Paper II

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Synthesis of Azeotropic Separation Systems by Case-Based Reasoning

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Abstract

This paper describes a case-based reasoning (CBR) approach that supports the design of azeotropic separation process structures. CBR finds the most similar existing separation processes and applies the knowledge of their concept for solving new problems. The method is applicable especially in the early phases of process design.

1. Introduction

The objective of this paper is to introduce a method for finding feasible azeotropic separation processes by case-based reasoning (CBR). CBR is a method of reusing information of existing design cases for new designs. This means finding most alike existing processes and applying the knowledge of their separation capacity and design for solving new problems in process design. This is especially important in the early phases of process design when many alternatives should be quickly screened before a more detailed study. There is a great need for these kinds of screening tools in practice (Cornider, 2001).

The problem of synthesis of a simple separation sequences from the selection of single separations is studied in earlier papers (Pajula et al., 2001a and 2001b). However the use of CBR for synthesis of azeotropic separations is not yet discussed in detail. When dealing with multicomponent mixtures, the number of possible separation methods, their combinations and process structures to be screened is huge as well as the work involved. The synthesis method studies the physical and chemical properties of the species to be separated and uses the properties presenting most favourable possibilities for successful separation for retrieving the nearest cases to the current problem.

2. CBR in Process Synthesis

The main benefit of CBR approach is that readily available existing knowledge can be utilised systematically also in very large and complex problems like process synthesis and design. In this way the time-consuming conceptual screening phase of a design project can be fastened. Because generalisations are not needed in CBR, no data is lost. CBR gives answers to design problems in a straightforward way, but the results are dependent on the retrieval parameters and the adaptation applied. The strong interaction with the user makes the flexible and interactive use of existing data and design experience possible. The CBR search can be focused on different aspects by defining new

search criteria and in this way the same case base can be used for several types of tasks. The system learns by updating the information in the database.

3. Complex Separation System

The presence of azeotropes adds some difficulties to separations and also the synthesis problem becomes much more complex. In order to separate azeotropic mixtures several technologies may be used: (Hilmen, 2000).

1. Pressure-swing distillation where a series of column operating at different pressures are used to separate binary azeotropes, which change appreciably in composition over a moderate pressure range or where a separating agent which forms a pressure-sensitive azeotrope is added to separate a pressure-insensitive azeotrope.
2. In homogeneous azeotropic distillation, a third component is added to modify the components relative volatility.
3. Heterogeneous azeotropic distillation is based on the same principle as homogeneous azeotropic distillation, but the added third component is partially miscible with one of the components, Solvent reprocessing is easy by means of a liquid-liquid separation system.
4. Reactive distillation is based on the transformation of one of the components into a component, which does not form an azeotrope with the other components.
5. Salted distillation consists in adding a ionic salt that dissociates in the liquid mixture and changes the azeotrope composition.

4. The General CBR Synthesis Algorithm

Distillation is the most feasible way to separate components in the majority of cases. Therefore the distillation related properties are studied first in the methodology, step 1. The strategy is to find first a feasible distillation system for the separations where ordinary distillation is possible. The distillation sequence is adapted from the strategy of the nearest existing design found. The remaining separation problems are solved with further reasoning which applies separation methods other than ordinary distillation. For this relative properties are calculated and the values that show potential for separation are used as retrieval parameters. The main steps in the approach are following (Pajula et al., 2001a):

Step 1: Distillation is applied whenever the relative volatility (α) is large enough. This decision to prefer distillation is up to the user. The first search for the solution is made using α's and reactivities as retrieval parameters. To make the search simpler, α's are classified as easy ($\alpha \geq 1.2$), possible, where mass separating agent (MSA) could be useful ($1.1 < \alpha < 1.2$) and difficult ($\alpha \leq 1.1$). A more accurate search is made (capacity and component types also as retrieval parameters) if several alternatives are found. The nearest strategy found is then applied in all the separations where ordinary distillation is applicable. If ordinary distillation is not feasible for all separations, the method continues to step 2.

Step 2: A suitable MSA is searched for each binary component pair that cannot be separated by conventional distillation. The retrieval parameters used are; types of components, concentrations, relative solubility parameter, dipole moment and dielectric con-

stant. The found MSA is used for defining solubilities and other separation related properties for step 3.
Step 3: Relative physical property parameters (Jaksland et al., 1995) are calculated for each component pair that can't be separated by ordinary distillation. The parameter values are compared to the feasibility limits of different separation methods to find the feasible separation methods and to limit the search space.
Step 4. Separation strategy is searched using the relative parameters (min and max values) that are within the feasibility limits as retrieval parameters. For example crystallisation is considered very feasible if the relative melting point is greater or equal to 1.2. A more detailed search (concentration, capacity and component types also as retrieval parameters) is defined if several alternatives are found. If there are still several alternatives left, an economical comparison is needed. The separation strategy of the nearest found case is applied to the components that can't be separated by distillation.

5. Synthesis of Azeotropic Separations by CBR

The synthesis of azeotropic separations in the previous algorithm can be done by using the CBR approach. The hierarchy of CBR searches is done in the following order:
1. Separation in single column in atmospheric or non-atmospheric pressure
3. Separation in multiple columns in non-isobaric pressure
4. Separation by using MSA
5. Separation by using MSA and non-isobaric pressure
6. Separation by other means; reactive, membrane, extraction etc.
7. Separation by hybrid separations

When the separation problem is complicated, as in the case when azeotropes are present in the mixture, the definition of case description and retrieval parameters is more complex. One idea is to use the relative similarity based on the similarity of feed, product and azeotropic points. To be able to compare separation methods, where mass separating agent (MSA) is needed, a suitable MSA is searched for each binary component pair that cannot be separated by conventional distillation. The retrieval parameters used are types of components to be separated. A more accurate search is defined (concentrations, relative solubility parameter, polarity and dielectric constant also as retrieval parameters), if several alternatives are found. The found MSA is used for defining solubilities and other separation related properties. If the MSA has not been used earlier for same components, more rigorous studies, simulations and/or experiments are needed to confirm the suitability.

6. Examples for THF/Water Separation

6.1 Searching for a feasible non-isobaric distillation system

Task: Separate tetrahydrofuran (15 wt-%) from water. Purity requirement for tetrahydrofuran product is 99 wt-%.
This cannot be reached with ordinary distillation, because tetrahydrofuran and water form an azeotrope at 64 °C with 96 wt-% THF (Smallwood, 1993).

Search criteria:

1) Feed composition: 15 wt-% THF
2) Product compositions: 99 wt-% THF
3) Use pressure swing distillation
4) More than one column
5) No MSA

Using these parameters the nearest case found is:

Components:	Tetrahydrofuran (THF) and water
Feed:	10 wt-% THF
Products:	99 and 3 wt-% THF
Separation:	Distillation in a two column system operating at different pressure (p_1=1 bar, p_2=7,6 bar)

THF/water mixture contains minimum azeotrope, whose position can be shifted by changing system pressure in a two columns system (Figure 1.).

6.2: Selection of mass transfer agent

Task: Find suitable MSA for THF/water separation.
The search is made using following retrieval parameters: component type, solubility parameter, dipole moment and dielectric constant (these three describe solvent's separation capability). The nearest cases are shown in Table 1.

Table 1. Query and nearest cases in Example 6.2

	Query	Found 1	Found 2
Component 1 type	Water	Water	Water
Component 2 type	Ether	Ether	Acetate
Component 1	Water	Water	Water
Component 2	THF	Diethyl ether	Ethyl acetate
Solubility parameter	9.9	7.4	9.1
Dipole moment / D	1.75	1.3	1.7
Dielectric constant	7.6	4.34	6.02
MSA's		n-Hexane, Benzene, Toluene	n-Pentane, 2,2-Dimethyl-butane, Dichloromethane
Similarity		0.92	0.85

The found MSA is used for defining solubilities and other separation related properties for step 3. If the MSA has not been used earlier for exactly the same components, more rigorous studies, simulations and/or experiments are needed to confirm the suitability. In this case n-pentane has been reported for THF/water separation (Smallwood, 1993).

6.3: Finding alternative separation methods

Task: Dehydrating of THF to containing less than100 ppm water.
The search is made for finding single separation method to THF dehydration. Adsorption and pervaporation seem possible separation methods based on the search.

Table 2. Query and nearest cases in Example 6.3

	Query	Found 1	Found 2	Found 3
Component types	water, ether	water, ether	water, ether	ether
Component 1	water	water	water	methanol
Component 2	THF	THF	THF	MTBE
Feed composition	5 wt-% THF	3 wt-%	15 wt-%	-
Product composition	100 ppm water	200 ppm	250 ppm	-
Separation method		Adsorption	Pervaporation	Reactive distillation
Comments		Type 5Å molecular sieves	Easily dehydrated to a few hundred ppm water	
Similarity		0.90	0.88	0.2

6.4: Finding hybrid operations

Possibility of further combined or hybrid operations need also to be taken into account. After reasoning a feasible separation system, the user should consider combining the unit operations one by one. This kind of combined operations may also be found in the retrieved cases. The query case is similar to example 6.3. The nearest case found is shown in Figure 2.

Table 3. Query and nearest cases in Example 6.4

	Query	Found 1	Found 2	Found 3
Component 1	water	water	water	water
Component 2	THF	THF	THF	THF
Feed comp.	5 wt-%	10 wt-%	15 wt-%	20 wt-%
Product comp. water	100 ppm	100 ppm	> 1 wt-%	> 1 wt-%
Separation methods	distillation/ extraction, distillation/ decant.	distillation/ extraction	distillation/ extraction	distillation/ decantation
Nr. of columns		3	3	2
MSA/solvent		NaOH	DMF	n-pentane
Similarity		0.90	0.82	0.80

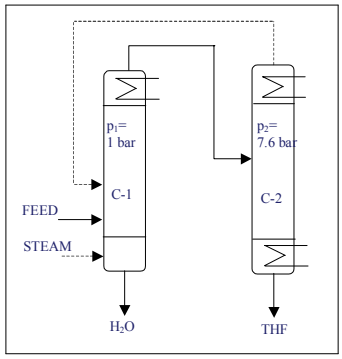

Figure 1. Separation of THF/Water mixture in two columns system.

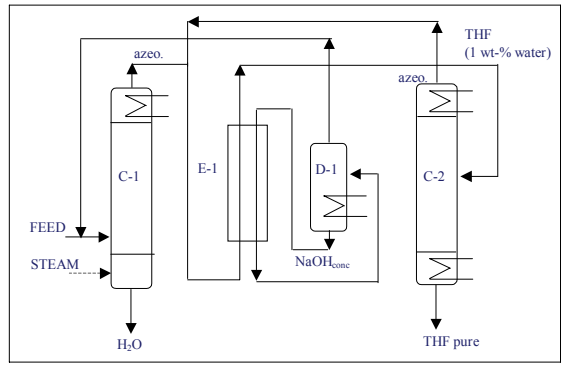

Figure 2. Separation of THF/water mixture by distillation and extraction (salting-out).

7. Creativity and learning aspects

When new separation techniques emerge, for example hybrid membrane/distillation processes, the case base needs to be updated. When new cases are added to database process maturity factors (Pajula et al. 2001b) and feasibility limits need to be considered. Creativity of separation concepts can be enhanced by applying analogies in CBR queries. The queries can be made e.g. based on relative physical properties.

8. Conclusions

CBR separation synthesis algorithm for finding feasible separation processes and separation process structures utilising earlier design cases was extended to azeotropic separations. The main phases are CBR searches for; single column separations, multiple column separations in variable pressures, use of MSA in isobaric of non-isobaric conditions, the use of other separation methods and use of hybrid separations.

The method is useful especially in the early stages of a design, since it fasten conceptual design. The advantage compared to rule-based methods is that all the existing knowledge is available as cases and can be utilised in a non-reduced form. The method is flexible, since the user can focus the search by defining more accurate search parameters, if several nearly similar solution possibilities are available.

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