alcohol.

Comparison with process without solvent

A process without solvent can be designed in which the alcohol is completely consumed in the reaction zone, similarly with the lauric acid the esterification with methanol (Omota et al., 2001). Concentration profiles are displayed in Fig. 9 (left). The concentration of 1-propanol goes to zero at the top of the reaction zone, where by consequence the reaction rate is low. The maximum reaction rate is recorded in this case on the stage number five (Fig. 9, right).
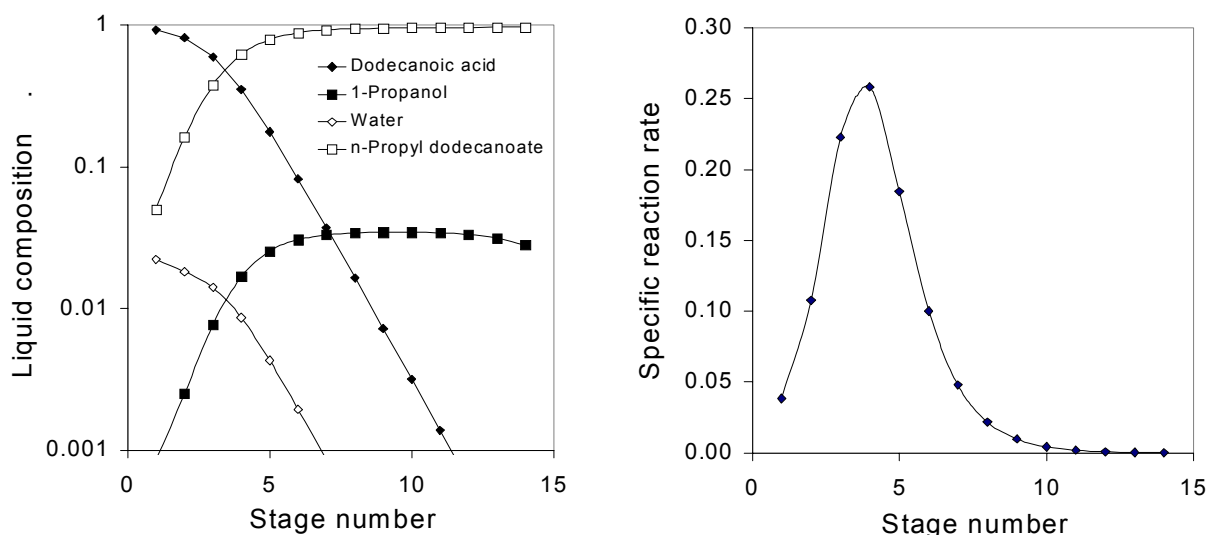

Figure 9 Concentration and reaction rate profiles of a process without solvent (complete alcohol consumption in top)

The advantage of using entrainer can be measured by comparing the catalyst consumption necessary to achieve the same conversion in the process with entrainer (Fig. 10, Case 1) against the process without entrainer (Fig. 10, Case 2). It may be seen that a reduction of about 40-50% can be noted, the effect being more important at higher purities. The beneficial action of the entrainer can be explained by a higher reaction rate at the top of the reactive zone, because of increased concentration of alcohol.
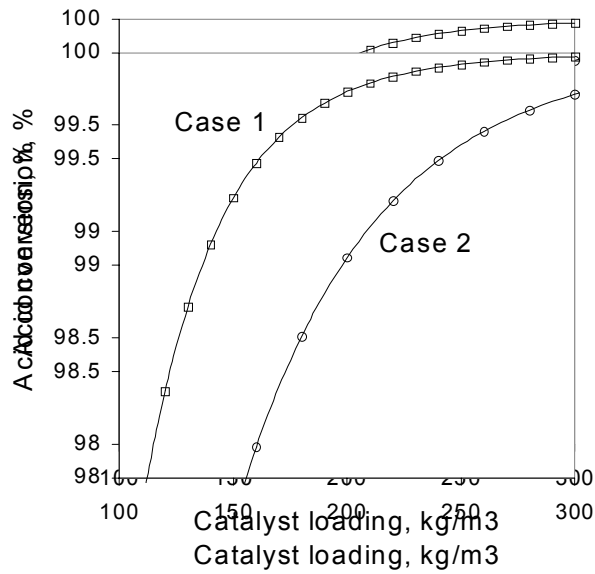
Figure 10 Comparison of processes with and without entrainer
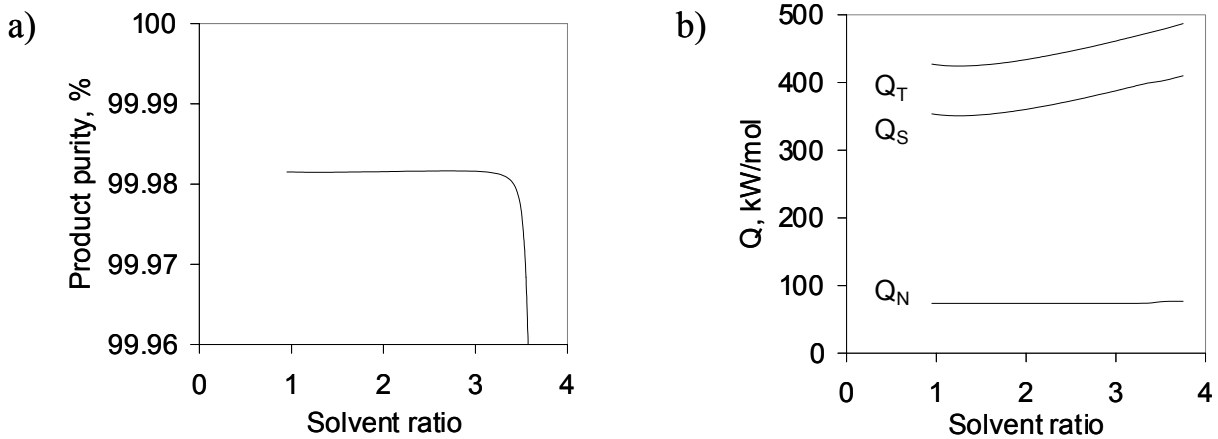
OPTIMISATION

Figure 11 Effect of solvent ratio on product purity and energetic consumption.

The computer simulation indicates that the product purity remains high over a large interval of the entrainer/reactant ratio. The energy increases with the solvent/reactant ratio, while the reboiler duty remains constant, the side-heater duty is proportional (Fig. 11). Therefore, solvent/reactant ratio turns out to be an optimisation variable between purity and energy requirements. In this case the optimum entrainer/reactant ratio is about 1.3.

CONCLUSIONS

The use of an entrainer as Mass Separation Agent in catalytic reactive distillation processes can bring significant advantages, by overcoming limitations set by distillation boundaries, and offering better opportunities for the reconciliation of reaction and separation conditions.

The principle has been demonstrated by the catalytic esterification of fatty acids with C2-C4 alcohols. Suitable entrainers have been found in the class of hydrocarbons, aliphatics and aromatics, as well as oxygenated and halogenated components

The entrainer should form a heterogeneous ternary azeotrope, from which the water product could be removed by decantation, eventually followed by a simple stripping. In this way the simultaneous removal of alcohol with water from the reaction space is prevented. A second costly distillation unit for alcohol recovery is not necessary, or limited to a simple stripping device.

As example the article presents the catalytic esterification of lauric acid with 1-propanol using n-propyl-acetate as entrainer, for which a feasible flowsheet is proposed. The examination of the concentration profiles indicates that the role of entrainer is to enhance and facilitate the water removal, allowing simultaneously direct recycle of the alcohol to the reaction zone. By consequence, the reaction rate can increase substantially. The comparison with a process without entrainer in similar conditions shows that the catalyst loading can be reduced up to 50%.

Minimum and maximum entrainer ratios have been identified. The first comes from the material balance constraint set by the azeotrope composition, the second from the Residue Curve Map characteristics. At higher entrainer ratio the distillation boundary alcohol-entrainer can be crossed, with negative effects on the process.

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