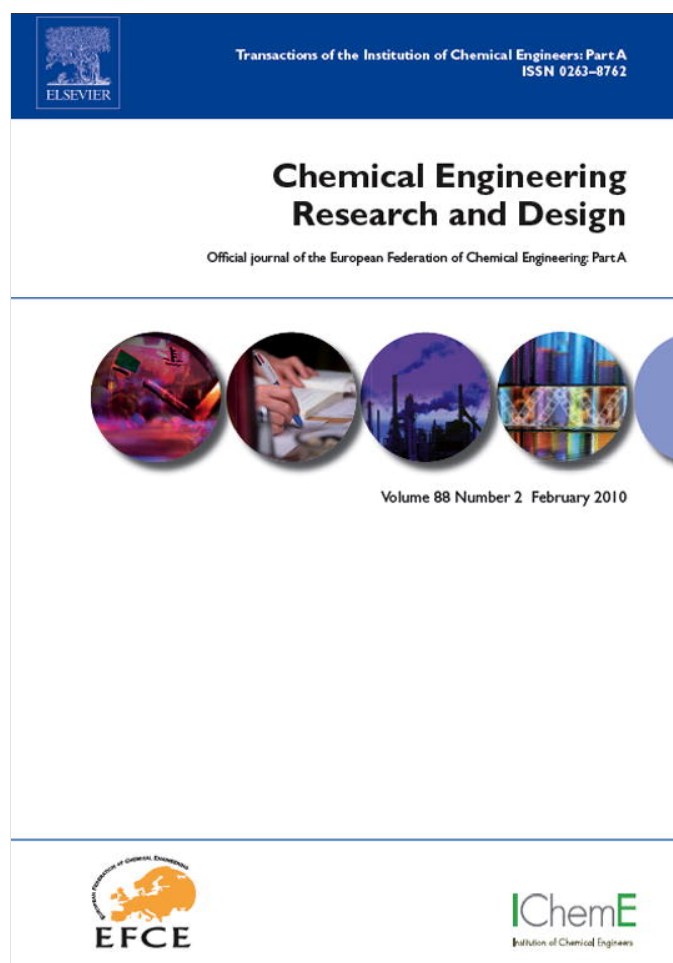


Provided for non-commercial research and education use.
Not for reproduction, distribution or commercial use.



This article appeared in a journal published by Elsevier. The attached copy is furnished to the author for internal non-commercial research and education use, including for instruction at the authors institution and sharing with colleagues.

Other uses, including reproduction and distribution, or selling or licensing copies, or posting to personal, institutional or third party websites are prohibited.

In most cases authors are permitted to post their version of the article (e.g. in Word or Tex form) to their personal website or institutional repository. Authors requiring further information regarding Elsevier's archiving and manuscript policies are encouraged to visit:

<http://www.elsevier.com/copyright>



Contents lists available at ScienceDirect

Chemical Engineering Research and Design

IChemE

journal homepage: www.elsevier.com/locate/cherd

Reducing energy consumption and CO₂ emissions in extractive distillation: Part II. Dynamic behavior

José de Jesús Ibarra-Sánchez, Juan Gabriel Segovia-Hernández*

Universidad de Guanajuato, Campus Guanajuato, Departamento de Ingeniería Química, División de Ciencias Naturales y Exactas, Noria Alta s/n, 365050 Guanajuato, Mexico

ABSTRACT

The structure of thermally coupled distillation systems offers several control challenges arising from the transfer of vapor (or liquid) streams between columns. In particular, the presence of recycle streams for coupled schemes has led to the notion that control problems might be expected during the operation of these systems, in contrast to the rather well-known behavior of conventional distillation sequences. In this work, we analyze the control properties of thermally coupled extractive distillation schemes studied previously (Gutiérrez-Guerra, R., Segovia-Hernández, J.G. and Hernández, S., 2009, Reducing energy consumption and CO₂ emissions in extractive distillation. *Chem Eng Res Des*, 87: 145–152). Control properties are analyzed with the application of the singular value decomposition technique and a closed-loop analysis. The results showed that the energy savings predicted in the complex extractive distillation sequence can be achieved along with good dynamic behavior and reductions in greenhouse gas emissions.

© 2009 The Institution of Chemical Engineers. Published by Elsevier B.V. All rights reserved.

Keywords: Extractive distillation; Thermally coupled systems; Energy savings; Dynamic behavior

1. Introduction

The separation of azeotropic mixtures or close boiling components is a challenging task in many chemical processes as it is impossible using a single conventional distillation column. Therefore, many nonconventional distillation techniques have been proposed to solve this problem (Widagdo and Seider, 1996; Doherty and Malone, 2001, among others). The most common alternatives involve changing the operating pressure or adding a so-called entrainer compound. The pressure option is economically feasible only for mixtures that are very sensitive to pressure. Consequently, the second alternative is the typical nonconventional distillation process encountered in industry and concerns so-called azeotropic and extractive distillation processes. In both cases an additional component, the so-called entrainer, is introduced into the original mixture to facilitate separation. Because of the easier separation of the entrainer through liquid–liquid splitting in a decanter, heterogeneous azeotropic distillation is often preferred over homogeneous azeotropic distillation (Widagdo and Seider, 1996). Extractive distillation, however, can be more energy efficient than heterogeneous azeotropic

distillation (Lei et al., 2003). This is especially true when thermally coupled sequences are used (Gutiérrez-Guerra et al., 2009). Extractive distillation is commonly applied in industry, and is becoming an increasingly more important separation method in petrochemical engineering. The product scale in industrial equipment ranges widely, from several kilotons (column diameter of about 0.5 m) to one hundred kilotons (column diameter about 2.5 m) per year (Lei et al., 2003). In the case of extractive distillation, the entrainer facilitates separation by interacting with the original azeotropic mixture in the extractive and stripping sections of a distillation column. In the classical extractive distillation setup (DS; Fig. 1), the entrainer is fed into the extractive column above the process feed with the azeotrope-forming components. One of these azeotrope-forming components is withdrawn at the top of the extractive column, while the other, together with the entrainer, forms the bottoms product of the extractive column. In a second column, the entrainer is separated from the second feed component and recycled to the first column. The separation in the second column is easier when a large boiling point difference between the high-boiling entrainer and the second feed component exists and no additional azeotropes occur in the mixture

* Corresponding author. Tel.: +52 473 732 0006x8142.

E-mail address: gsegovia@quijote.ugto.mx (J.G. Segovia-Hernández).

Received 2 May 2009; Received in revised form 5 July 2009; Accepted 9 August 2009

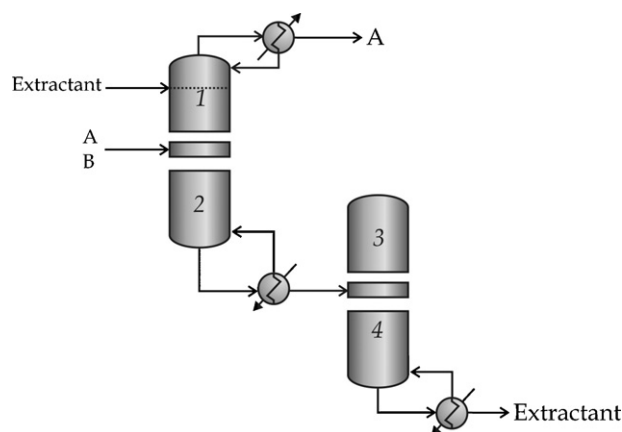


Fig. 1 – Conventional extractive distillation sequence (DS).

(Rodríguez-Donis et al., 2007; Kossack et al., 2008). Extractive distillation is widely used in several different processes: recovery of aromas or fragrances (Pollien et al., 1998; Chaintreau, 2001), separation of aqueous alcohol solutions (Pinto et al., 2000; Zhigang et al., 2002; Llano-Restrepo and Aguilar-Arias, 2003), mixtures which exhibit an azeotrope (Wu et al., 2007; Gil et al., 2009) and separation of hydrocarbons with close boiling points (Wentink et al., 2007; Abushwreb et al., 2007). Recently, the use of ionic liquids as entrainers in the extractive distillation of certain mixtures has also been introduced (Shiflett and Yokozeki, 2006; Zhang et al., 2007). Additionally, few publications deal with the separation of azeotropic mixtures by batchwise extractive distillation, a combination of batch distillation and absorption, so far not widely applied in the industry (Lang et al., 1994; Düssel and Stichlmair, 1995; Safrit and Westerberg, 1997; Low and Sorensen, 2002). This area requires more study comparing it with the conventional extractive distillation process, due to the success of both distillation as an efficient unit operation for the separation of multicomponent mixtures into pure components at low capital cost.

Contrary to the conventional distillation process, the dynamic of extractive columns has been explored very little in published literature, although some authors have attacked this problem. Grassi II (1992) presents case studies to gain insight into the process and develop a methodology for process design and control of extractive distillation systems. The work attempts to bridge the gap between process design and control by introducing dynamic methods into process design. The results show that extractive distillation processes are controllable for a preferred control scheme. Wolf-Maciel and Brito (1995) analyzed the sensitivity and stability of conventional extractive distillation through perturbations in the main variables, in order to recommend the best variables for manipulation. Yao et al. (2007) studied the operation and control of batch extractive distillation for the separation of mixtures with minimum-boiling azeotrope. The operating variables, including the pre-load amount with the mixture, continuous feed rate of the entrainer, and reflux ratio at each operating step are determined in the operating sequence. The constant reflux ratio and constant entrainer feed rate operating policy, and another policy to allow these two operating variables to be varied, will be compared in order to further improve batch operation.

Arifin and Chien (2008) have investigated the control of an isopropyl alcohol (IPA) dehydration process via extractive distillation. The heavy-boiling entrainer used to aid the

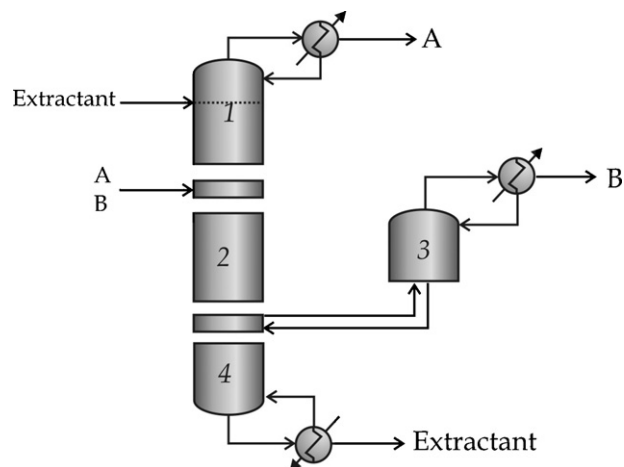


Fig. 2 – Thermally coupled extractive distillation sequence (TCEDS-SR).

separation is dimethyl sulfoxide. A very simple overall control strategy has also been proposed which requires only one tray temperature control loop in each column to hold the high-purity specifications of the two products. Dynamic simulations reveal that fixing the reflux ratio is not a suitable control strategy. Instead, the strategy to fix the two reflux flowrates should be used to reject feed disturbances.

Recently, Luyben (2008a) studied the dynamic performance of the conventional extractive distillation sequence in the separation of the acetone/methanol system with several different solvents. Dynamic simulation results show that all systems are controllable, but product quality variability is poorest when the methanol is driven overhead in the extractive column. One explanation for this difference is that methanol is higher boiling than acetone and preferentially wants to go out the bottom. In another study, Luyben (2008b) explores the design and control of the maximum-boiling azeotropic acetone/chloroform distillation system. A control structure that is capable of handling very large disturbances in throughput and feed composition is developed. The control of two tray temperatures in the extractive column is found to be necessary to handle feed composition disturbances. Luyben (2008c) has also compared the dynamic control of extractive distillation and pressure-swing distillation. Results show that the dynamic controllabilities of the two alternative processes are quite similar.

Gutiérrez-Guerra et al. (2009) proposed a design and optimization procedures for a thermally coupled extractive distillation scheme (TCEDS-SR; Fig. 2). The results showed that the energy savings predicted in the complex extractive distillation sequence can be achieved with reductions in greenhouse gas emissions, higher thermodynamic efficiencies and lower minimum total annual operating cost. This study is the continuation of the work of Gutiérrez-Guerra et al. (2009). We analyze the dynamic behavior of the cases of study designed in the aforementioned paper and compare them to extractive conventional distillation arrangements.

2. Singular value decomposition (SVD)

Open loop dynamic responses to set point changes around the assumed operating point (which corresponds to that with minimum energy consumption for each configuration) were obtained. The responses were obtained using Aspen Dynamics. Transfer function matrices (G) were then collected for each

Table 1 – Mixtures analyzed.

Mixture	Feed components	Feed component flows (kmol/h)	Extractant
M1	Tetrahydrofuran/water	40.82/4.53	1,2-Propanediol
M2	Acetone/methanol	45.35/45.35	Dimethyl sulfoxide (DMSO)
M3	n-Heptane/toluene	90.72/90.72	Aniline

case, and these were subjected to singular value decomposition (SVD):

$$G = V\Sigma W^H \quad (1)$$

where $\Sigma = \text{diag}(\sigma_1, \dots, \sigma_n)$, σ_i = singular value of $G = \lambda_i^{1/2}(GG^H)$; $V = (v_1, v_2, \dots)$ matrix of left singular vectors, and $W = (w_1, w_2, \dots)$ matrix of right singular vectors. Two parameters of interest are the minimum singular value, σ^* , and the ratio of maximum to minimum singular values, or condition number:

$$\gamma = \frac{\sigma_{\max}}{\sigma_{\min}} \quad (2)$$

The minimum singular value is a measure of the invertibility of the system and represents a measure of the potential problems of the system under feedback control. The condition number reflects the sensitivity of the system under uncertainties in process parameters and modeling errors (Klema and Laub, 1980; Lau et al., 1985). These parameters provide a qualitative assessment of the theoretical control properties of the alternate designs. The systems with higher minimum singular values and lower condition numbers are expected to show the best dynamic performance under feedback control (Gabor and Mizsey, 2008). In this case we cover a sufficiently complete range of frequencies. Similar studies have been reported by Jantes-Jaramillo et al. (2008) and Gómez-Castro et al. (2008), among others, for control analysis in studies of thermally coupled distillation systems.

3. Closed-loop analysis

One of the key parts of the dynamic analysis is the selection of control outputs and manipulated variables for each control loop. Although more formal techniques to define the control loops for the complex columns may be used [for instance, the relative gain array method proposed by Bristol (1966) for selecting control loops in order to minimize the amount of interaction among the resulting loops], we based our selection on practical considerations. In the case of distillation columns, however, such loops are fairly well established and used successfully in practice, at least for conventional columns. A well-known structure is based on energy balance considerations, which yields the so-called LV control structure in which the reflux flowrate L and the vapor boilup rate V (affected directly by the heat duty supplied to the reboiler) are used to control the distillate and bottom output compositions (see, for instance, Häggblom and Waller, 1992). Control loops for the integrated systems were chosen from extensions of the practical considerations observed for conventional distillation columns. The control objective was to preserve the output streams at their design purity specifications. Thus, for any sequence, the control of the lightest component of the ternary mixture was manipulated with the top reflux flowrate. The control of the intermediate component was paired to the second column reflux flowrate. In this study we do not analyze the control of entrainer (heavy component) due to the fact

Table 2 – Design variables for TCEDS-SR (M1; E/F = 2.0).

	Main column	Side rectifier
Pressure (atm)	1.14	1.14
Stages	33	17
Feed stage	17	
Extractant stage	3	
Interconnection stage	24	
FV (kmol/h)	4.98	

that, in industrial practice, the control focuses principally on the components of the original binary mixture. The closed-loop analysis was based on proportional-integral controllers. There are several possible alternatives for tuning controller parameters. We attempted to establish a common ground for comparison by optimizing controller parameters, proportional gains (K_c) and reset times (τ_i) for each conventional and integrated scheme following the integral of the absolute error (IAE) criterion. For integrated arrangements, the procedure is particularly complicated because of the interactions of the multivariable control problem. For these cases, the tuning procedure was conducted taking one control loop at a time; the parameters thus obtained were taken for the following control loop until the three loops had been considered.

4. Case of study

We analyze the configurations designed in the first part of this study (Gutiérrez-Guerra et al., 2009) where three ternary mixtures were considered (Table 1). The UNIQUAC model was used to predict thermodynamic properties. Different extractant/feed (E/F) ratios were investigated. The design pressure for each separation was chosen to ensure the use of cooling water in the condensers. Purities of 99% in mole in the products were assumed. As far as energy consumption is concerned, the optimized steady-state complex design provides energy savings of ~30% (and reduction in CO₂ emissions) over the most energy-efficient sequence based on conventional extractive distillation columns. The tray arrangements and some important design variables for this sequence after the optimization task are given in Tables 2–7.

5. Results

The controllability analysis was conducted in two parts. The theoretical control properties of the three schemes were first predicted through the use of the singular value decomposition (SVD) technique, and then closed-loop dynamic simulations were conducted to analyze the control behavior of each system

Table 3 – Design variables for DS (M1; E/F = 2.0).

	Column 1	Column 2
Pressure (atm)	1.36	1
Stages	25	25
Feed stage	17	17
Extractant stage	3	

Table 4 – Design variables for TCEDS-SR (M2; E/F = 2.0).

	Main column	Side rectifier
Pressure (atm)	1.36	1.36
Stages	33	18
Feed stage	21	
Extractant stage	3	
Interconnection stage	30	
FV (kmol/h)	75.57	

Table 5 – Design variables for DS (M2; E/F = 2.0).

	Column 1	Column 2
Pressure (atm)	1.36	1
Stages	31	20
Feed stage	21	18
Extractant stage	3	

Table 6 – Design variables for TCEDS-SR (M3; E/F = 2.5).

	Main column	Side rectifier
Pressure (atm)	1.36	1.36
Stages	53	17
Feed stage	20	
Extractant stage	13	
Interconnection stage	39	
FV (kmol/h)	172.36	

Table 7 – Design variables for DS (M3; E/F = 2.5).

	Column 1	Column 2
Pressure (atm)	1.36	1
Stages	40	30
Feed stage	20	17
Extractant stage	13	

and to compare those results with the theoretical predictions provided by SVD.

5.1. Singular value decomposition

The theoretical control properties of conventional and thermally coupled extractive distillation sequences were obtained. The SVD technique requires transfer function matrices, which are generated by implementing step changes in the manipulated variables of the optimum design of the distillation sequences and registering the dynamic responses of the three products. Open-loop dynamic simulations were carried out in Aspen Dynamics in order to obtain the transfer function

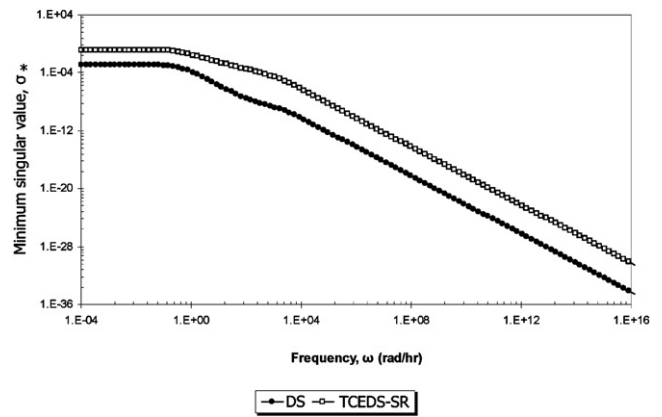


Fig. 3 – Minimum singular value, mixture M1 (E/F = 2.0).

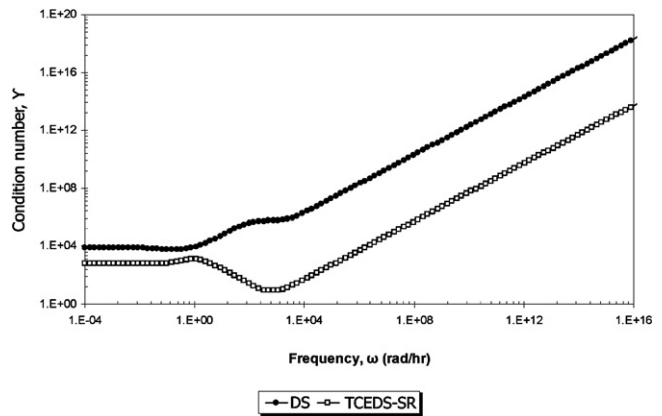


Fig. 4 – Condition number, mixture M1 (E/F = 2.0).

matrix. For the distillation sequences presented in this work, three controlled variables were considered: product compositions A–C. Similarly, three manipulated variables were defined: the reflux ratios (in both columns) and reboiler duty. For the case of study considered here, Tables 8 and 9 show some representative transfer function matrices generated by using step changes in the manipulated variable and recording the dynamic behavior of the three product compositions (A–C). The transfer function matrix shown in Table 8 corresponds to TCEDS-SR (M1; E/F = 2.0). It can be observed that dynamic responses can be adjusted to first or second order or parallel processes. Table 9 shows the transfer function matrix for the DS (M1; E/F = 2.0). Similar transfer function matrices can be obtained for all cases of study.

For the case of study of TCEDS-SR and DS, we obtained the following results: for the case M1; E/F = 2.0 (Figs. 3 and 4), the

Table 8 – Transfer function matrix for coupled extractive system (M1; E/F = 2.0).

$$\begin{bmatrix} \frac{0.2174}{4.190s + 1} & \frac{-0.001}{(0.332s + 1)(0.856s + 1)} & \frac{-0.0010}{0.828s + 1} \\ \frac{72.0382}{(1.026s + 1)(10.026s + 1)} & \frac{71.4646}{(1.142s + 1)(1.142s + 1)} & \frac{-3.865}{(0.518s + 1)(0.518s + 1)} \\ \frac{-0.0001}{0.828s + 1} & \frac{-0.0001}{0.828s + 1} & \frac{0.7020}{2.594s + 1} \end{bmatrix}$$

Table 9 – Transfer function matrix for conventional extractive system (M1; E/F = 2.0).

$$\begin{bmatrix} \frac{0.2577}{(0.701s + 1)(1.681s + 1)} & \frac{0.0013}{24.762s + 1} & \begin{pmatrix} 0.023 & -0.1618 \\ 3.857s + 1 & 1.772s + 1 \end{pmatrix} \\ \frac{2.8522}{(1.951s + 1)(1.951s + 1)} & \frac{0.0723}{(5.087s + 1)(0.793s + 1)} & \begin{pmatrix} 4.2582 & 4.2972 \\ 5.119s + 1 & 17.179s + 1 \end{pmatrix} \\ 0 & 0 & \frac{0.1324}{16.264s + 1} \end{bmatrix}$$

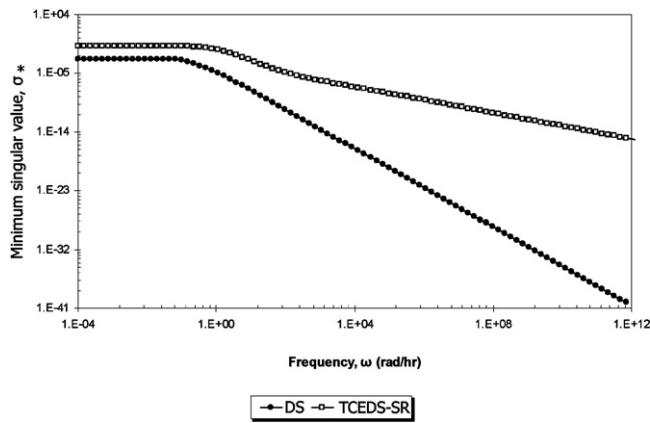


Fig. 5 – Minimum singular value, mixture M1 ($E/F = 2.5$).

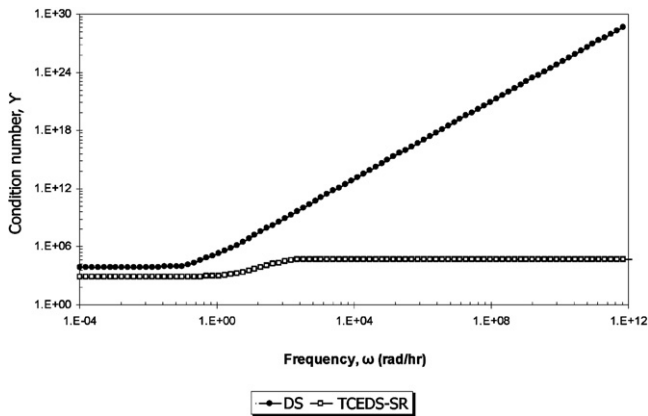


Fig. 6 – Condition number, mixture M1 ($E/F = 2.5$).

TCEDS-SR arrangement presents higher values of the minimum singular value and lower condition number for the entire frequency range; therefore, it can be expected that the TCEDS-SR system will exhibit better control properties than the other sequence under feedback control, and is better conditioned to the effect of disturbances than the other distillation scheme. Figs. 5 and 6 show the minimum singular value and condition number for the case of study M1; $E/F = 2.5$. The TCEDS-SR presents higher values of σ^* and lower values of γ for the entire frequency range. Therefore, the TCEDS-SR is expected to require less effort control under feedback operation and is better conditioned to the effect of disturbances than the conventional extractive scheme. For the case of M1; $E/F = 3.0$, Figs. 7 and 8 show that, at low frequencies, TCEDS-SR exhibits higher values of σ^* than the other scheme, but as the frequency increases, the minimum singular value is similar to

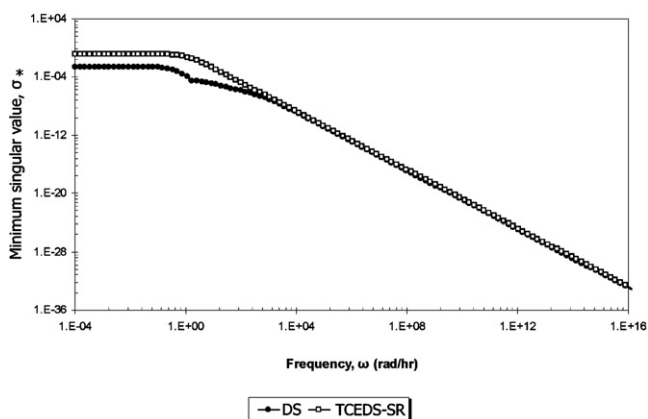


Fig. 7 – Minimum singular value, mixture M1 ($E/F = 3.0$).

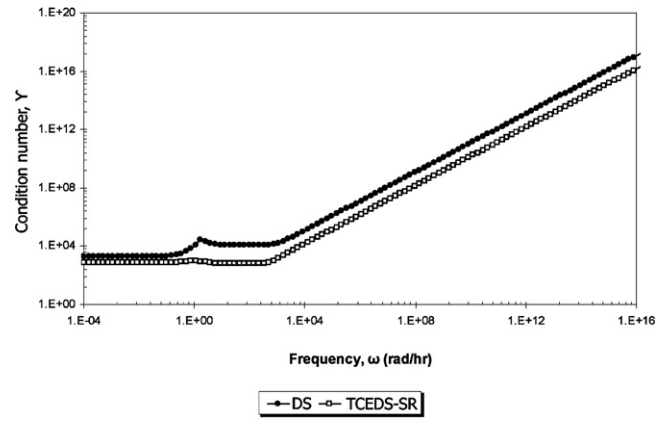


Fig. 8 – Condition number, mixture M1 ($E/F = 3.0$).

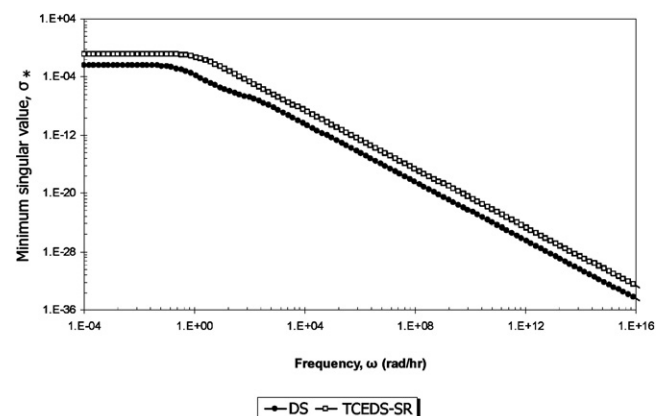


Fig. 9 – Minimum singular value, mixture M1 ($E/F = 3.5$).

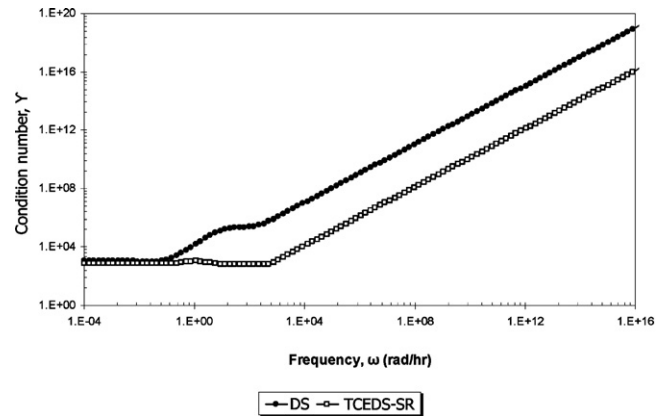


Fig. 10 – Condition number, mixture M1 ($E/F = 3.5$).

the values of the DS scheme. As for the condition number, TCEDS-SR shows the lowest values at low frequencies. In general, we can say that TCEDS-SR offers better conditioning properties for model uncertainties and process disturbances than the other arrangement at low frequencies. According to SVD (Figs. 9 and 10) for the case of M1; $E/F = 3.5$, TCEDS-SR shows better control properties than a conventional extractive arrangement, presenting lower values for condition number and similar minimum singular values when compared to the DS arrangement. For the case shown in Figs. 11 and 12 (M1; $E/F = 4.0$), the SVD results are similar to the case $E/F = 3.5$. Based on the trends observed, two distinctions are seen between the TCEDS-SR and DS: in general, the arrangement with thermal coupling is expected to require less control effort under feedback operation, and, as E/F ratios increase, the control properties of the complex extractive scheme are observed to

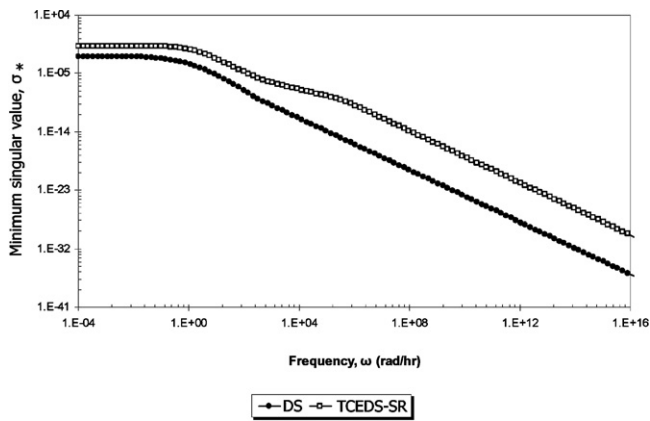


Fig. 11 – Minimum singular value, mixture M1 ($E/F = 4.0$).

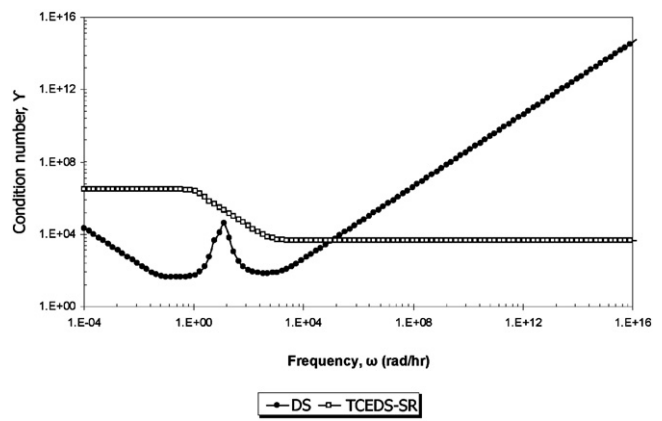


Fig. 14 – Condition number, mixture M2 ($E/F = 2.0$).

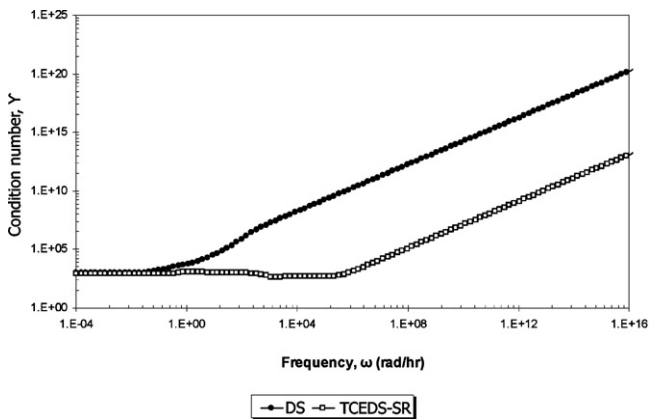


Fig. 12 – Condition number, mixture M1 ($E/F = 4.0$).

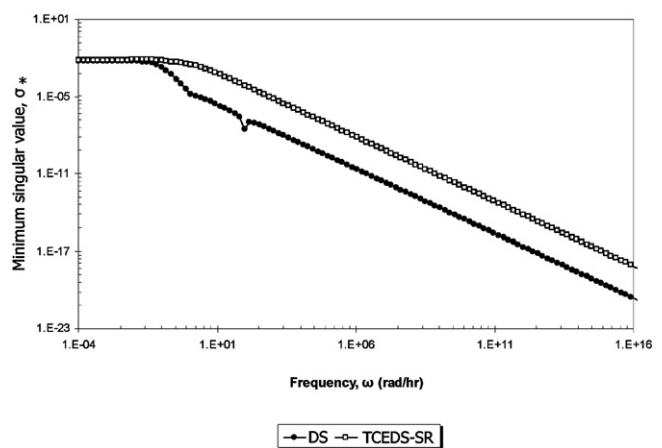


Fig. 15 – Minimum singular value, mixture M3 ($E/F = 2.5$).

be similar to those of the conventional extractive scheme. In other words, at low E/F values, the coupled extractive columns present the best values for minimum singular value and condition number as compared to the conventional extractive column, and therefore these E/F ratio values (~ 2.0 – 3.0) are the best option for the operation of the complex arrangements.

In the case of M2, $E/F = 2.0$ (Figs. 13 and 14), TCEDS-SR seems to be the best choice because it has the highest values of σ^* and the lowest condition number at low frequencies when compared to the DS arrangement (Figs. 15 and 16).

Similar results can be obtained for case of study M3 and for all E/F options. In general, it can be concluded that TCEDS-SR presents better control properties than DS and the best option is to operate the complex arrangements at low E/F ratio values, in all cases of study. The results also indicate that the presence

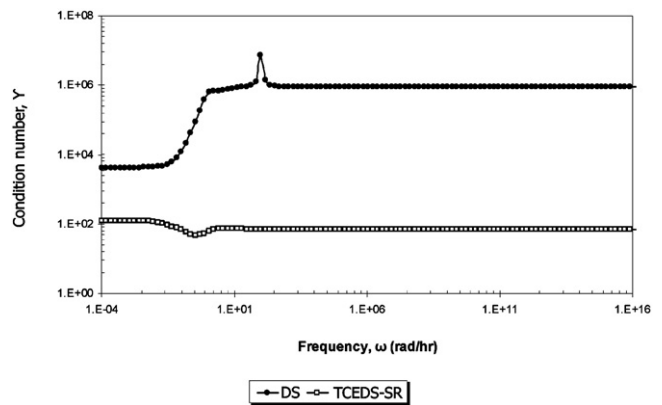


Fig. 16 – Condition number, mixture M3 ($E/F = 2.5$).

of interconnections, in coupled extractive systems, provide an improvement in controllability properties.

5.2. Closed-loop simulations

For the dynamic analysis, individual set point changes for product compositions were implemented for each of the two product streams (we do not analyze the closed loop for the entrainer stream). For all cases (conventional and integrated extractive sequences), the two control loops were assumed to operate as closed loops. The performance of the sequences under analysis was compared through the evaluation of IAE values for each test, and using Aspen Dynamics. Table 10 shows the IAE values obtained for each E/F ratio and for each control loop of the two distillation sequences for mixture M1.

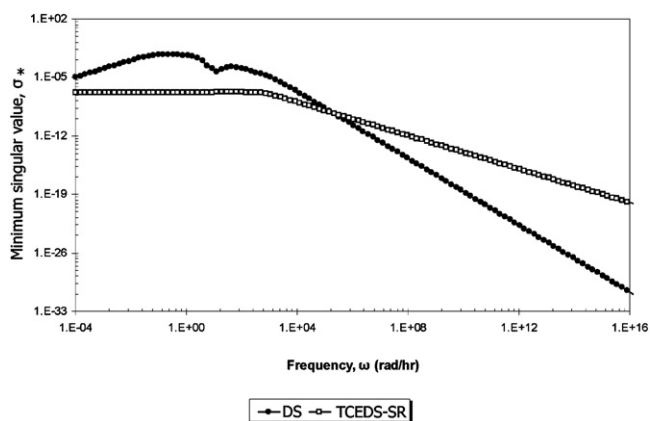


Fig. 13 – Minimum singular value, mixture M2 ($E/F = 2.0$).

Table 10 – IAE results for mixture M1.

Sequence	Tetrahydrofuran			Water		
	K_c	τ_i (min)	IAE	K_c	τ_i (min)	IAE
<i>E/F = 2.0</i>						
DS	14	1	5.725E-4	500	15	1.658 E-4
TCEDS-SR	249	50	3.366E-4	500	16	3.196E-5
<i>E/F = 2.5</i>						
DS	42	2	6.116E-4	500	525	9.140E-5
TCEDS-SR	107	371	3.253E-4	500	31	4.094E-5
<i>E/F = 3.0</i>						
DS	57	1	6.714E-4	500	370	1.110E-4
TCEDS-SR	21	340	1.145E-3	500	14	3.354E-5
<i>E/F = 3.5</i>						
DS	500	122	1.144E-4	500	399	2.389E-4
TCEDS-SR	100	338	2.791E-4	500	15	3.204E-5
<i>E/F = 4.0</i>						
DS	500	99	2.329E-4	500	434	1.269E-4
TCEDS-SR	21	335	1.080E-3	500	28	3.126E-5

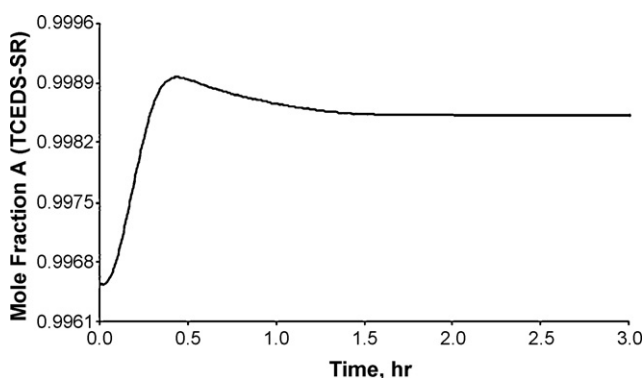


Fig. 17 – Closed-loop dynamic response for tetrahydrofuran, coupled system ($E/F = 2.0$).

When the ratio $E/F = 2.0$ was considered, the TCEDS-SR system offered the best dynamic behavior – based on the lowest IAE values – for the control of the two product streams, as compared to the conventional extractive configuration. The control of light or intermediate components (Figs. 17–20) does not create any significant problems in the complex system case. However, one may notice how the conventional extractive sequence shows some oscillations before arriving at the settling time. These results are consistent with IAE values. In general, the thermally coupled extractive system offers the highest energy savings and also shows the best dynamic performance as compared to the DS arrangement under con-

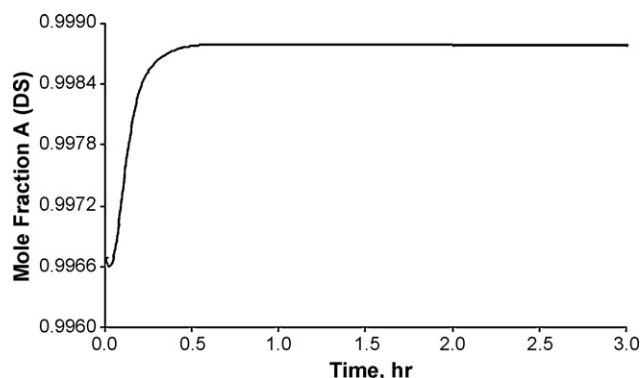


Fig. 18 – Closed-loop dynamic response for tetrahydrofuran, conventional system ($E/F = 2.0$).

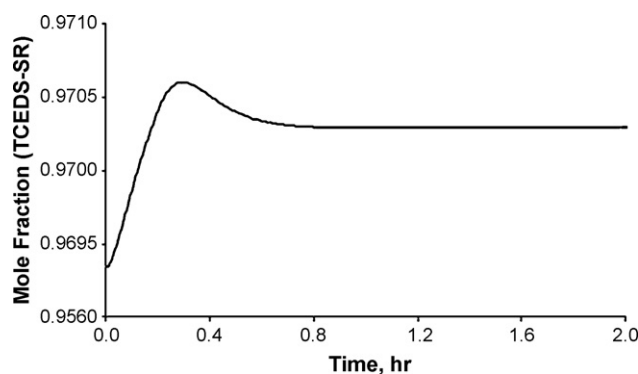


Fig. 19 – Closed-loop dynamic response for water, coupled system ($E/F = 2.0$).

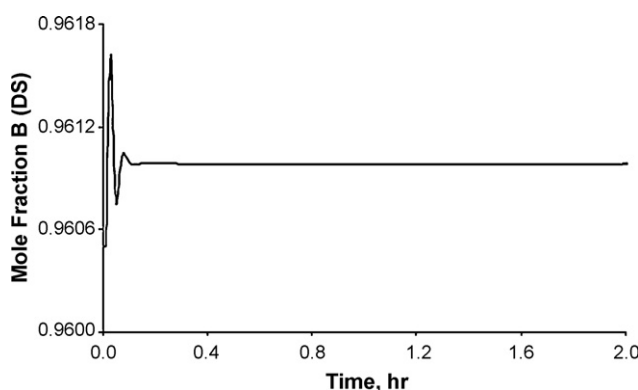


Fig. 20 – Closed-loop dynamic response for water, conventional system ($E/F = 2.0$).

sideration. Table 10 shows IAE values when the E/F ratio has the value of 2.5. In this case, results similar to the case of $E/F = 2.0$ are obtained. The TCEDS-SR presents the lowest values of IAE. These results show that the complex separation system is a better option than the conventional distillation system. Both cases are consistent with those obtained by means of the SVD technique. When the E/F ratio was raised from 2.5 to 3.0, significant changes in the dynamic responses of the distillation systems were observed (Table 10): the IAE value for control of the light component is highest in the coupled system, whereas the IAE value for the control of the intermediate component is the lowest in the coupled system. Similar

Table 11 – IAE results for mixture M2.

Sequence	Acetone			Methanol		
	K_c	τ_i (min)	IAE	K_c	τ_i (min)	IAE
<i>E/F</i> = 2.0						
DS	500	1	1.385E–3	63	26	7.209E–5
TCEDS-SR	3	12	2.052E–4	500	252	1.046E–5
<i>E/F</i> = 2.5						
DS	500	12	7.990E–4	1	400	1.010E–2
TCEDS-SR	500	899	1.003E–5	61	19	1.199E–4
<i>E/F</i> = 3.0						
DS	500	35	6.853E–5	64	17	5.700E–5
TCEDS-SR	1	11	3.267E–4	500	247	1.638E–5
<i>E/F</i> = 3.5						
DS	500	55	6.279E–5	62	15	4.627E–5
TCEDS-SR	6	11	1.224E–4	500	13	7.899E–6
<i>E/F</i> = 4.0						
DS	500	62	5.352E–5	57	16	5.006E–5
TCEDS-SR	6	10	1.161E–4	500	365	1.098E–5

Table 12 – IAE results for mixture M3.

Sequence	n-Heptane			Toluene		
	K_c	τ_i (min)	IAE	K_c	τ_i (min)	IAE
<i>E/F</i> = 2.5						
DS	500	4	1.822E–5	1	700	4.027E–2
TCEDS-SR	150	1	7.676E–5	19	300	9.057E–3
<i>E/F</i> = 3.0						
DS	71	1	2.579E–5	1	700	2.869E–2
TCEDS-SR	500	1	2.661E–5	20	707	9.435E–3
<i>E/F</i> = 3.5						
DS	500	4	1.394E–5	2	700	2.384E–2
TCEDS-SR	500	6	1.607E–5	45	660	1.811E–3
<i>E/F</i> = 4.0						
DS	84	1	2.812E–5	2	700	2.279E–2
TCEDS-SR	500	5	1.918E–5	45	667	1.781E–3

results are obtained for the cases where the *E/F* ratio has values of 3.5 and 4.0. These last three cases analyzed show that the complex sequence is not the best option when dynamic behavior is compared against the conventional arrangement. The conclusions obtained by means of SVD analysis (for the case M1) indicate that low *E/F* ratios (~2.0–3.0) are the best option for operating the complex systems. The results from operating the sequences in the closed-loop fashion are consistent with those estimated using the SVD technique.

For the case M2 (Table 11), TCEDS-SR shows the lowest IAE values (as compared to DS) at low *E/F* ratio values. When the *E/F* ratio is from 3.0 to 4.0, the thermally coupled extractive distillation design is no longer a good option because the IAE value for control of the light component is highest in the coupled system. Similar results can be observed for the case of study M3 (Table 12). In general, these results are also consistent with those obtained by means of the SVD methodology: low *E/F* ratios are the best option for the operation of the thermally coupled extractive systems.

5.3. Study of the bioethanol purification process

To complement this study, we analyze control properties in a bioethanol purification process (reported by Hernández, 2008), which, in one of its stages, uses extractive distillation. Fig. 21 shows the two options analyzed for the purification of the

mixture. A dilute feed of 100 lb-mol/h ethanol in water [10% in moles of ethanol in water—this is a typical yield for fermentation of sugarcane bagasse (Kummar et al., 2009)] as saturated liquid at 1 atm is introduced into a conventional distillation column that removes the binary homogeneous azeotrope as distillate. This study focuses on the separation stage for ethanol with a high mass fraction (0.995). The bottoms product of the first distillation column is almost pure water. This conventional distillation column is needed in both distillation options. The first option (Fig. 21a) uses a conventional extractive distillation column with ethylene glycol as entrainer; the distillate of the column is ethanol with a mass fraction of 0.995. The bottoms product of the extractive distillation column is principally a binary mixture of water and ethylene glycol. This mixture is fed to a third distillation column in order to recover the entrainer as bottoms product. The second option (Fig. 21b), in the extractive stage of the separation, uses a thermally coupled extractive distillation scheme (design and optimization methods used for thermally coupled extractive distillation are reported in Gutiérrez-Guerra et al., 2009). For this case of study, we only analyzed the option with an *E/F* ratio of 2.0. The optimized steady-state thermally coupled extractive design provides energy savings of ~30% (and thus a decrease in greenhouse gas emissions) over the most energy-efficient sequence based on conventional extractive distillation columns. For the systems presented in this case of

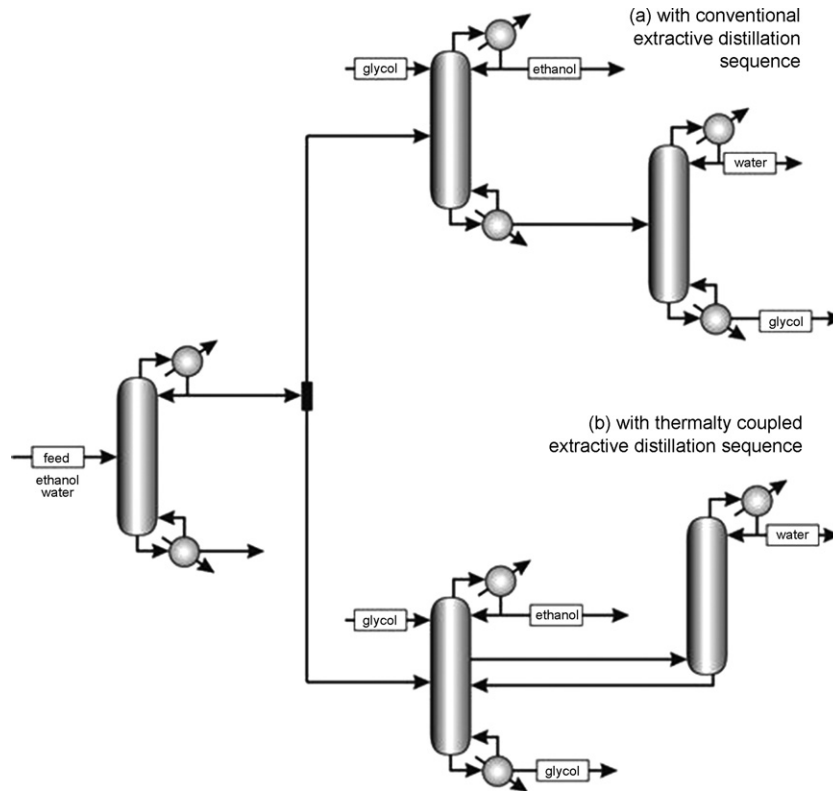


Fig. 21 – Bioethanol purification process using schemes with: (a) conventional extractive distillation structure and (b) thermally coupled extractive distillation sequence.

Table 13 – Transfer function matrix for coupled extractive system (bioethanol/water mixture).

$$G(s) = \begin{bmatrix} \frac{0.0227}{1.363s + 1} & \frac{-0.0011}{(13.399s + 1)(2.375s + 1)} & \frac{-0.0192}{(0.028s + 1)(1.0641s + 1)} & \frac{-0.0179}{1.811s + 1} \\ \frac{-0.2046}{(5.915s + 1)(0.644s + 1)} & \frac{0.0254}{(8.801s + 1)(0.560s + 1)} & \frac{0.7642}{(3.493s + 1)(0.552s + 1)} & \frac{0.2624}{(5.261s + 1)(1.508s + 1)} \\ \begin{pmatrix} 0.0081 & 0.1566 \\ 1.802s + 1 & 1.118s + 1 \end{pmatrix} & \frac{-0.0078}{(7.155s + 1)(0.669s + 1)} & \begin{pmatrix} 0.4843 & 0.0081 \\ 0.893s + 1 & 1.168s + 1 \end{pmatrix} & \frac{-0.3138}{1.285s + 1} \\ \frac{-0.0004}{2.243s + 1} & \frac{-0.0004}{(0.332s + 1)(0.856s + 1)} & \frac{-0.0004}{0.828s + 1} & \frac{0.0441}{0.737s + 1} \end{bmatrix}$$

Table 14 – Transfer function matrix for coupled extractive system (bioethanol/water mixture).

$$G(s) = \begin{bmatrix} \frac{0.3136}{0.721s^2 + 1.213s + 1} & \frac{-0.0006}{0.356s^2 + 0.759s + 1} & \frac{-0.0006}{0.351s^2 + 0.754s + 1} & \begin{pmatrix} 0.0629 & 0.0479 \\ 1.042s + 1 & 2.189s^2 + 2.373s + 1 \end{pmatrix} \\ \frac{0.2709}{4.690s + 1} & \frac{0.0774}{(5.002s + 1)(0.218s + 1)} & \frac{-0.4191}{(3.949s + 1)(0.813s + 1)} & \frac{1.091}{(5.113s + 1)(1.669s + 1)} \\ \frac{-0.0008}{0.828s + 1} & \frac{-0.0003}{0.828s + 1} & \frac{0.0598}{(4.597s + 1)(4.597s + 1)} & \frac{-0.0018}{0.828s + 1} \\ 0 & 0 & 0 & \frac{0.0052}{0.571s + 1} \end{bmatrix}$$

study, four controlled variables were considered: bioethanol product composition, water, entrainer, and the bottoms product of the first distillation column. Similarly, four manipulated variables were defined: two reflux ratios (belonging to the columns of the extractive system, in both arrangements) and two reboiler duties (belonging to the first conventional distil-

lation column in both cases, and the reboiler duty associated with the second column of the conventional extractive distillation configuration or the thermal load associated with the main column of the thermally coupled extractive distillation sequence). Tables 13 and 14 show the transfer function matrix generated for the systems using TCEDS-SR and DS.

Table 15 – IAE results for bioethanol/water mixture.

Sequence	Bioethanol			Water		
	K_c	τ_i (min)	IAE	K_c	τ_i (min)	IAE
DS	4	34	9.9777E-1	500	1	7.8294E-3
TCEDS-SR	500	1	1.1032E-3	500	7	6.9558E-3

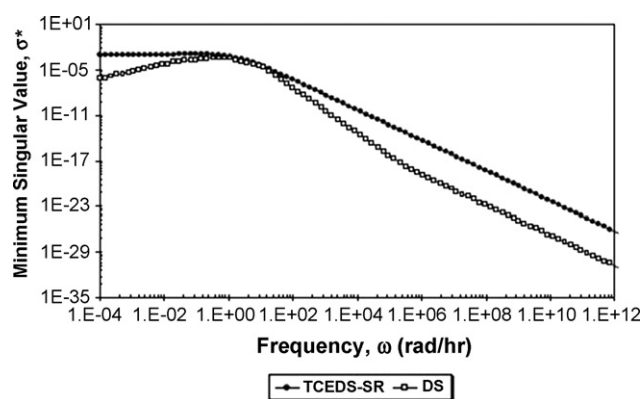


Fig. 22 – Minimum singular value, bioethanol/water mixture.

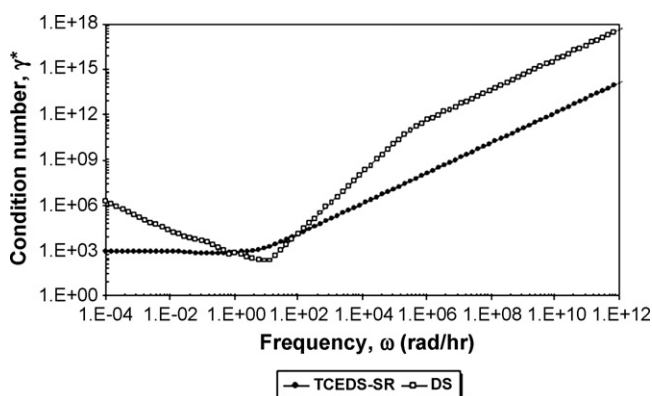


Fig. 23 – Condition number, bioethanol/water mixture.

Figs. 22 and 23 display the results obtained for minimum singular value and condition number. The system using the TCEDS-SR arrangement presents higher minimum singular values and lower condition number for the entire frequency range; therefore, it can be expected that the configuration using the TCEDS-SR arrangement will exhibit better control properties than the other system under feedback control, and is better conditioned to the effect of disturbances than the other distillation scheme. Closed-loop analysis was based on proportional-integral controllers. Individual set point changes for product compositions were implemented for each of the two product streams (bioethanol and water obtained in extractive sequences). Table 15 gives the summary of IAE values for this case of study. A similar trend was observed: the system using a TCEDS-SR shows the best dynamic behavior for the control (the lowest IAE values) as compared to the arrangement using the DS option. As a representative test,

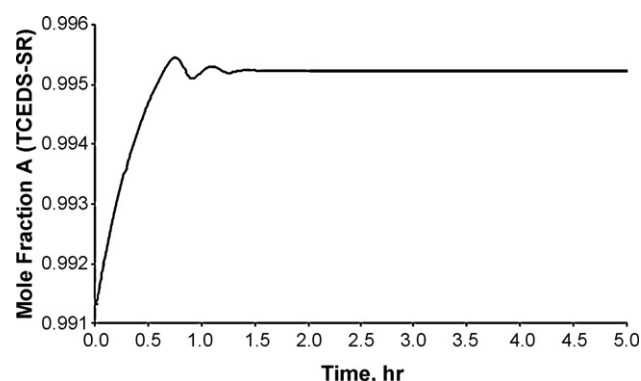


Fig. 24 – Closed-loop dynamic response for bioethanol, coupled system.

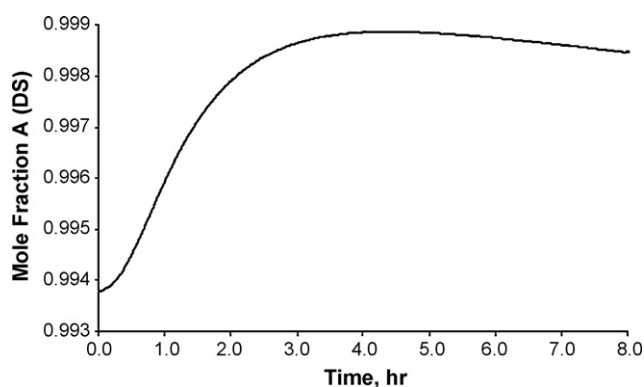


Fig. 25 – Closed-loop dynamic response for bioethanol, conventional system.

Figs. 24 and 25 show the closed-loop results for a bioethanol stream. The configuration using a coupled extractive sequence provides proper dynamic behavior: a smooth response, with a relatively short settling time as compared to the system using the conventional extractive arrangement. These results are in agreement with those obtained using the SVD technique. Again it is possible to establish that the best option is to use systems where one finds a thermally coupled extractive distillation sequence present.

6. Conclusions

We have conducted a comparison of the dynamic behavior of two extractive distillation sequences: conventional and with thermal coupling. Dynamic analysis was based on the SVD technique and PI controllers, for which the parameters were tuned through a minimization procedure of the integral of absolute error. Results indicate, in general, that the TCEDS-SR system is better than the DS scheme. The results also indicate that a lack of interconnections (as in the case of DS) does not necessarily provide the operational advantages originally expected given the resulting simpler structural design. It is apparent that the presence of recycle streams, instead of worsening the dynamic behavior of separation sequences, may contribute positively to their dynamic properties. Additionally, the results suggest that coupled extractive columns present the best minimum singular values and condition numbers at low E/F values, as compared to conventional extractive columns, and therefore these low E/F ratios are the best option for the operation of the complex arrangements. In summary, the results show that in certain cases not only do integrated extractive sequences provide significant energy savings and reduction in CO_2 emissions over conventional extractive arrangements, but they may also offer dynamic advantages.

Acknowledgements

We acknowledge the financial support provided by Universidad de Guanajuato, CONACyT and CONCyTEG (Mexico).

References

- Abushwreb, F., Elakrami, H. and Emtir, M., 2007, Recovery of aromatics from pyrolysis gasoline by conventional and energy-integrated extractive distillation, In *Proceedings of European Symposium on Computer Aided Process Engineering-17 (ESCAPE)* (p. 243).

- Arifin, S. and Chien, I.L., 2008, Design and control of an isopropyl alcohol dehydration process via extractive distillation using dimethyl sulfoxide as an entrainer. *Ind Eng Chem Res*, 47: 790.
- Bristol, E.H., 1966, On new measure of interaction for multivariable process control. *IEEE Trans Autom Control*, AC-11: 133.
- Chaintreau, A., 2001, Simultaneous distillation–extraction: from birth to maturity. *Flavour Fragr J*, 16: 136.
- Doherty, M.F. and Malone, M.F., (2001). *Conceptual Design of Distillation Systems, Chemical Engineering Series*. (McGraw-Hill, New York).
- Düssel, R. and Stichlmair, J., 1995, Separation of azeotropic mixtures by batch distillation using an entrainer. *Comput Chem Eng*, 19: S113.
- Gabor, M. and Mizsey, P., 2008, A methodology to determine controllability indices in the frequency domain. *Ind Eng Chem Res*, 47: 4807.
- Gil, I.D., Botía, D.C., Ortiz, P. and Sánchez, O.F., 2009, Extractive distillation of acetone/methanol mixture using water as entrainer. *Ind Eng Chem Res*, 48: 4858.
- Grassi II, V.G., 1992, Process Design and Control of Extractive Distillation, in *Practical Distillation Control*, Luyben, W.L. (ed). (Van Nostrand Reinhold, NY)
- Gómez-Castro, F.I., Segovia-Hernández, J.G., Hernández, S., Gutiérrez-Antonio, C. and Briones-Ramírez, A., 2008, Dividing wall distillation columns: optimization and control properties. *Chem Eng Technol*, 31: 1246.
- Gutiérrez-Guerra, R., Segovia-Hernández, J.G. and Hernández, S., 2009, Reducing energy consumption and CO₂ emissions in extractive distillation. *Chem Eng Res Des*, 87: 145.
- Hägglom, K.E. and Waller, K.V., 1992, Control structures, consistency, and transformations, in *Practical Distillation Control*, Luyben, W.L. (ed). (Van Nostrand Reinhold, NY)
- Hernández, S., 2008, Analysis of energy-efficient complex distillation options to purify bioethanol. *Chem Eng Technol*, 31: 597.
- Jantes-Jaramillo, D., Segovia-Hernández, J.G. and Hernández, S., 2008, Reduction of energy consumption and greenhouse gas emissions in a plant of separation of amines. *Chem Eng Technol*, 31: 1462.
- Klema, V.C. and Laub, A.J., 1980, The singular value decomposition its computation and some applications. *IEEE Trans Automat Control*, AC-25: 164.
- Kossack, S., Kraemer, K., Gani, R. and Marquardt, W., 2008, A systematic synthesis framework for extractive distillation processes. *Chem Eng Res Des*, 86: 781.
- Kummar, S., Singh, S.P., Mishra, I.M. and Adhikari, D.K., 2009, Recent advances in production of bioethanol from lignocellulosic biomass. *Chem Eng Technol*, 32: 517.
- Lang, P., Yatim, H., Moszkowicz, P. and Otterbein, M., 1994, Batch extractive distillation under constant reflux ratio. *Comput Chem Eng*, 18: 1057.
- Lau, H., Álvarez, J. and Jensen, K.F., 1985, Synthesis of control structures by singular value analysis: dynamic measurements of sensitivity and interaction. *AIChE J*, 31: 427.
- Llano-Restrepo, M. and Aguilar-Arias, J., 2003, Modeling and simulation of saline extractive distillation columns for the production of absolute ethanol. *Comput Chem Eng*, 27: 527.
- Lei, Z., Li, C. and Chen, B., 2003, Extractive distillation: a review. *Sep Purif Rev*, 32: 121.
- Low, K.H. and Sorensen, E., 2002, Optimal operation of extractive distillation in different batch configurations. *AIChE J*, 48: 1034.
- Luyben, W.L., 2008, Effect of solvent on controllability in extractive distillation. *Ind Eng Chem Res*, 47: 4425.
- Luyben, W.L., 2008, Control of the maximum-boiling acetone/chloroform azeotropic distillation system. *Ind Eng Chem Res*, 47: 6140.
- Luyben, W.L., 2008, Comparison of extractive distillation and pressure-swing distillation for acetone–methanol separation. *Ind Eng Chem Res*, 47: 2696.
- Pinto, R.T.P., Wolf-Maciel, M.R. and Lintomen, L., 2000, Saline extractive distillation process for ethanol purification. *Comput Chem Eng*, 24: 1689.
- Pollien, P., Ott, A., Fay, L.B., Maignial, L. and Chaintreau, 1998, A simultaneous distillation–extraction: preparative recovery of volatiles under mild conditions in batch or continuous operations. *Flavour Fragr J*, 13: 413.
- Rodríguez-Donis, I., Papp, K., Rev, E., Lelkes, Z., Gerbaud, V. and Joulia, X., 2007, Column configurations of continuous heterogeneous extractive distillation. *AIChE J*, 53: 1982.
- Safrit, B.T. and Westerberg, A.W., 1997, Improved operational policies for batch extractive distillation columns. *Ind Eng Chem Res*, 36: 436.
- Shiflett, M.B. and Yokozeki, A., 2006, Separation of difluoromethane and pentafluoroethane by extractive distillation using ionic liquid. *Chem Today*, 24: 28.
- Wentink, A.E., Kuipers, N.J.M., de Haanb, A.B., Scholtz, J. and Mulder, H., 2007, Olefin isomer separation by reactive extractive distillation: modeling of vapour–liquid equilibria and conceptual design for 1-hexene purification. *Chem Eng Proc*, 46: 800.
- Widagdo, S. and Seider, W.D., 1996, Azeotropic distillation. *AIChE J*, 42: 96.
- Wolf-Maciel, M.R. and Brito, R.P., 1995, Evaluation of the dynamic behavior of an extractive distillation column for dehydration of aqueous ethanol mixtures. *Comput Chem Eng*, 19: S405.
- Wu, L.L., Chang, W.X. and Guan, G.F., 2007, Extractants design based on an improved genetic algorithm. *Ind Eng Chem Res*, 46: 1254.
- Yao, J.Y., Lin, S.Y. and Chien, I.L., 2007, Operation and control of batch extractive distillation for the separation of mixtures with minimum-boiling azeotrope. *J Chin Inst Chem Eng*, 38: 371.
- Zhang, L., Han, J., Deng, D. and Ji, J., 2007, Selection of ionic liquids as entrainers for separation of water and 2-propanol. *Fluid Phase Equilibria*, 255: 179.
- Zhigang, L., Jinchang, Z. and Biaohua, C., 2002, Separation of aqueous isopropanol by reactive extractive distillation. *J Chem Technol Biotechnol*, 77: 1251.