SHORTCUT EVALUATION OF ABSORPTION FOR SYNTHESIS OF GAS SEPARATION NETWORKS

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A systematic and quantitative methodology for synthesis of gas separation networks is being developed to allow generation of effective and economic separation schemes. Synthesis includes selection of appropriate separation methods, e.g. absorption, low-temperature separation processes and membrane permeation. In the screening step of the methodology, a quick assessment of alternative separation techniques is needed. This work focuses on methods and performance indicators for such an assessment of physical absorption.

To identify whether physical absorption is a promising technology, solubility differences of the components of a mixture in a non-volatile solvent may be assessed using heuristic rules. However, the selective solubility, which has been proposed previously as a performance indicator, is shown to be inconclusive. Instead, this work proposes two complementary performance indicators: the separation factor and the distribution coefficient. This study derives relationships for these for two process configurations of equilibrium stages: countercurrent and crossflow. The relationships derived for the countercurrent configuration can be rearranged into a form analogous to the Kremser relationships.

An analysis of the impact on the separation factor and distribution coefficient of key process design parameters (solvent-to-feed ratio and number of stages in the column) provides a criterion for process evaluation which is in agreement with existing heuristics for absorption column design: if an absorption column with an infinite number of stages allows complete removal of at least one component, the split is taken to be feasible. In such cases, the operating solvent-to-feed ratio lies between the equilibrium constants of the key components. This provides a quantitative basis for preliminary selection of the solvent-to-feed ratio.

KEYWORDS: absorption, shortcut model, screening

INTRODUCTION

The separation of gas and vapour mixtures represents a large fraction of the vast number of industrial separation applications, such as the removal of acid gases from exhaust streams, the recovery of light gases from hydrocarbon gas streams and the production of enriched air.

There are incentives to substitute energy-intensive conventional processes with alternative separation schemes including novel separation techniques. The synthesis of a gas separation system involves the selection of the most appropriate separation technologies. There are typically several competing or complementary options. Whereas for liquid separations, distillation is the dominant separation technology, no such method exists for gases. In addition more than one separation task will frequently be required. The best sequence of separation tasks must be established considering that the component distribution in each intermediate stream may affect the suitability of the units downstream. Generally, many structural and parametric choices still have to be made to define the network configuration and to select its operating conditions. Accounting for energy integration options increases the size of the synthesis problem.

Thus separation system synthesis involves a number of interlinked decisions (Douglas, 1995) and influences strongly the overall process competitiveness. In this context, the open-ended synthesis activity requires systematic strategies assisting in the decision making process. The basic idea of using an existing design as a reference is perhaps the most straightforward approach. Heuristics and facts have been frequently employed in the literature to help generate flowsheet alternatives. The comprehensive collection of heuristics published by Barnicki and Fair (1992) typifies the knowledge-based approach for synthesis of separation networks for multicomponent gas/vapour mixtures. This rule-driven methodology for preliminary process design aims to formulate a limited number of feasible separation systems. In this work, the adequacy of a given technology to carry out a split between two groups of components depends on quantity and extent requirements, and ultimately on the value of certain component properties critical to the process effectiveness. The suitability of the technology is relative to the difference between these properties of the key components. The knowledge input is the common denominator in each of the qualitative heuristic strategies and may be misleading or detrimental to the generation of innovative solutions. Moreover the dynamics of the industrial practices, constraints and economics urge a reevaluation of the design heuristics, which are based on accepted tradeoffs between factors. As a result the validity of the heuristic rules is questionable as is the quality of the related designs.

THE NEED FOR SCREENING

Grossmann (2004) reports on the computational limitations related to large-scale flowsheet synthesis problems. When a design problem dealing with multicomponent mixtures and a variety of separation methods is approached in a systematic way, the number of separation alternatives is generally very large. There is a need for a screening tool that reduces the number of design options in the early phases of the design to allow the alternatives be enumerated for external superstructure construction. Screening provides a quick estimate of alternatives with no need for a detailed simulation-based analysis and can be used to make early decisions at various levels.

Pre-screening of separation technologies uses the driving principle for the separation of exploiting the differences in certain physicochemical properties of components of a mixture. In the identification of the feasible splits for a given separation method, those differences are assessed using some heuristic rules based on approximate performance indices. However, these may be inadequate: the indicator of the separation performance is not always effective, and the feasibility indices are only qualitative estimates. In many cases the characteristic property that a given separation method exploits is not unique, and the methods for property prediction are often insufficient. While the performance of distillation as a separation method can be effectively and simply captured by the relative volatility between components or the boiling point difference, such a criterion does not exist for physical absorption. Absorption exploits the preferential solubility of the components of the gas mixture in a non-volatile liquid which acts as the separating agent. Typically the feasibility and viability of this method depends on the solvent and it is closely tied to the operating conditions. These differences in solubility result from the differences in intermolecular forces between the gaseous solutes and the absorptive liquid. Fundamental intermolecular force calculations, involving the dipole moments and polarizabilities of the species are not accurate enough to give a qualitative indication of the feasibility of the operation. Therefore, thermodynamic calculations are required for the estimation of the solubilities. According to England (1986), absorption properties can be calculated with good confidence from scarce data. Equations can be used to calculate the solubilities of components, and also to investigate the sensitivity of these properties to temperature.

THE NEED FOR PROCESS EVALUATION THROUGH SHORTCUT MODELLING

Optimisation-based strategies provide a systematic framework for many process synthesis problems (Wang and Smith (2005), Kookos (2002, 2003)). Quantitative solutions can only be achieved through process evaluation and optimisation with respect to certain criteria, and this requires adequate models of the separation processes. According to Li and Kraslawski (2004), these strategies are limited by extensive computational requirements. Therefore simple models of the separation unit operations are required for the resolution of the optimisation problem. Also at the initial stages of design, when there is little information about the separation tasks beyond the design specifications, less input demanding models are essential. To date, the required shortcut evaluation methods are not available for all separation processes of interest.

The established shortcut model for multicomponent absorption columns is the Kremser model (King, 1980), based on the absorption/stripping factor. The Kremser model assumes fixed equilibrium constants and constant molar overflow. These simplifications are acceptable for preliminary design in nearly ideal systems.

PRE-SCREENING FOR PHYSICAL ABSORPTION

FEASIBILITY CRITERIA

When the separation between two key components is to be effected by physical absorption, non-preferential transfer occurs if the exit gas bears exactly the same concentration ratio between the key components as the feed gas. In this case, the relative proportions in the gas are preserved, although the exit solvent stream may or may not exhibit the same ratio (depending on the concentration of key components in the feed solvent). While this process could achieve high removals of both key components from the feed, no preferential enrichment takes place. Non-preferential separation between A and B is illustrated in Figure 1, where y_{i-in} is the mole fraction of key component i (A or B) in feed gas; y_{i-out} is the mole fraction of key component i (A or B) in exit gas; x_{i-in} is the mole fraction of key component i (A or B) in feed solvent; x_{i-out} is the mole fraction of key component i (A or B) in exit solvent.

Barnicki and Fair (1992) take the selective solubility $S_{A,B}$ as a feasibility indicator of the split A/B by absorption, and formulate the following feasibility rule: "If $S_{A,B}$ is 3 or greater for an enrichment process, or 4 or greater for a sharp separation, then physical absorption should be considered as a feasible separation method for the split concerned." The solubility selectivity ($S_{A,B}$) is defined as the ratio of the liquid phase mole fractions of the key components in equilibrium with the given feed gas composition:

$$S_{A,B} = \frac{X_{A\,(\text{in eqm. with } y_{A-in})}}{X_{B(\text{in eqm. with } y_{B-in})}} \tag{1}$$

In certain cases, $S_{A,B}$ may be high enough to render the method applicable according to this criterion. However the separation will not be effective if no preferential separation is realised, regardless of how large the selective solubility is. In the example in Figure 1, if the composition of the liquid in equilibrium with the feed gas is taken to be that of the exit solvent, a value of $S_{A,B} = 3$ is obtained. The criterion above would regard this split as feasible. However, the separation is not preferential. This example shows that the selective solubility proposed in the literature is not always an effective feasibility indicator and that the selective solubility rule on feasibility is inconclusive.

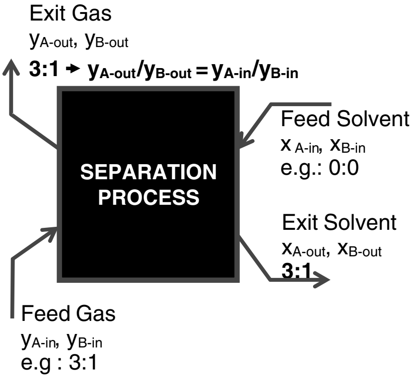


Figure 1. No preferential separation of A from B

TWO COMPLEMENTARY PERFORMANCE INDICATORS

It follows that preferential separation is said to occur if the process modifies the ratio of concentrations of the two key components in the gas stream. Therefore an indicator of preferential separation is needed to indicate feasibility. This work proposes two complementary performance indicators: the separation factor and the distribution coefficient.

A measure of the extent of transfer of a component to the liquid phase gives a meaningful performance indication. The distribution coefficient, DC_A, indicates the extent of the removal of A quantifying the relative partition of A between the phases:

$$DC_A = \frac{x_{A-out}}{y_{A-out}} \tag{2}$$

The relationship between the distribution coefficients for the key components or between the key components ratios in the outlet streams is suggested as an improved measure of the performance of the separation, which corresponds to the classical definition of separation factor:

$$SF_{A,B} = \frac{ratio_{L,\,out}}{ratio_{G,\,out}} = \frac{x_{A-out}/x_{B-out}}{y_{A-out}/y_{B-out}} = \frac{x_{A-out}\,y_{B-out}}{x_{B-out}\,y_{A-out}} \tag{3}$$

$SF_{A,B} \neq 1$ indicates preferential separation when using a pure solvent or one where the same key components ratio is equal to that in the feed gas.

Table 1 illustrates by example the discrepancy between the indicators and proves that an assessment based on the selective solubility alone is inconclusive. Whereas the selective solubility favours the split methane/argon, the separation factor indicates that the split ethane/methane is easier. The distribution coefficient leads to the same result.

SHORTCUT EVALUATION FOR ABSORPTION

This section investigates the effect of key process variables (number of stages, N, and solvent-to-feed ratio, L/G) on the separation performance using the proposed performance indicators (separation factor and distribution coefficients).

RELATIONSHIPS FOR $SF_{A,B}$ AND DC_A FOR A SERIES OF COUNTERCURRENT EQUILIBRIUM STAGES

Analytical techniques are applied to derive mathematical relations between the key parameters and the performance indicators. The following conventions and assumptions are used:

- Linear LV equilibrium, Henry's constants fixed (only for dilute systems and low partial pressures).
- Pure solvent feed ($x_{A-in} = x_{B-in} = 0$).
- Concentrations on absorbate-free basis for simplicity: strictly linear operating line (negligible deviation from linear equilibrium for dilute systems).

Table 1. Gas absorption in ethylene oxide (1,2-epoxyethane). Components are ranked in order of solubility

Gas	y_i	Henry's Constants H_{p-i} (atm) (50°C)	Henry's Constants P = 10 atm H_i (dimensionless)/(50°C)	x_i	$S_{i,\ i+1}$	$DC_i = \frac{x_{i-out}}{y_{i-out}} = \frac{1}{H_i}$	$SF_{i,i+1} = \frac{H_{i+1}}{H_i}$
C_2H_6	0.15	129	12.9	1.2E-02	1.98	7.8E-02	4.61
CH_4	0.35	595	59.5	5.9E-03	74.71	1.7E-02	2.13
Ar	0.01	1270	127.0	7.9E-05	0.03	7.9E-03	1.43
N_2	0.49	1820	182.0	2.7E-03		5.5E-03	

For a typical configuration of an absorption column consisting of a countercurrent series of ideal equilibrium stages, the following relationships are obtained:

$$SF_{A,B} = \frac{E_A(E_B - 1)\,E_A^N - 1}{E_B(E_A - 1)\,E_B^N - 1}$$

$$\text{with the absorption factors: } E_A = \frac{L}{G}\frac{1}{H_A}; \quad E_B = \frac{L}{G}\frac{1}{H_B} \tag{4}$$

$$DC_A = \frac{1}{H_A}\frac{E_A^N - 1}{E_A - 1} = \frac{1}{H_A}\sum_{n=0}^{N-1} E_A^n \left(\text{For } E_A = 1,\ DC_A = \frac{N}{H_A}\right) \tag{5}$$

An analysis of the dependence of $SF_{A,B}$ and DC_A on L/G and N is conducted, occasionally aided by numerical techniques. Growth patterns and operating limits are identified. The increment in N and in L/G has the net effect of raising the separation factor and the distribution coefficients.

A GRAPHICAL TOOL FOR EVALUATION

The individual mole balance or operating line gives the relative location of the bottom and top concentrations when represented in a XY plot:

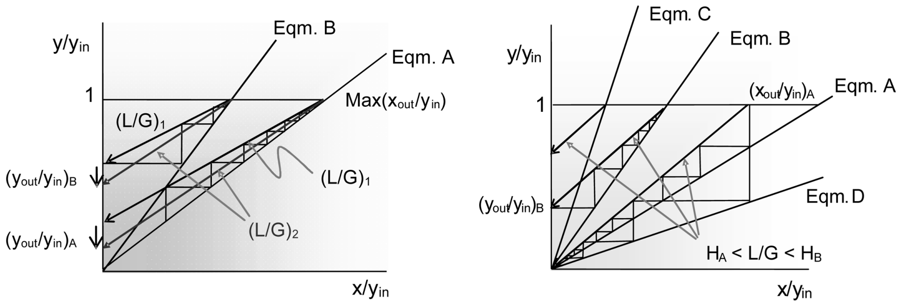
$$\frac{y_{bottom} - y_{top}}{x_{bottom} - x_{top}} = \frac{L}{G} \tag{6}$$

Some insights about the separation efficiency between keys can be obtained from graphical analysis at infinitely high N. This requires merging the XY diagram of the components in a novel representation. This includes the equilibrium and the operating lines. The coordinates are normalised with respect to the gas inlet concentrations so that the operating lines start from the same ordinate. Since the two axes are rescaled by the same factor, the slopes of the equilibrium and the operating lines are preserved. The operating lines have the same slope, but they are distinct because of the different input/output concentrations.

Two scenarios can be distinguished for the relative position between the operating line and the equilibrium:

$$\text{a)}\ \frac{L}{G} < H_A, \quad \forall\ H_B > H_A$$

The slope of the operating lines is less than the slope of any equilibrium line. For infinite N, the operating lines cross the equilibrium lines at the bottom of the column, as in



(a) (b)

Figure 2. Novel representation of absorption column performance. (a) Incomplete removal of any of the two key components. L/G does not favour splits. (b) Complete removal of A and D for $H_A < L/G < H_B$

Figure 2(a). The removal of any of the components is incomplete, and it is not possible to favour significantly the splits by adjusting L/G.

$$\text{b)}\quad \frac{L}{G} \geq H_A, \quad \forall\ H_B > H_A$$

For infinite N, the operating line for A crosses the equilibrium line at the top of the column, as in Figure 2(b). The solutes A and D can be completely removed from the feed gas. Component B is only partially removed if $L/G < H_B$. The operating line for B crosses the equilibrium line at the bottom of the column.

SELECTION CRITERION

It has been shown in the previous section that if L/G can be adjusted to above the equilibrium constant of a component, then this component can be sharply removed at an infinite number of stages. Components with a higher solubility will be removed completely as well. This result is in agreement with heuristics for absorption column design (usually L/G is between 1.2 and 1.5 times H_A). An strategy for split selection can be devised whereby, by selecting L/G within a given interval of consecutive equilibrium constants, a specific split can be performed. This is only feasible if L/G is within the hydraulic limits.

AN EXAMPLE

The proposed methodology is illustrated by a case study. The data source is a simulation in Aspen Plus for light hydrocarbons separations, designed to meet real plant specifications. The process involves two absorption units as seen in Figure 3. First a hydrocarbon gas feed

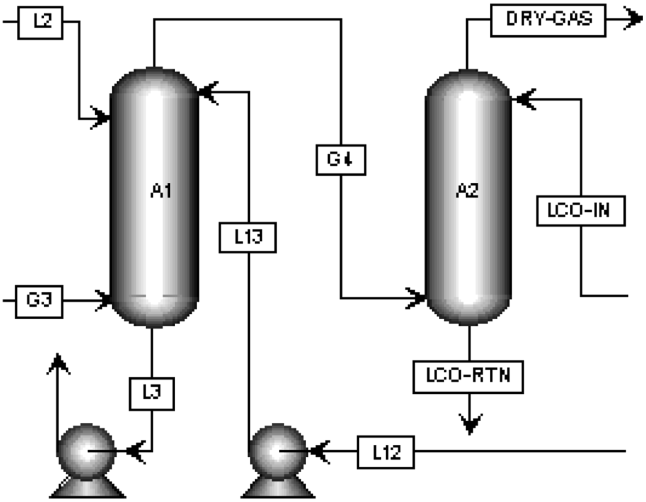


Figure 3. Flowsheet diagram for the absorption sequence

is fed to the absorber A1, which uses recycle gasoline as the solvent. The rich gasoline from A1 is stripped and stabilised downstream prior to being recycled to A1. The gas exit is directly fed to the second absorber A2, which employs a light cycle oil (LCO) as the solvent.

The procedure to test the evaluation criterion starts with the calculation of the Henry's equilibrium constants for the components of the two gas feeds. These can be retrieved from a backward flash calculation in which the pressure, the compositions and the flowrates of the solvent in and the gas out are specified. Aspen Hysys can handle reverse flow of information and it is therefore used for the flash simulation.

The pressures are taken to be the same as in the corresponding absorption units in the real process. The gas out concentrations of solvent components are set to arbitrarily small values. In a flash, given the pressure and the compositions of the vapour out, the temperature is fixed. The equilibrium compositions obtained are then used to determine the solubility equilibrium constants of each component in the given solvent. Subsequently the components are ranked in ascending order of solubility as listed in Table 2. The results presented correspond to the SRK property package, which is also specified for the plant simulation in Aspen Plus. The temperatures at which the Henry's law constants are determined must be close to the actual temperatures in the columns. However the absorption columns exhibit non-flat temperature profiles due to the mixing effects and the adiabatic operation. Also the temperature is not uniform when pumparounds with lateral coolers for enhanced absorption are employed, as in A1. Table 2 includes the results for the temperatures in the two flashes and in the top and the bottom of the column, which satisfy the temperature check.

Table 2. Absorption data from the case study and application of the methodology

Henry's constants H_i (dimensionless)	Absorber A1		Absorber A2		Compo nent split fractions	Absorber A1 OUTLET streams		Absorber A2 OUTLET streams	
Solvent	Gasoline to A1		LCO to A2			G4	L3	DRY-GAS	LCO-RTN
Solute	H_2	17.16	H_2	137.38	H_2	0.969 ✓	0.031	0.985 ✓	0.015
	N_2	8.24	N_2	56.41	N_2	0.931 ✓	0.069	0.967 ✓	0.033
	O_2	5.72	O_2	27.11	O_2	0.888 ✓	0.112	0.944 ✓	0.056
	CH_4	3.95	CH_4	20.53	CH_4	0.821 ✓	0.179	0.910 ✓	0.090
	CO_2	2.20	CO_2	7.03	H_2O	0.552	0.448	0.721 ✓	0.279
	H_2O	2.09	C_2H_4	6.37	C_2H_4	0.397	0.603 ✓	0.694 ✓	0.306
	C_2H_4	1.62	H_2O	5.48	CO_2	0.318	0.682 ✓	0.655 ✓	0.345
	C_2H_6	1.21	C_2H_6	4.44	C_2H_6	0.107	0.893 ✓	0.562 ✓	0.438
	C_3H_6	0.54	C_3H_6	1.64	C_3H_6	0.019	0.981 ✓	0.001	0.999
	C_3H_8	0.49	C_3H_8	1.44	C_3H_8	0.019	0.981 ✓	0	1
	i-C_4H_8	0.23	i-C_4H_{10}	0.64	i-C_4H_{10}	0.012	0.988 ✓	0	1 ✓
	i-C_4H_{10}	0.23	i-C_4H_8	0.56	i-C_4H_8	0.010	0.990 ✓	0	1 ✓
	1-C_4H_8	0.22	1-C_4H_8	0.54	1-C_4H_8	0.010	0.990 ✓	0	1 ✓
	n-C_4H_{10}	0.20	n-C_4H_{10}	0.46	n-C_4H_{10}	0.008	0.992 ✓	0	1 ✓
	trans-C_4H_8	0.20	trans-C_4H_8	0.44	trans-C_4H_8	0.007	0.993 ✓	0	1 ✓
	cis-C_4H_8	0.19	cis-C_4H_8	0.40	cis-C_4H_8	0.006	0.994 ✓	0	1 ✓
Flash P (bar)	15.20		14.50						
Flash T (°C)	40.96		49.69						
Top & Bottom T (°C)	47.1	38.3	42.8	44.6					
Top & Bottom L/G	2.36	2.99	1.03	1.23					

Next step in the procedure is the computation of the actual operating L/G for each column, which fluctuates slightly along the column. The L/G at the top and the bottom of the columns are obtained from the simulation and presented in Table 2.

At this point the evaluation rule is applied, starting by locating the operating L/G span of each column on the solubility ranked list. According to this rule, the components below the operating L/G in the list could be completely removed to the solvent if the column had an infinite number of equilibrium stages. Therefore, an infinitely high A1 would be able to remove all the carbon dioxide and the more soluble components when operating at its actual L/G (≥ 2.36). Similarly, an infinitely long A2 would be able to remove all the isobutane and the more soluble components when operating at its usual L/G (≥ 1.03). The components can be lumped into two characteristic groups for each column as sketched on Table 2.

These results are then compared with the actual recoveries or split fractions in A1 and A2 for their respective number of stages ($N = 30$). These are included in Table 2. Real columns do not generally achieve a sharp separation between components, since they operate at a limited number of stages. Instead the partition of the components between the exit streams (which components predominate in which phase) is analysed. The information that derives from the table is that the components with a predominant distribution in the solvent phase coincide with those predicted by the proposed evaluation rule with a few exceptions. In the absorber A1, for example, water does not predominate in the solvent as predicted for infinite N. Also differently to the shortcut evaluation, in A2 propylene and propane do not predominate in the gas. A reason for this is may be that the actual operating temperature in A2 is up to 8°C below than the temperature employed for the Henry's constants calculation. In fact, the solubility is very sensitive to the temperature, and colder conditions may well reduce the Henry's constants of these components so as to shift them to the group of absorbable components at the preliminary assessment. In addition, the values for the Henry's constants evaluated from different physical property packages vary, and the SRK model may differ between the two programs used. The blend characterisation of the two solvents and the decomposition into pseudocomponents may also increase the discrepancy between the models. Finally the shortcut evaluation was deduced for absorbate-free basis. Differently in this example no account is taken of this convention to correct concentrations and molar flowrates.

CONCLUSIONS

A quantitative rule is proposed for evaluation of absorption processes and column design that conforms to current heuristics: if an absorption column operates at $H_A < L/G < H_B$, A and B become the key components of the non-sharp separation, and two groups of components are defined (predominating in the gas of in the solvent phase). The rule presented in this work gives an upper bound for L/G which cannot be obtained from heuristics. In the examples used, the shortcut rule based in conditions of infinite N predicts correctly the predominance of more than 90% of the components in real columns (with limited N).

The performance indicators allow quantifiable assessment of whether absorption is a suitable technology for a given separation objective. This approach will be implemented in a broader framework for the screening of separation technologies, and the generation, evaluation and optimisation of gas separation networks.

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REFERENCES

Barnicki S. D. and Fair J. R., Separation system synthesis: A knowledge-based approach. 2. Gas/Vapor Mixtures. *Industrial and Engineering Chemistry Research* 31 (1992) 1679–1694.

Douglas J. M., Synthesis of Separation System Flowsheets. *AIChE Journal* 41, 12 (1995) 2522–2536.

England C., Gas solubilities in physical solvents. *Chemical Engineering* 28 (1986) 63–66.

Grossmann I., Challenges in the new millennium: product discovery and design, enterprise and supply chain optimisation, global life cycle assessment. *Computers and Chemical Engineering* (2004).

King C. J., Separation Processes. McGraw-Hill (1980) 2nd Ed.

Kookos I. K., A targeting approach to the synthesis of membrane networks for gas separations. *Journal of Membrane Science* 208, 1–2 (2002) 193–202.

Kookos I. K., Optimal design of membrane/distillation column hybrid processes. *Industrial and Engineering Chemistry Research* 42, 8 (2003) 1731–1738.

Li X. and Kraslawski A., Conceptual process synthesis: past and current trends. *Chemical Engineering and Processing* (2004) 589–600.

Wang J. and Smith R., Synthesis and Optimization of Low-Temperature Gas Separation Processes. *Industrial and Engineering Chemistry Research* 44 (2005) 2856–2870.