Thermodynamic modeling, synthesis and optimization of extraction — dehydration processes

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Abstract

The synthesis problem of a new separation operation (dehyextraction) with near critical fluids is formulated as a mixed integer nonlinear programming (MINLP) problem. The key separation properties of the dehyextraction process are predicted by the group contribution with association equation of state (GCA-EOS) that supports property predictions of a rigorous process simulator. The simulator is integrated to a MINLP optimization program. Optimal schemes and operating conditions are determined for different aqueous solutions in a wide range of oxychemical compositions. A detailed study for the recovery and dehydration of ethanol, 2-propanol and acetone and mixtures of these solutes from aqueous solutions using supercritical gases as propane, propylene and isobutane is presented. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Thermodynamic modeling; Near critical fluid; Synthesis; Optimization; MINLP synthesis

1. Introduction

The use of light hydrocarbons at near critical conditions for the recovery of dehydrated oxychemicals from azeotropic or dilute aqueous mixtures has been studied by several authors (Brignole, Andersen & Fredenslund, 1987; Zabaloy, Mabe, Bottini & Brignole, 1992; Horizoe, Tanimoto, Yamamoto & Kano, 1993). The process is based on a process cycle in which the aqueous mixture is fed to an extractor and the solvent and the extracted product are separated in a solvent recovery column. This is the simplest two-column (extraction + distillation) separation process, typical of liquid or supercritical extraction. A distinct advantage of this process is that the distillation column besides recovering the solvent, also completely removes the water from the bottom product. In this way, dehydrated products can be obtained without additional columns to remove the water. The solvents that are suitable for this type of separation process (dehyextraction) are called dual effect solvents. They should offer good selectivity for the oxychemical recovery and also exhibit the water entrainment effect (water–solvent relative volatility greater than one at the solvent recovery column). Moreover, no azeotrope formation between the solvent

and the extracted product is required. A thorough study of process alternatives for the recovery of ethanol from water using this approach has been presented by Gros, Diaz and Brignole (1998). This separation is just an example of a wide class of separation problems related to the recovery and dehydration of oxychemicals from aqueous solutions. Depending on the solutes to be recovered, concentration and near critical solvent selected, different optimum schemes and operating conditions are obtained. The great variety of separation problems calls for suitable modeling, simulation and optimization tools for process synthesis and design.

In this work, the synthesis and optimization of the dehyextraction process is performed with a rigorous process simulator that is integrated to a mixed integer nonlinear programming (MINLP) optimization program (Diaz, Serrani, De Beistegui & Brignole, 1995). The phase equilibrium properties are based on a Group Contribution with Association Equation of State, GCA-EOS (Gros, Bottini & Brignole, 1996). In Section 2, the thermodynamic modeling is described and key thermodynamic properties are discussed. In Section 3, different process alternatives are analyzed and the process mathematical model is presented together with the optimization algorithm description. In Section 4, the dehyextraction operation is studied for the recovery and dehydration of several aqueous mixtures with oxy-

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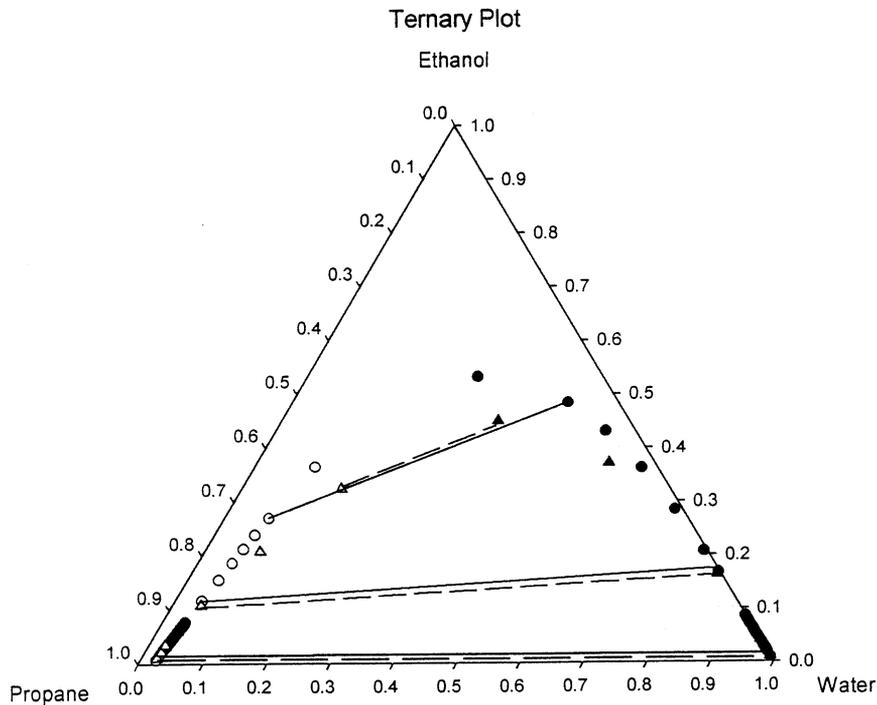chemicals such as ethanol, 2-propanol and acetone at different concentrations. The potential of many dual effect solvents is investigated and special attention has been devoted to propane and isobutane.

2. Thermodynamic modeling

'Semi-empirical' equations of state, such as GC-EOS (Skjold-Jorgensen, 1988), MHV2 (Dahl, Fredenslund & Rasmussen, 1991) and GCA-EOS (Gros et al., 1996) have been proposed to model the dehyextraction of oxychemicals from aqueous solutions with near critical solvents. Simplicity for engineering applications, extrapolation capacity in wide ranges of temperature and pressure and efficiency in handling highly nonideal azeotropic mixtures at near critical conditions justify their application.

2.1. Group contribution equation of state with association

Gros et al. (1998) have proposed the GCA-EOS as a reliable method for modeling the recovery of dehydrated alcohols using near critical light hydrocarbons as solvents. Three types of energetic contributions are taken into account in this equation of state: repulsive, attractive and associative. The repulsive hard sphere and attractive dispersive terms are the same as in the original GC-EOS model (Skjold-Jorgensen, 1988). The third term has been proposed by Gros et al. (1996) to take into account the association effects due to the hydrogen bonding between the O and H sites of an unique associating OH group, the same for all alcohols and water. The Helmholtz function due to association is calculated with a modified form of the expression used in the SAFT equation (Chapman, Gubbins, Jackson & Radosz, 1990; Huang & Radosz, 1990, 1991).

Due to the addition of associating parameters, new dispersive pure energy parameters (g_{ii}) have been obtained for the associating groups (CH_2OH, H_2O, etc.) and revised binary interaction parameters (k_{ij} and α_{ij}) have been estimated for pairs of groups in which one or both depict associating behavior (gases, alcohols, ketones and paraffinic groups; Gros et al., 1996; Diaz, Gros, Zabaloy & Brignole, 1999). The original definition of groups and the values for the reference temperature T_i^* and group surface area q_i are those proposed by Skjold-Jorgensen (1988). A detailed description of the GCA-EOS thermodynamic model is given in Appendix A.

Table 1 shows the matrix of available parameters for these mixtures. Fig. 1 shows GCA-EOS ternary equilibrium predictions compared with experimental data for the ethanol–water–propane system (Horizoe et al., 1993) at 403 K and 100 bar.

2.2. Key thermodynamic properties in extraction and dehydration with near critical fluids

In a basic dehyextraction scheme, the main units are: a high-pressure extractor and solvent recovery columns, as it is shown in Fig. 2. The near critical fluid (NCF) solvent stream enters the extraction column at the bottom, while the water–oxychemical stream is fed to the top of the column. The extraction column is operated at conditions near the critical temperature of the solvent and at pressure above the critical. The extract (oxychemical and solvent) contains a small amount of water. The raffinate mainly consists of water and a very small amount of oxychemical and almost no solvent. The extract is reduced in pressure through a valve and fed to a distillation column to recover the solvent. In this column the solvent is recovered and the complete dehydration of the oxychemical is obtained, by the entrainment of water by the near critical solvent. The

Table 1
Available pure group and binary interaction parameters for GCA-EOS in aqueous azeotropic mixtures and dual effect solvents

		1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	CH_3	x	x	x	x		x	x	x	x	x	x	x	x	x
2	CH_2		x	x	x		x	x	x	x	x	x	x	x	x
3	(ws)CH_3			x	x		x	x	x	x	x	x	x	x	x
4	(ws)CH_2				x		x	x	x	x	x	x	x	x	x
5	CH_3OH					x				x	x				x
6	CH_2OH						x	x	x	x	x	x	x	x	x
7	CHOH							x	x	x	x	x		x	
8	CH_3CO								x	x	x	x	x	x	x
9	H_2O									x	x	x	x	x	x
10	Propane										x	x	x	x	x
11	Propylene											x	x	x	x
12	Butane												x	x	x
13	Isobutane													x	x
14	CO_2														x

Ternary Plot

Fig. 1. Liquid–supercritical fluid equilibrium for the ethanol–water–propane system (weight fractions). Experimental data: (△--▲) Horizoe et al. (1993); (○—●) GCA-EOS.

distillate is returned as the NCF solvent to the extractor and almost absolute oxychemical is obtained at the bottom of the distillation unit.

Simulation results in this process strongly depend on the accuracy of the thermodynamic model predictions of the following phase equilibrium properties:

1. Distribution coefficient of the oxychemical between the aqueous phase and the solvent phase at the extractor operating conditions. The solvent flowrate is directly determined by this variable. Figs. 3 and 4 show distribution coefficients of different oxychemicals between the near critical solvent and the aqueous phase, as predicted by GCA-EOS. Fig. 3 shows the ethanol distribution coefficient between propane and aqueous phase, together with experimental data (Horizoe et al., 1993) at 99 bar and 5% ethanol molar concentration. The distribution coefficients for acetone are also shown in this figure at 80 bar and 4% acetone molar concentration. Fig. 4 shows distribution coefficients for 2-propanol at dilute solute concentrations for two near critical solvents: propane and isobutane. In all cases, distribution coefficients increase with temperature; therefore higher extraction temperatures result in lower solvent requirements. Acetone presents higher distribution coefficients than alcohols.

2. The concentration of water in the extract, which determines the selectivity of the extraction process and is a key variable for the operation of the dehydration column.

3. The relative volatility of water with respect to the solvent under the dehydration column conditions, it should be greater than one to obtain the water entrainment effect, i.e. to obtain water and solvent as top product in the distillation column. Fig. 5 shows water/propane relative volatility for several mixtures. For acetone or 2-propanol mixtures; a water/oxychemical ratio of 1/40 has been considered. The water relative volatility is greater than one
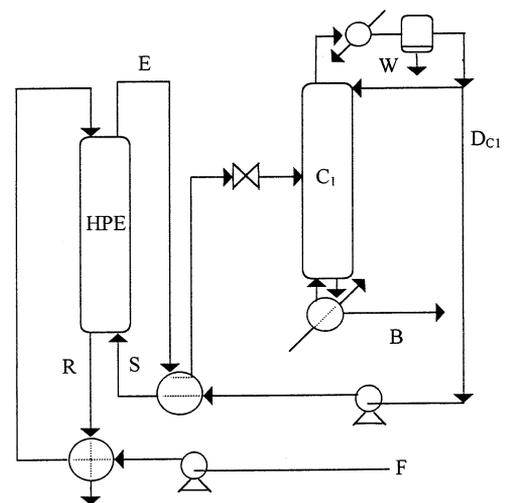
Fig. 2. Simple extraction–dehydration cycle. HPE: high-pressure extractor, C_1: dehydration column, F: aqueous feed, R: raffinate, B: dehydrated oxychemical, S: solvent.
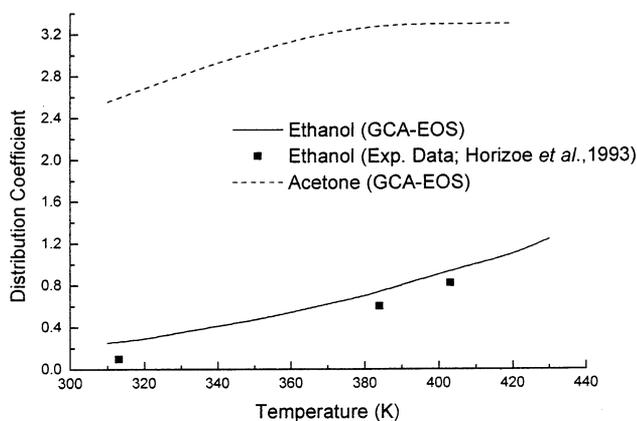
Fig. 3. Ethanol and acetone distribution coefficients between near critical propane and aqueous phase.
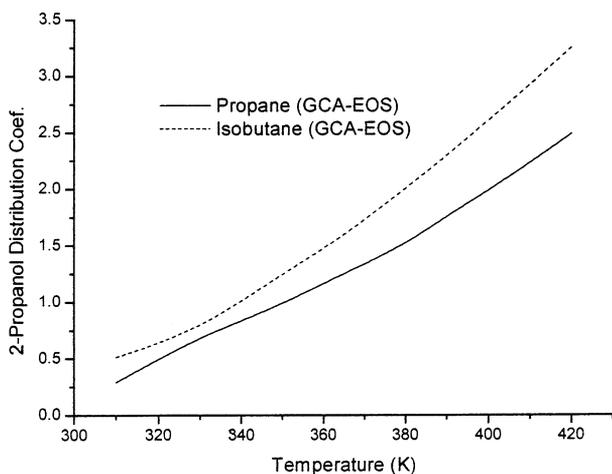
Fig. 4. Distribution coefficients for 2-propanol between water and propane or isobutane as function of temperature for dilute solutions ($x_{IPA} = 0.04$), at $P = 80$ bar.
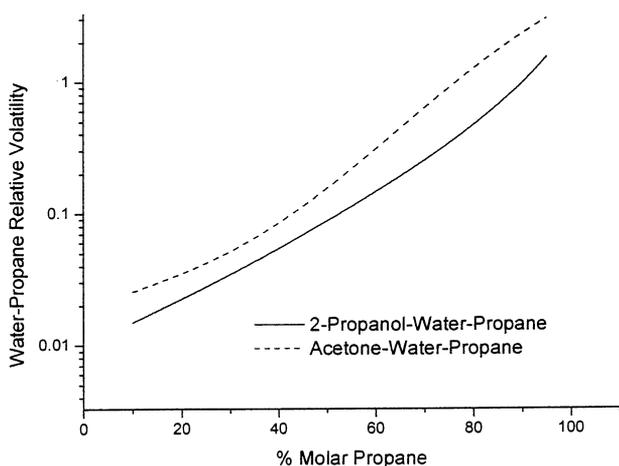
Fig. 5. Water–propane relative volatility dependence on molar propane concentration and temperature. Water/oxychemical ratio equal to 1/40.

above 75% propane concentration in acetone mixtures. In the case of water–propane–alcohol mixtures, propane concentrations have to be above 90% to achieve water–propane relative volatility greater than one. This is due to the strong association of water and alcohol in the propane phase.

4. The relative volatility of the oxychemical with respect to the solvent, under the conditions of the dehydration column, which determines the feasibility of the separation (no azeotrope formation between solvent and oxychemical) and in many cases the energy consumption of this unit.

5. Three phase formation (l-l-v) in the top of the solvent recovery column. If a third aqueous phase appears, water cannot be entrained by the solvent and it is obtained as bottom product together with the oxychemical (no dehydration is achieved in the column).

When the first conceptual dehyextraction schemes were presented (Brignole et al., 1987) the simulation and evaluation of process alternatives were based on the GC-EOS model (Skjold-Jorgensen, 1988). The model parameters were estimated on the basis of binary high-pressure vapor liquid equilibria information. However there was a lack of experimental information on ternary mixtures, to assess the quality of the predictions for the five key phase equilibrium properties. When measurements of ternary experimental information were available, the limitation of the GC-EOS model to handle high-pressure mixtures of non polar + associating components, was realized and Gros et al. (1996) developed the GCA-EOS to improve the model predictions. Recently Gros, Bottini and Brignole (1997) made a thorough testing of the capability of the GCA-EOS model to accurately describe, the key thermodynamic properties of the dehyextraction process

3. Process synthesis and optimization

Based on the previously described extraction–dehydration process, different process alternatives can lead to more efficient and economic designs. A thorough thermodynamic analysis results in the formulation of structural process modifications to improve process performance.

Aqueous solutions of different oxychemicals, concentrations and supercritical solvents require different process schemes and operating conditions. Different process alternatives have been formulated as a MINLP problem to systematize the decision-making procedure and to be able to easily embed more alternatives in dealing with real and industrial processes in the extraction and dehydration of a wide family of oxychemicals with near critical fluids.

3.1. Alternative NCF schemes

In oxychemicals + propane mixtures the boiling point increases when the oxychemical concentration is rather small (if the oxychemical concentration is of the order of 50% molar or lower). This feature justifies the use of a two distillation column scheme. In the first column, all the water and almost all the NCF solvent are removed as top product. An equimolar oxychemical + NCF solvent mixture is obtained as bottom product. The second distillation completes the oxychemical + solvent separation. This two-column approach has several advantages: (a) low reboiler temperature of the main distillation column which facilitates heat integration; (b) operation of the first column at higher pressure; this fact gives greater water concentration at saturation, avoiding the formation of a third aqueous phase on the top section of the distillation column; (c) the second column can operate at much lower pressure with low reboiler temperature and reduced energy consumption (less reflux). The use of a two-column scheme also allows the application of a heat pump in the first distillation column, that leads to considerable energy saving.

In this process, the main contribution to energy consumption is the near critical solvent recirculation rate; moreover, the solvent requirement at given operating conditions is directly proportional to the feed rate. Therefore, a reduction of the feed flow to the extractor is an attractive alternative. The recovery of oxychemicals from dilute aqueous solutions can be achieved with low energy consumption by ordinary distillation, if the separation goal is the complete alcohol removal from the solution. The high alcohol–water relative volatility for dilute aqueous mixtures allows the increase of the alcohol or oxychemical concentration using a simple stripping column. In this way, the preconcentration of the process feed reduces the flowrate of the aqueous solution to the extractor, and therefore the solvent requirements. The use of the two-column approach discussed before, makes possible the energy integration between the feed preconcentration and first solvent recovery column, such as matching the vapor of the preconcentrator top stream, with the reboiler of the first solvent recovery column. However, the stream matches depend on the preconcentrator operating pressure.

Table 2
Bounds on design variables

Variable	Lower bound	Upper bound
Extractor temperature (K)	325	420
Extractor pressure (bar)	40	100
Solvent (Kmol/h)	45	1500
Reflux ratio	0.3	2.5

The formation of a third (aqueous) phase can be avoided by the cooling of the extract after leaving the near critical extractor. The extract cooling gives place to the formation of an aqueous phase that can be recycled to the extractor.

If the top vapor of the dehydration column is compressed, this stream can be thermally integrated to the reboiler and the energy consumption is mainly determined by the overhead vapor compression. The required energy in the column reboiler/condenser is supplied by the condensation of the recompressed vapor and no external heating services are required. A vapor recompression scheme can be used if there is a low temperature difference between top and bottom at the dehydration column; this operating condition can be obtained if a rather high concentration of solvent is kept in the bottom product.

3.2. Process model

The synthesis problem of the dehyextraction process can be formulated as the following mixed integer non-linear programming (MINLP) model:

$$\text{Min } f(x, y)$$
$$x, y$$
s.t.
$$h(x, y) = 0$$
$$g(x, y) \leq 0$$
$$y \varepsilon \{0, 1\}^{\mathrm{m}}, x \varepsilon \mathscr{R}^{\mathrm{n}}, x_{\mathrm{L}} \leq x \leq x_{\mathrm{U}},$$

where x represents continuous optimization variables and y corresponds to binary variables that represent discrete decisions.

Four design variables have been selected to represent main continuous decisions associated to the NCF extraction–dehydration process; they correspond to operating conditions at the high-pressure extractor (temperature and pressure), solvent flowrate and reflux ratio at the dehydration column. Table 2 shows bounds on these variables.

Binary variables (y) account for discrete decisions such as including one unit in the process flowsheet or not. The high-pressure extractor and the dehydration column are always included in the NCF process flowsheet, but the preconcentrator, the vapor compressor, the cooler and the second solvent recovery column are potential units and their existence is associated to binary variable values, as shown in Table 3 and Fig. 6.

Equality constraints (h) represent the NCF plant mathematical model and they are solved within a sequential process simulator (De Beistegui, Bandoni & Brignole, 1992) with a black box strategy. This program includes rigorous models for a high-pressure multistage extractor (Kehat & Ghitis, 1981), low and high-pressure distillation columns (Naphtali & Sandholm, 1971), and

Table 3
Binary variables and corresponding units

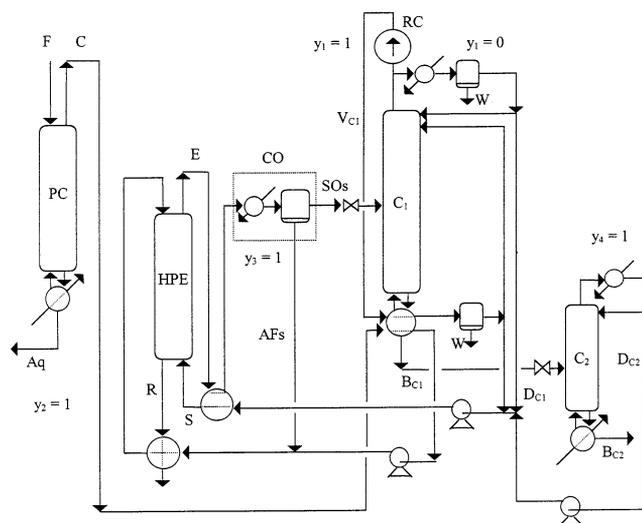| Unit	Binary variable
Vapor compressor	y_1
Preconcentrator	y_2
Flash (cooling option)	y_3
Second solvent recovery column	y_4

Fig. 6. Dehyextraction process superstructure. HPE: high-pressure extractor, C_1: dehydration column, C_2: second solvent recovery column, CO: cooling unit, PC: preconcentrator, RC: recompressor, F: aqueous feed, R: raffinate, B_{C_2}: dehydrated oxychemical, S: solvent.

a multiphase flash (Michelsen, 1982). The GCA-EOS has been integrated as thermodynamic support for these model unit simulation routines.

Inequality constraints (**g**) include process specifications, operating bounds and bounds on potential units. A detailed description of constraints and bounds is given in Table 4. Constraints r5, r6 and r7 are handled as mixed integer nonlinear ones, where y_2 is the binary variable.

Pure integer constraints stand for the forbidden combination of a preconcentrator and a vapor compressor:

$$y_1 + y_2 \leq 1,$$

and for the existence of a vapor recompressor only if a second solvent recovery column exists:

$$y_1 - y_4 \leq 0.$$

Objective function (f): The process is thermodynamically feasible so the objective is to minimize equivalent thermal energy consumption to optimize its economical performance. Energy consumption has been selected as the economical objective function because utility costs depend on local conditions. The objective function is composed of several terms corresponding to pumping energy for solvent and aqueous solution and heating requirements for the distillation columns. Electricity cost is higher than steam cost. To carry out the evaluation of the different alternatives on a similar cost basis, mechanical energy (kJ/kg) has been affected by a factor of 3.0 (Streich & Bolkart, 1982) so as to convert it in an amount of thermal energy of equivalent cost. To avoid products between continuous and binary variables, additional continuous variables have been defined.

$$f = \Delta H_1^* y_1 + \Delta H_2^* y_2 + \Delta H_3^* (1 - y_2 - y_1) + \Delta H_4^* y_4$$
$$+ \Delta H_5 + \Delta H_6,$$

where

ΔH_1 vapor compression energy (kJ/kg dehydrated oxychemical)

ΔH_2 preconcentrator heating requirement (kJ/kg dehydrated oxychemical)

ΔH_3 dehydration column heating requirement (kJ/kg dehydrated oxychemical)

ΔH_4 second solvent recovery column heating requirement (kJ/kg dehydrated oxychemical)

ΔH_5 solvent pumping energy to high-pressure extractor conditions (kJ/kg dehydrated oxychemical)

ΔH_6 aqueous feed pumping energy (kJ/kg dehydrated oxychemical)

When a preconcentrator exists, its top stream is thermally integrated to the dehydration column reboiler. Heat integration between the preconcentrator and the dehydration column reboiler has been handled

Table 4
Description of nonlinear inequality constraints

Unit	Constraint	Description	Bound
Extractor	r1	Oxychemical recovery (%)	≥ 98.5
Solvent recovery column C1	r2	Water composition in top vapor phase	$\leq Y_{H2O}(sat)$
Solvent recovery column C1	r3	Oxychemical recovery (%)	≥ 98
Solvent recovery column C1	r4	Oxychemical (solvent free basis) in bottom	≥ 99
Preconcentrator	r5	Oxychemical recovery (%molar)	≥ 99.5
Preconcentrator	r6	Energy available from preconcentrator vapor	$\geq QreboilerC1$
Preconcentrator	r7	Preconcentrator vapor — reboilerc1 temperature difference	≥ 15

with nonlinear constraints. The top stream of the pre-concentrator (which comes from a partial condenser) must be able to provide at least the entire energy required in the reboiler. Ideal heat integration can be overcome by imposing that a certain percentage of the energy available from the condensation of this top stream provides the entire heat for the dehydration column reboiler. In most cases, this constraint is active at the optimum; however, if there is additional energy available, it could be used for other services, for example, to heat the aqueous feed. If a vapor recompression scheme is included, only compression energy is accounted for because the compressed stream provides the reboiler heating requirement.

3.3. Optimization strategy

The optimization is performed by the integration of a rigorous sequential modular simulator to an optimization program (Diaz et al., 1995). The optimization algorithm is an ad hoc extension of the outer approximations (Duran & Grossmann, 1986) that interacts with a process simulator in a black box way. Nonlinear programming subproblems have been solved with OPT (Biegler & Cuthrell, 1985). An additional problem in the rigorous modeling with a sequential modular simulator is to take into account the effect of nonexisting units to build up the MILP problem. Linearization coefficients for continuous variables that do not belong to the analyzed configuration have been determined by perturbations around the current NLP optimum. For convex problems, the algorithm guarantees convergence to global optimum. The use of a black box simulator for function evaluation does not guarantee problem convexity and outer approximations may cut off parts of the feasible region and converge to locally optimal solutions. To validate the local optimum quality, the program has been run from different continuous and integer initial points that converged to the same MINLP optimum and results indicate that nonconvex solutions greatly improve the objective function.

4. Numerical results

The extraction of different alcohols, ketones and mixtures of alcohol and acetone has been studied for typical fermentation solutions of 10 000 kg/h of aqueous mixtures, using propane ($T_c = 369.8$ K, $P_c = 41.9$ bar) or isobutane ($T_c = 408.2$ K, $P_c = 36.$ bar) as near critical solvents. Mixture compositions ranging from 5 to 50% have been studied.

The following units specifications have been considered (Gros et al., 1998): *extractor*: 10 stages; *first solvent recovery column:* 35 stages, pressure: 25 bar;

second solvent recovery column: pressure: 12 bar; reflux ratio: 0.7.

4.1. Dehyextraction of ethanol from water

The optimal process scheme for the dehyextraction of ethanol from a 10 wt.% aqueous solution with supercritical propane is shown in Fig. 7; it is a plant that includes a feed preconcentrator ($y_2 = 1$) integrated to the reboiler of the dehydration column and a second solvent recovery column ($y_4 = 1$) (Gros et al., 1998). Table 5 shows main variable values and equivalent thermal energy consumption for the initial configuration (simple extraction–dehydration scheme) and for the MINLP optimum. Total energy consumption has been reduced from 26 200 kJ/kg of dehydrated ethanol
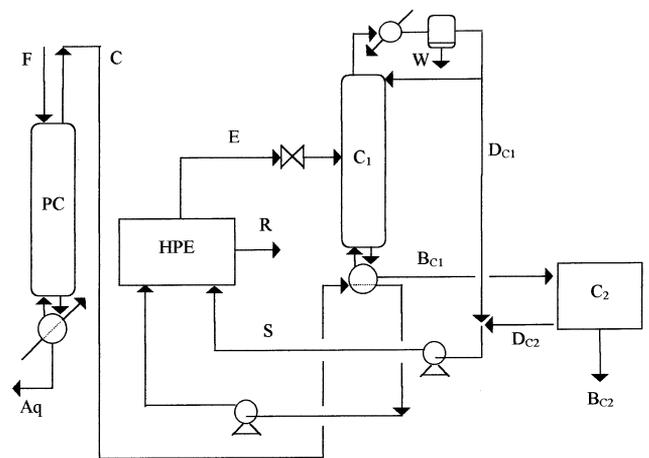
Fig. 7. MINLP optimum for the extraction and recovery of ethanol from a 10 wt.% ethanol aqueous solution with propane: NCF cycle with preconcentrator (0 1 0 1).

Table 5
Dehyextraction of ethanol with propane[a]

	Initial dehyextraction optimum	MINLP optimum
Textr (K)	397.	365.
Pextr (bar)	100.	60.
Solvent (kmol/h)	760.	176.
Reflux ratio	1.5	0.86
Binary variables	0 0 0 1	0 1 0 1
Preconcentrator (kJ/kg)	–	3500.
Solvent recovery column 1 (kJ/kg)	22200.	3500.
Solvent recovery column 2 (kJ/kg)	500.	500.
Pumping (kJ/kg) (thermal)	3500.	370.
Utility costs (US$/h)	54.68	9.12
Total thermal energy eq.(kJ/kg)	26200.	4370.

[a] Optimal operating conditions and energy consumption for initial configuration and MINLP optimum.

Table 6
Matrix of active constraints for dehyextraction of a 10% ethanol aqueous mixture with propane

Scheme	y_1, y_2, y_3, y_4	r_1	r_2	r_3	r_4	r_5	r_6	R_7
Basic Dehyextraction	(0,0,0,1)	▨	▨	▨				
Basic Dehyextraction + Cooling	(0,0,1,1)	▨		▨				
Vapor Recompression	(1,0,0,1)	▨	▨	▨				
Vapor Recompression+Cooling	(1,0,1,1)	▨						
Preconcentration	(0,1,0,1)		▨		▨	▨	▨	
Preconcentration+Cooling	(0,1,1,1)			▨		▨		

(the NLP optimal value for the simple NCF scheme) to 4370 kJ/kg of dehydrated alcohol in the preconcentration/energy integration option (MINLP optimum). The values 3500 and 370 kJ/kg associated to pumping energy correspond to actual pumping energy requirements of 1167 and 123 kJ/kg, respectively that have been affected by a weighing factor to convert them to amounts of thermal energy of equivalent cost. This process scheme also shows lower operating pressure and temperature in the extractor and an important reduction in solvent requirements. Utility costs have also been determined as associated to energy consumption for the processing of 10 000 kg/h of aqueous mixture. Electricity cost is 0.023 US$/(kW/h) and low pressure steam cost is 4.54 US$/ton. In the extraction and dehydration of a 10 wt.% ethanol aqueous solution with near critical propane, each alternative flowsheet has been analyzed as an NLP problem and the matrix of active nonlinear constraints for these different process schemes is shown in Table 6. It can be noted that both in the simple extraction–dehydration cycle optimum and in the vapor recompression option, there are three active constraints: r_1, r_2 and r_3; the optimum is more sensitive to r_2 (the water composition in top vapor phase), as the Lagrange multiplier associated to this constraint is much higher than the other two. This active constraint is removed by cooling the extract, as it is shown in the simple extraction + cooling option. For the feed preconcentration scheme using extract cooling/water elimination, the internal reflux/vapor requirements at column C_1 are determined by the specified ethanol–propane separation ($r_3 = 0$). These requirements are lower than those for the scheme without water elimination and, consequently, the required energy at column C_1 results lower than the available. The additional energy (about 22% of the total available) can be used for other services.

4.2. Dehyextraction of 2-propanol from water

The extraction and recovery of 2-propanol has been studied for two different near critical solvents: propane and isobutane. Aqueous solutions from 5 to 50 wt.% 2-propanol have been analyzed. Table 7 shows a comparison between equivalent thermal energy consumption and utility costs at the simple NCF cycle optimum and at the MINLP optimum for different aqueous solution concentrations; binary and continuous design variables at the MINLP optimum are also reported. For dilute solutions, the feed preconcentration option is the best design. For concentrations above 20 wt.% of 2-propanol, the feed preconcentration is not required and the optimal configuration is the vapor recompression scheme, as it is shown in Fig. 8.

Table 8 shows equivalent thermal energy consumption and main operating variables for the initial NLP optimum in the simple NCF cycle and in the MINLP optimum for two alternative near critical solvents: propane and isobutane respectively. The use of isobutane as near critical solvent provides lower energy consumption. In the case of the simple dehyextraction cycle with isobutane, it is possible to operate the extractor at higher temperature with lower solvent requirements

Table 7
Comparison between simple dehyextraction cycle optimum and MINLP optimum for the extraction and recovery of 2-propanol from aqueous solutions with near critical propane

| Variable	5 wt.%	10 wt.%	20 wt.%	50 wt.%
Simple NCF cycle: NLP optimum				
y_o	0 0 0 1	0 0 0 1	0 0 0 1	0 0 0 1
Total energy consumption (kJ/kg)	22008.	10505.	4870.	2962.
Total utility cost (U$S/h)	22.96	21.92	20.33	30.91
MINLP optimum				
y	0 1 0 1	0 1 0 1	1 0 0 1	1 0 0 1
Text (K)	363.5	350.0	366.2	350.0
Pext (bar)	40.0	40.0	61.0	67.0
Solvent flowrate (kmol/h)	100.0	121.7	490.5	605.0
Reflux ratio	0.84	1.5	0.59	1.50
Total utility cost (U$S/h)	7.36	8.01	9.60	16.71
Total energy consumption (kJ/kg)	7058.	3836.	2300.	1601.
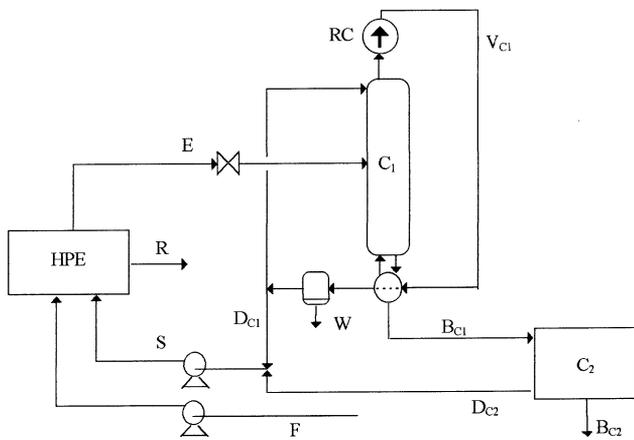
Fig. 8. MINLP optimum scheme (vapor recompression) for the dehyextraction of 2-propanol from concentrated aqueous solutions (above 20 wt.% 2-propanol).

Table 9
Energy consumption and design variables for the extraction and dehydration of 2-propanol from a 20 wt.% aqueous solution with isobutane

Variable	Simple NCF cycle optimum	MINLP optimum
Binary	0 0 0 1	1 0 0 1
Solvent recovery column 1 (kJ/kg)	3826.	3826.
Solvent recovery column 2 (kJ/kg)	327.	327.
Recompression (kJ/kg)	–	960.
Pumping (kJ/kg) (thermal eq.)	226.	226.
Total utility costs (US$/h)	18.28	6.31
Total energy (kJ/kg)	4379.	1513.

because the distribution coefficient of the alcohol between the solvent and the aqueous phase increases with temperature, as shown in Fig. 4. This operation can be done without loss in selectivity because isobutane has a higher critical temperature than propane. When using isobutane as NCF, the dehydration column operates at 11 bar (it operates at 25 bar with propane) and the second solvent recovery column, at 4 bar (12 bar for propane as NCF). It is important to note that isobutane cannot be used for ethanol extraction because there is an azeotrope between ethanol and isobutane as reported by Zabaloy, Gros, Bottini and Brignole (1994).

Table 9 shows optimization results for the extraction and dehydration of a 20 wt.% 2-propanol aqueous solution with isobutane. There is a 21% decrease in utility costs with respect to the dehyextraction with propane. The use of isobutane does not change the fact that the MINLP optimum corresponds to a vapor compression scheme for concentrations above 10 wt.%

2-propanol. In this case, the same continuous optimization variable values have been obtained for both the initial and the optimal scheme, i.e. the extractor optimal conditions are 393.8 K and 35 bar with a solvent flowrate of 233.6 kmol/h. The MINLP optimum corresponds to the same operating condition, but with the integration of the compressed vapor to the column reboiler.

4.3. Dehyextraction of acetone from water

The recovery of acetone from aqueous solution has been investigated using propane as near critical solvent. Both the distribution coefficient of acetone between water and propane and the selectivity are considerably higher than for ethanol and 2-propanol, as shown in Fig. 3. Therefore, acetone can be extracted and dehydrated by an extraction stage at subcritical conditions. However, we study the potential of this technology for the extraction and dehydration of acetone.

Table 8
Comparison of optimal conditions in the dehyextraction of 2-propanol with two different near critical solvents (propane and i-butane) from an aqueous solution of 10 wt.% 2-propanol

Variable	Simple NCF cycle optimum		MINLP optimum	
	Propane	i-butane	Propane	i-butane
Textr (K)	380.00	416.66	350.00	351.5
Pextr (bar)	72.60	63.95	40.00	35.00
Solvent (kmol/h)	458.9	204.67	121.7	47.8
Reflux Ratio	0.79	1.68	1.50	1.70
Binary	0 0 0 1	0 0 0 1	0 1 0 1	0 1 0 1
Preconcentrator (kJ/kg)	–	–	3161.5	2188.3
Solvent recovery column 1 (kJ/kg)	8820.7	8462.9	2820.5	1357.2
Solvent recovery column 2 (kJ/kg)	311.5	359.1	296.7	446.7
Recompression (kJ/kg)	–	–	–	–
Pumping (kJ/kg) (thermal eq.)	1372.8	850.0	95.6	59.3
Total energy (kJ/kg)	10505.	9673.1	3836.	2694.

Table 10 shows optimal operating conditions for the simple NCF cycle and for the MINLP optimum. Even for dilute solutions, the best process scheme is the vapor compression integrated to the column reboiler; it is not necessary to concentrate the aqueous solution due to the higher distribution coefficient between acetone and near critical propane and to the high selectivity of the separation. These processes offer an interesting alternative to the conventional distillation process, which requires more than 6000 kJ/kg dehydrated acetone.

4.4. Separation of multicomponent mixtures: water–acetone–2-propanol

The dehyextraction of an aqueous solution of 2-propanol and acetone (10 and 3 wt.%, respectively) has also been analyzed (Table 11). The optimal energy consumption of the simple near critical fluid solvent scheme is almost the same as the one required for the dehyextraction of 2-propanol from water plus the additional separation by conventional distillation of 2-propanol and acetone. A 99.99% 2-propanol can be obtained, with no acetone; operating variables are also comparable to 2-propanol cycle. However, the MINLP optimum scheme includes a vapor compressor with a 44% reduction in total energy consumption.

5. Conclusions

The wide family of problems covered by the conceptual process of extraction and dehydration of organic

Table 10
Dehyextraction of acetone from water with propane[a]1

Variable	Simple NCF cycle optimum	MINLP optimum
Textr (K)	382.56	360.00
Pextr (bar)	67.48	40.00
Solvent (kmol/h)	192.06	207.67
Reflux ratio	0.94	0.99
Binary variables	0 0 0 1	1 0 0 1
Solvent recovery column 1 (kJ/kg)	3759.6	4144.1
Solvent recovery column 2 (kJ/kg)	207.3	207.3
Pumping (kJ/kg) (thermal eq.)	686.4	324.2
Recompression (kJ/kg) (thermal eq.)	–	1379.7
Total utility cost (US$/h)	9.71	3.99
Total energy (kJ/kg)	4653.3	1911.2

[a] Aqueous solution: 10 000. Kg/h; 10 wt.% acetone.

Table 11
Dehyextraction of a mixture of 2-propanol and acetone from water with propane[a]1

Variable	Simple NCF cycle optimum	MINLP optimum
Textr (K)	379.62	379.40
Pextr (bar)	72.86	62.57
Solvent (kmol/h)	462.85	455.96
Reflux ratio	0.81	0.92
Binary variables	0 0 0 1	1 0 0 1
Solvent recovery column 1 (kJ/kg)	9040.5	7810.7
Solvent recovery column 2 (kJ/kg)	162.4	131.9
Recompression (kJ/kg) (thermal eq.)	–	3614.6
Pumping (kJ/kg) (thermal eq.)	1385.0	908.6
Total utility costs (US$/h)	28.72	12.63
Total energy (kJ/kg)	10587.8	4655.1

[a] Aqueous solution: 10000 kg/h; 10 wt.% 2-propanol, 3 wt.% acetone.

compounds from aqueous solutions is identified as a new separation operation: *dehyextraction*. The synthesis of process schemes for different applications has been addressed combining MINLP techniques with reliable thermodynamic models. The process thermodynamic analysis indicated that the economics of the process is dependent on several phase equilibrium variables. Therefore, the process simulation is supported by a group contribution thermodynamic model that gives reliable predictions of phase equilibria for low and high-pressure operations of vapor–liquid and liquid–near critical fluid phase equilibria, of highly nonideal azeotropic mixtures.

This methodology has been applied to the recovery of dehydrated alcohols and ketones using supercritical hydrocarbons as solvents. The MINLP optimization program has proved to be a robust and efficient tool for the systematic determination of both optimal schemes for different aqueous mixtures and their associated operating conditions. Furthermore, numerical results have shown that different feed concentrations and NCF solvents require different optimal schemes.

Finally, it has been shown that the dehyextraction operation using propane or isobutane is a feasible and economic process for the recovery and dehydration of oxychemicals from aqueous solutions.

Appendix A. Group contribution equation of state with association (GCA-EOS)

The GCA-EOS, as proposed by Gros et al. (1996), is derived from the computation of the residual Helmholtz function. This function is obtained as sum of three terms representing the contributions of different intermolecular forces. The first term, A^{hs}, accounts for the repulsive (hard sphere) interactions, the second term, A^{disp}, is due to the presence of attractive dispersive mean field interactions and the third term, A^{assoc}, accounts for the increment in the residual function due to site-site attractive specific interactions (e.g. hydrogen bonding). The general expression for the residual Helmholtz function is given by

$$A^{res} = A^{hs} + A^{disp} + A^{assoc} \tag{1}$$

Hard sphere and dispersive terms

The repulsive hard sphere and attractive dispersive terms are the same as in the original GC-EOS model (Skjold-Jorgensen, 1988). The repulsive only requires one pure component parameter, namely the hard sphere diameter. This is obtained from acentric factors, normal boiling points or vapor pressure data. The hard sphere diameter is assumed temperature dependent following the generalized expression

$$d = 1.06565 d_c (1. - .12 \exp(-2T_c/3T)). \tag{2}$$

The dispersive part is a group contribution version of a density dependent local composition (NRTL) expression for the dispersive Helmholtz function. The pure group parameters are the group surface q_i and the dispersive energy between like groups

$$g_{ii} = g_{ii}^*(1. + g_{ii}'(T/T_i^* - 1.) + g_{ii}'' \ln(T/T_i^*)). \tag{3}$$

T_i^* is an arbitrary but fixed temperature for group i. Binary parameters are the asymmetric non-randomness factor α_{ij} and the dispersive energy between unlike groups

$$g_{ij} = k_{ij}\sqrt{g_{ii}g_{jj}}. \tag{4}$$

$$k_{ij} = k_{ij}^*(1. + k_{ij}' \ln(T/T_{ij}^*)) \tag{5}$$

is a symmetric, temperature dependent, binary interaction parameter and

$$T_{ij}^* = (T_i^* + T_j^*)/2. \tag{6}$$

Expressions for the compressibility factors and fugacity coefficients are reported by Skjold-Jorgensen (1988).

Association term

The Helmholtz function due to association is calculated with a modified form of the expression used in the SAFT equation (Chapman et al., 1990). This expression is formulated in terms of associating groups. Therefore,

$$A^{assoc}/RT = \sum_{i=1}^{NGA} n_i^* \left[\sum_{k=1}^{M_i} \left(\ln X^{(k,i)} - \frac{X^{(k,i)}}{2} \right) + \frac{1}{2} M_i \right] \tag{7}$$

where n_i^* represents the total number of moles of associating group i, M_i the number of association sites assigned to group i and $X^{(k,i)}$ the mole fraction of group i non-bonded at site k. The group definitions from the association point of view do not necessarily have to agree with those in the dispersive term; this means for example, that whilst a distinction can be made between primary (CH₂OH), secondary (CHOH) and tertiary (COH) dispersive alcohols groups, a unique hydroxyl (OH) associating group is considered to represent the contribution of association to non-ideality in any possible alcohol solution. The number of moles of the associating group i is

$$n_i^* = \sum_{m=1}^{NC} \gamma_{assoc}^{(i,m)} \cdot n_m, \tag{8}$$

where $\gamma_{assoc}^{(i,m)}$ represents the number of associating groups i in molecule m and n_m the total number of moles of molecule m; the summation includes all NC components in the mixture. The mole fraction of group i not-bonded at site k is determined by

$$X^{(k,i)} = \left[1 + \sum_{j=1}^{NGA} \sum_{l=1}^{M_i} \rho_j^* X^{(l,j)} \Delta^{(k,i,l,j)} \right]^{-1} \tag{9}$$

where the summation includes all association groups and sites. As it can be seen in Eq. (9) $X^{(k,i)}$ depends on the molar density of the associating group j

$$\rho_j^* = n_j^*/V \tag{10}$$

and on the association strength between site k of group i and site l of group j

$$\Delta^{(k,i,l,j)} = \kappa^{(k,i,l,j)}[\exp(\varepsilon^{(k,i,l,j)}/kT) - 1]. \tag{11}$$

The association strength is a function of the temperature T(K) and the characteristic association parameters $\varepsilon^{(k,i,l,j)}$ and $\kappa^{(k,i,l,j)}$. These parameters have been proposed for a square well model of specific interactions between the two sites k and l (Chapman et al., 1990). The parameter $\varepsilon^{(k,i,l,j)}$ characterizes the association energy (well depth) and $\kappa^{(k,i,l,j)}$ (cm³/mol) the associating volume (well width). The energy of association, and hence the association strength between two like-sites from the same or different associating groups (for example the interactions oxygen–oxygen and hydrogen–hydrogen), are set equal to zero. Compared to other expressions proposed in the literature (Chapman et al., 1990) for the association strength, Eq. (11) does not include a radial distribution function. The simpler expression for $\Delta^{(k,i,l,j)}$ used in this work allows a straightforward group contribution formulation for the

Table 12
Association parameters for the common hydroxyl group[a1]

Associating Group	ε/k (K)	κ (cm3/mol)	Type of Data	Reference
OH	2700.	.8621	Non bonded mole fraction of associating molecules at liquid like densities	Chapman et al. (1990)

[a] Energy ε/k and volume κ.

association term. Eqs. (9)–(11) are sufficient to describe the density effects on association.

Model parameters

The values for the energy ε and volume κ association parameters corresponding to the 'common' hydroxyl group are shown in Table 12. They were fitted in such way that similar values to the ones reported by Chapman et al. (1990) were obtained for the molar fraction of non-bonded associating group as a function of temperature. Water and methanol at liquid like densities were the hydrogen bonding molecules considered.

On the basis of these associating parameters, new dispersive pure energy parameters (g_{ii}) have been obtained for the associating groups (CH$_2$OH, H$_2$O, etc.) and revised binary interaction parameters (k_{ij} and α_{ij}) have been estimated for pairs of groups in which one or both depict associating behavior.

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