Spreadsheets in Chemical Engineering Education—A Tool in Process Design and Process Integration*

EUGÉNIO C. FERREIRA
*Centro de Engenharia Biológica, Universidade do Minho, Campus de Gualtar, 4710-057 Braga, Portugal.
E-mail: ecferreira@deb.uminho.pt*

RICARDO LIMA and ROMUALDO SALCEDO
Departamento de Engenharia Química, Universidade do Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal

Recent developments in embedding numerical optimization procedures with linear and nonlinear solvers within a spreadsheet environment have greatly enhanced the use of these tools for teaching chemical process design and process integration. Student skills with respect to these topics are usually gained by complex and expensive modular simulators, e.g. ASPEN Plus® or algebraic tools such as GAMS® or AMPL®. However, modular simulators have a significant learning curve, and algebraic modeling languages are usually ignored once students commence careers. This paper demonstrates how the Solver feature of the Excel® spreadsheet is used for the optimization of several chemical engineering systems, including pollution prevention problems and mass-exchange networks. Three nonlinear problems are examined: the (a) recovery of benzene from a gaseous emission; (b) design of a chemical reactor network; and (c) solution of material balances in the production of vinyl chloride from ethylene. Dephenolization of aqueous wastes is presented as a linear case. The ease with which these and similar process problems can be formulated and solved within the Excel® environment constitutes a major step towards teaching practical optimization and design concepts for university students.

INTRODUCTION

UNDERGRADUATE ENGINEERING students are attracted to the powerful 'what-if' spreadsheets with optimization capabilities, such as the EXCEL® Solver (Microsoft Co.) and What's Best (Lindo Systems, Inc.). They require a minimum amount of effort in building a typical simulation/optimization problem, in comparison with standard high level language coding such as GAMS® or AMPL®. Undergraduate instructors are adopting Excel Solver for introducing students to solving and optimizing process design and integration [1, 2]. In addition, several engineering textbooks now include coverage of the Excel Solver [3–6]. The new edition of the classical textbook *Optimization of Chemical Processes* [4] dedicates several pages to the use of Excel Solver as an optimization tool. The book includes a new co-author, Leon Lasdon, a recognized authority in operations research optimization software and implementation of the Excel Solver [7].

Practicing engineers also use spreadsheets for many tasks, and process optimization is steadily becoming a common task in process synthesis, design and integration. Therefore, it is important

to establish to what extent these tools are capable of solving optimization problems.

The present authors studied recently an interesting problem dealing with the concepts of process synthesis including heat integration and solvent recovery [1, 2, 8]. The Solver feature of the Excel® spreadsheet is demonstrated for the optimization of several chemical engineering systems, including pollution prevention problems and mass-exchange networks in the current paper. Three nonlinear problems (the recovery of benzene from a gaseous emission; the design of a chemical reactor network; and the solution of material balances in the production of vinyl chloride from ethylene), and one linear problem (the dephenolization of aqueous wastes) are examined. These case studies have been adapted for demonstration purposes in two courses run by the authors.

THE EXCEL SOLVER

The Microsoft Excel® spreadsheet was used as a development framework, coupled with the Solver add-on—a companion of Excel since 1991 (version 3.0). The Excel Solver has two nonlinear unconstrained optimizers, a quasi-Newton method and a reduced gradient method. These are used within a
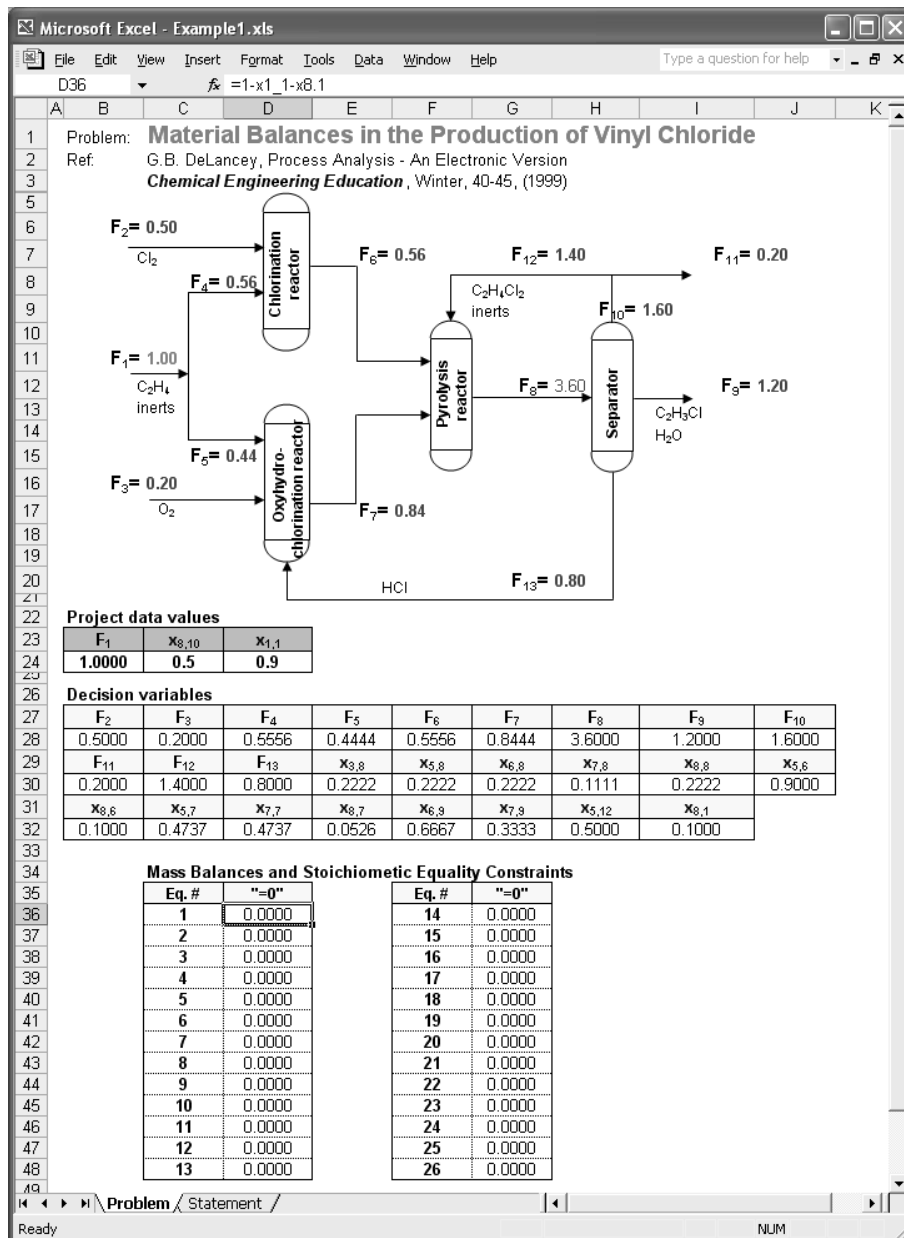
Fig. 1. Material balances in the production of vinyl chloride from ethylene.

Generalized Reduced Gradient algorithm [9] for solving constrained optimization problems. The linear simplex method with bounds on the variables, and the branch-and-bound method implemented by Fylstra *et al.* [7], can be used for solving linear and integer problems.

The approach used to obtain better initial estimates of the basic variables in each one-dimensional search can be specified in Solver options. Linear extrapolation from a tangent vector or quadratic extrapolation can be used, which may improve the results on highly nonlinear problems. It is also possible to specify the differencing method to estimate derivatives of the objective and constraint functions: 'Forward' when the constraint values change relatively slowly, or 'Central', used for problems when the constraints

change rapidly, especially near the boundaries of the active constraints. It is possible to control;

a) the solution process by limiting the time taken and the number of interim calculations by the solution process;
b) the precision within which constraints are considered binding;
c) the convergence criteria for the solutions.

Example 1: Material balances in the production of vinyl chloride

This case study illustrates the use of Excel Solver in the solution of simultaneous nonlinear equations associated with material balances in the production of vinyl chloride from ethylene. DeLancey [10] solved this example using Scientific Notebook

Table 1. Material balances and stoichiometric equations [10]

#	Equation	#	Equation
1	$x_{1,1} + x_{8,1} = 1$	14	$0.50(x_{5,6}F_6 + x_{5,7}F_7 + x_{5,12}F_{12}) = x_{5,8}F_8$
2	$F_2 = x_{1,1}F_4$	15	$0.50(x_{5,6}F_6 + x_{5,7}F_7 + x_{5,12}F_{12}) = x_{6,8}F_8$
3	$F_3 = 0.5x_{1,1}F_5$	16	$0.50(x_{5,6}F_6 + x_{5,7}F_7 + x_{5,12}F_{12}) = x_{3,8}F_8$
4	$F_4 + F_5 = F_1$	17	$x_{7,7}F_7 = x_{7,8}F_8$
5	$x_{5,6}F_6 = x_{1,1}F_4$	18	$x_{8,6}F_6 + x_{8,7}F_7 + x_{8,10}F_{12} = x_{8,8}F_8$
6	$x_{8,6}F_6 = x_{8,1}F_4$	19	$x_{3,8} + x_{5,8} + x_{6,8} + x_{7,8} + x_{8,8} = 1$
7	$x_{5,6} + x_{8,6} = 1$	20	$x_{3,8}F_8 = F_{13}$
8	$x_{7,7}F_7 = x_{1,1}F_5$	21	$x_{5,8}F_8 = x_{5,12}F_{10}$
9	$x_{5,7}F_7 = x_{1,1}F_5$	22	$x_{6,8}F_8 = x_{6,9}F_9$
10	$F_{13} = 2(x_{1,1}F_5)$	23	$x_{7,8}F_8 = x_{7,9}F_9$
11	$x_{8,7}F_7 = x_{8,1}F_5$	24	$x_{8,8}F_8 = x_{8,10}F_{10}$
12	$x_{5,7} + x_{7,7} + x_{8,7} = 1$	25	$x_{6,9} + x_{7,9} = 1$
13	$x_{5,12} + x_{8,10} = 1$	26	$F_{10} = F_{11} + F_{12}$

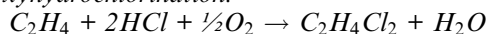(MacKichan Software, Inc.) primarily oriented for solving systems of nonlinear equations.

The flow diagram in Fig. 1 represents the main steps in the production of vinyl chloride (C_2H_3Cl) from ethylene (C_2H_4).

The reactions taking place separately in each reactor are:

Chlorination:
$$C_2H_4 + Cl_2 \rightarrow C_2H_4Cl_2$$

Oxyhydrochlorination:
$$C_2H_4 + 2HCl + \tfrac{1}{2}O_2 \rightarrow C_2H_4Cl_2 + H_2O$$
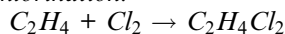
Pyrolysis:
$$C_2H_4Cl_2 \rightarrow C_2H_3Cl + HCl$$

The ethylene feed, F_1, is 90% molar ethylene and the remainders are inerts. The chlorine and oxygen feeds, F_2 and F_3, respectively, are pure. All of the ethylene, oxygen, and chlorine react and the conversion of the hydrochloric acid (HCl) fed to the oxyhydrochlorination is complete.

Only 50% of the total dichloroethane ($C_2H_4Cl_2$) fed to the pyrolysis reactor is converted, with the remainder being separated and recycled with inerts in stream F_{12}. The inert concentration in the recycle stream is 50% molar. Pure hydrochloric acid (HCl) is recycled in stream F_{13}. The final product stream, F_9, consists only of vinyl chloride and water.

Setting $F_1 = 1$ mole/hr results in a problem with 24 independent (unknown) variables and 26 equations issued from material balances (Table 1), with no degrees of freedom. The EXCEL Solver was used to determine all of the unknown flow rates, F_j, and mole fractions, x_{ij} (mole fraction i in stream j). The species are labeled in Table 2.

The Solver is used to compute the root of one equation subject to several equality constraints (Fig. 2). Equation 1 ($\$C\$36$) was set as 'Target Cell' with a required zero value and all the 26 equations were set as equality constraints. The initial values for the decision variables ('By Changing Cells') were 1.0 for all the flow rates (F_j) and 0.50 to all the mole fractions ($x_{i,j}$). The solution is obtained almost instantaneously.

Example 2: Dephenolization of aqueous wastes

This example is used to illustrate the synthesis of mass-exchange networks based on a mathematical programming approach. For an overview of this technique the reader is referred to El-Halwagi [11].

An oil-recycling plant is demonstrated in Fig. 3 as adapted from [11]. Two types of waste oil are handled: gas and lube oils. The two streams are

Table 2. Labeling of components

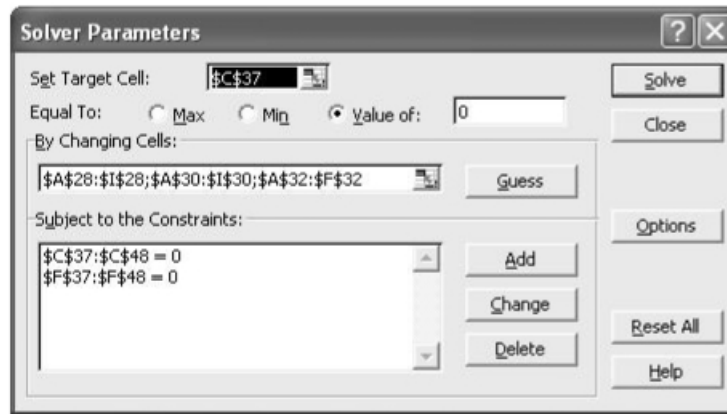| Index	1	2	3	4	5	6	7	8
Species	C_2H_4	Cl_2	HCl	O_2	$C_2H_4Cl_2$	C_2H_3Cl	H_2O	Inerts

Fig. 2. Solving simultaneous nonlinear equation associated with material balances in the production of vinyl chloride from ethylene.
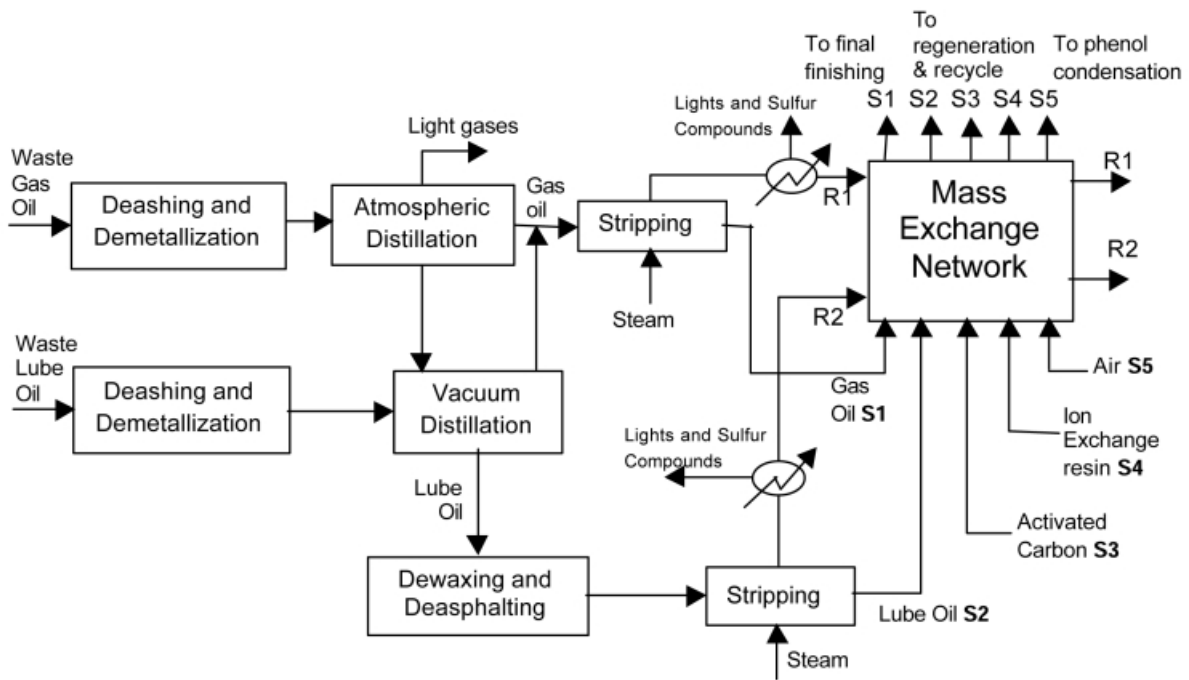

Fig. 3. Dephenolization of aqueous wastes in an oil recycling plant.

Table 3. Data on waste streams for the dephenolization example [11]

Stream	Description	Flow rate G_i, kg/s	Supply composition	Target composition
R_1	Condensate from first stripper	2	0.050	0.010
R_2	Condensate from second stripper	1	0.030	0.006

first de-ashed and de-metallized. Atmospheric distillation is used to obtain light gases, gas oil, and a heavy product. The heavy product is distilled under vacuum to yield lube oil. The gas and the lube oils can be further processed to attain other properties. The gas oil is steam stripped to remove light and sulphur impurities, then hydrotreated. The lube oil is dewaxed/deasphalted using solvent extraction followed by steam stripping. The process has two main sources of waste water. These are the condensate streams from the steam strippers.

The principal pollutant in both wastewater streams is phenol that can be separated using several techniques. Solvent extraction using gas oil (S1) or lube oil (S2) as process Mass Separation Agents (MSA) is an option. The data for the waste streams and the process MSA are given in Tables 3 and 4 respectively.

Three external technologies are also considered for the removal of phenol. These processes include adsorption using activated carbon, S3, ion exchange using a polymeric resin, S4, and stripping using air,

Table 4. Data process mass separation agents for the dephenolization example [11]

Stream	Description	Upper bound on flow rate L_j^c, kg/s	Supply composition x_j^s	Target composition x_j^t	Equilibrium distribution coefficient $m_j = y/x_j$	Cost C_j ($/kg of recirculation MSA)*
S_1	Gas oil	5	0.005	0.015	2.00	0.000
S_2	Lube oil	3	0.010	0.030	1.53	0.000
S_3	Activated carbon	∞	0.000	0.110	0.02	0.081
S_4	Ion-exchange	∞	0.000	0.186	0.09	0.214
S_5	Air	∞	0.000	0.029	0.04	0.060

* Including regeneration and make-up costs.

S5. The equilibrium data for the transfer of phenol to the jth lean stream is given by $y = m_j x_j$ where the values of m_j are given in Table 4. Also, listed are the supply and target compositions and unit cost data for each MSA. Throughout this example, a minimum allowable composition difference, ε_j, of 0.001 (kg phenol)/(kg MSA) is used.

An analysis based on 'pinch diagrams' (see [11] for details) indicates that 0.0184 kg phenol/s is the excess capacity for the process MSA and that 0.0124 kg phenol/s are to be removed using an external MSA.

The problem of minimizing the operating cost of mass separation agents was formulated in [11] by adopting the linear-programming approach solved using the LINGO package (Lindo Systems, Inc.). The objective function is:

$$min\{0.081L_3 + 0.214L_4 + 0.060L_5\}$$

subject to:
$$\delta_1 = 0.0052$$
$$\delta_2 - \delta_1 + 0.0101L_2 = 0.0308$$
$$\delta_3 - \delta_2 + 0.0010L_1 + 0.0013L_2 = 0.0040$$
$$\delta_4 - \delta_3 + 0.0066L_1 + 0.0086L_2 = 0.0396$$
$$\delta_5 - \delta_4 + 0.0024L_1 + 0.0537L_4 = 0.0144$$
$$\delta_6 - \delta_5 + 0.0222L_4 = 0.0060$$
$$\delta_7 - \delta_6 + 0.0444L_4 = 0.0040$$
$$\delta_8 - \delta_7 + 0.0420L_4 = 0.0000$$
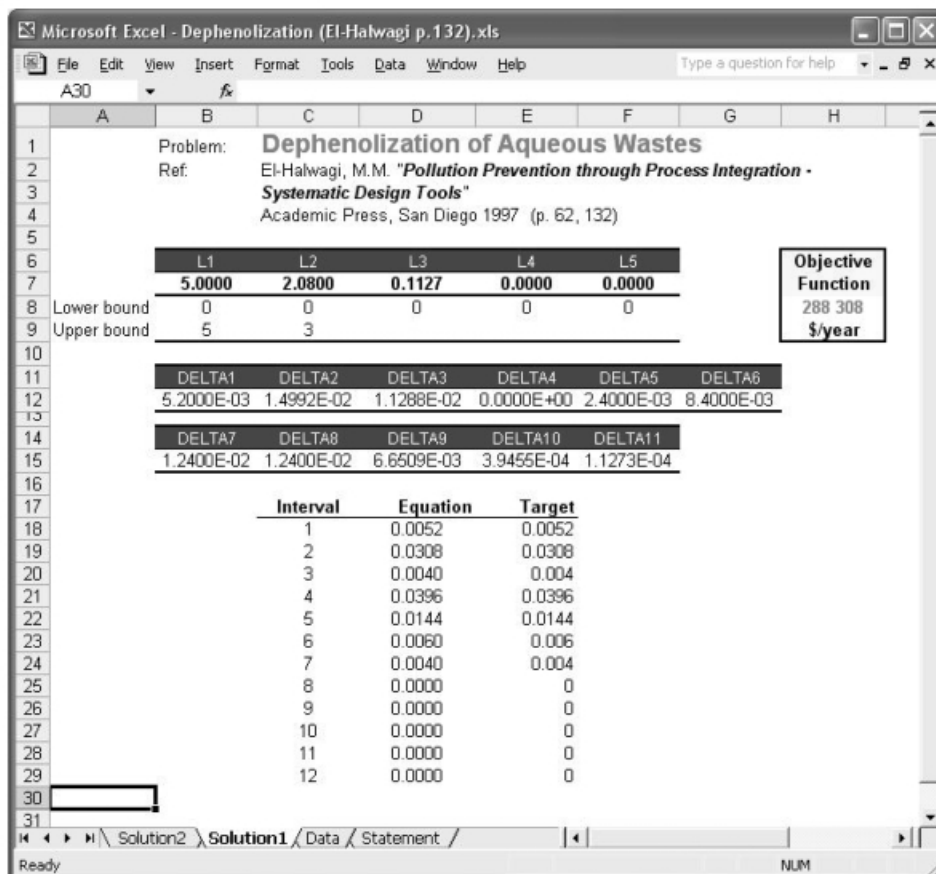$$\delta_9 - \delta_8 + 0.0510L_3 + 0.0114L_4 = 0.0000$$

Fig. 4. Minimizing operating cost in the dephenolization of aqueous wastes.
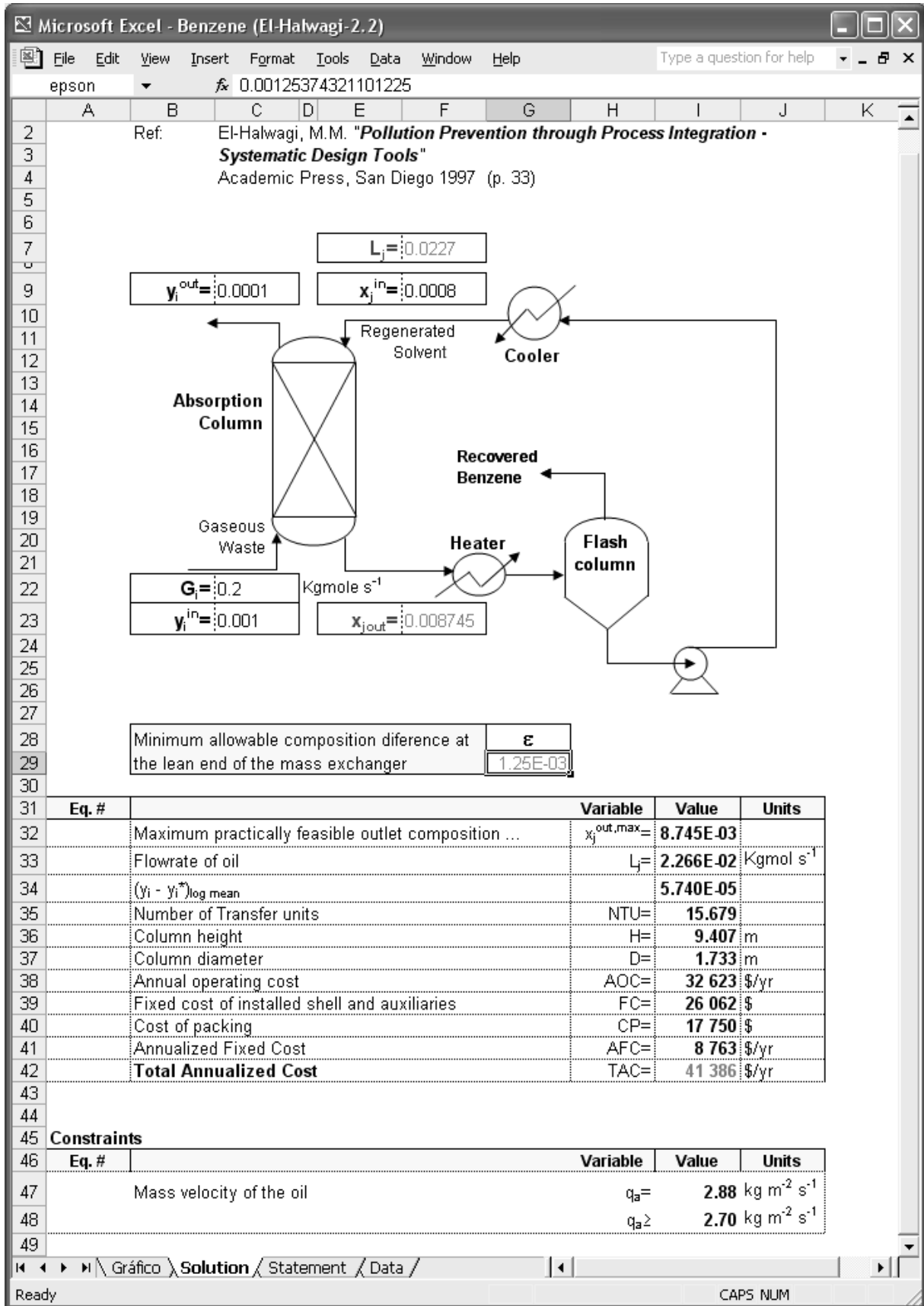
Microsoft Excel - Benzene (El-Halwagi-2.2)

File	Edit	View	Insert	Format	Tools	Data	Window	Help	Type a question for help

epson — f_x 0.00125374321101225

	A	B	C	D	E	F	G	H	I	J	K

Ref: El-Halwagi, M.M. "*Pollution Prevention through Process Integration - Systematic Design Tools*"
Academic Press, San Diego 1997 (p. 33)

L_j= 0.0227

y_i^{out}= 0.0001 x_j^{in}= 0.0008

Cooler

Regenerated Solvent

Absorption Column

Recovered Benzene

Gaseous Waste

Heater   **Flash column**

G_i= 0.2 Kgmole s^{-1}

y_i^{in}= 0.001 x_{jout}= 0.008745

Minimum allowable composition diference at the lean end of the mass exchanger | **ε** |
| 1.25E-03 |

Eq. #		Variable	Value	Units
	Maximum practically feasible outlet composition ...	$x_j^{out,max}$=	**8.745E-03**	
	Flowrate of oil	L_j=	**2.266E-02**	Kgmol s^{-1}
	$(y_i - y_i^*)_{log\ mean}$		**5.740E-05**	
	Number of Transfer units	NTU=	**15.679**	
	Column height	H=	**9.407**	m
	Column diameter	D=	**1.733**	m
	Annual operating cost	AOC=	**32 623**	$/yr
	Fixed cost of installed shell and auxiliaries	FC=	**26 062**	$
	Cost of packing	CP=	**17 750**	$
	Annualized Fixed Cost	AFC=	**8 763**	$/yr
	Total Annualized Cost	TAC=	41 386	$/yr

Constraints

Eq. #		Variable	Value	Units
	Mass velocity of the oil	q_a=	**2.88**	kg m^{-2} s^{-1}
		$q_a \geq$	**2.70**	kg m^{-2} s^{-1}

Gráfico \ **Solution** / Statement / Data /

Ready   CAPS NUM

Fig. 5. Recovery of benzene from a gaseous emission.

$\delta_{10} - \delta_9 + 0.0555L_3 + 0.0123L_4 + 0.0277L_5 = 0.0144$
$\delta_{11} - \delta_{10} + 0.0025L_3 + 0.0013L_5 = 0.0000$
$-\delta_{11} + 0.0010L_3 = 0.0000$
$\delta_k \geq 0, \ k = 1, 2, \ldots, 11$
$L_j \geq 0, \ j = 1, 2, \ldots, 5$
$L_1 \leq 5,$
$L_2 \leq 3.$

where L_j is the flow rate of the jth MSA, δ_{k-1} and δ_k are the residual masses of the key pollutant entering and leaving the kth interval. The first set of 11 equality constraints represents successive material balances around each composition interval. Setting $\delta_k \geq 0$ enables the waste streams to pass the mass of the pollutant downwards if it does not fully exchange it with the MSAs in a given interval. Setting $L_j \geq 0$ guarantees that the optimal flow rate of each MSA is non-negative. The last two constraints are upper bounds on flow rates less than the total available quantity of the corresponding lean stream.

The EXCEL Solver is used to optimize the objective function, which was set as the 'Target Cell' for minimization (Fig. 4). The initial values for the variables were set to 1.0 for all the flow rates (L_j) and to 0.001 for all the mole fractions (δ_k). The solution is quickly obtained by selecting the 'Linear Model' option in the Solver Parameters since all relationships are linear as is the objective function. The binding of the equality constraints determines the residual masses of the key pollutant entering and leaving the kth interval (δ_k). The solution for the MSA optimized flow rates is $\{L_1, L_2, L_3, L_4, L_5\} = \{5.0000, 2.0800, 0.1127, 0.0000, 0.0000\}$. Therefore, activated carbon (L_3) is the optimum external MSA. The same minimum operating cost can also be achieved by other combinations of the process MSA, since both L_1 and L_2 are inexpensive.

Example 3: Recovery of Benzene from a Gaseous Emission

This example is used to illustrate the application of the EXCEL Solver to solution of a nonlinear optimization problem [11] which is to remove benzene from a gaseous emission by contact with an absorbent (wash oil, molecular weight 300). The gas flow rate is 0.2 kmole/s and it contains 0.1% molar (1000 ppm) of benzene. The molar mass of the gas is 29 g/mole, its temperature is 300 K, at a pressure of 141 kPa. It is desired to reduce the benzene to 0.01 mole/mole% using the system shown in Fig. 5, where benzene is first absorbed
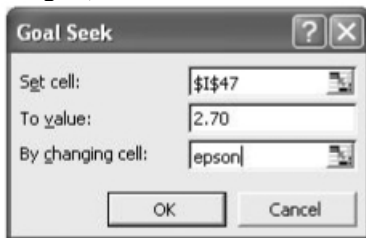
Fig. 6. Using 'Goal Seek' to find the value 2.70 for the mass velocity of oil (I47) by adjusting ε_j.

into oil. The oil is then fed to a regeneration system in which it is heated and passed on to a flash column that recovers benzene as a top product. The bottom product is the regenerated oil, which contains 0.08 mole/mole% benzene. Finally, the regenerated oil is cooled and pumped back to the absorber.

The EXCEL Solver is used to assess the optimal flow rate of recirculating oil that minimizes the total annualized cost (TAC) of the system.

The design equations for this process follow:

- *maximum practically feasible outlet composition of the MSA which satisfies the assigned driving force, ε_j:*

$$x_j^{out,max} = \frac{y_i^{in} - b_j}{m_j} - \varepsilon_j$$

- *Flow rate of oil:*

$$L_j = G_i \frac{(y_i^{in} - y_i^{out})}{(x_j^{out} - x_j^{in})}$$

-

$$(x_j - x_j^*)_{\log\ mean}$$

$$= \frac{\left[x_j^{out} - \left(\frac{y_i^{in} - b_j}{m_j}\right)\right] - \left[x_j^{in} - \left(\frac{y_i^{out} - b_j}{m_j}\right)\right]}{\ln\left\{\frac{\left[x_j^{out} - \left(\frac{y_i^{in} - b_j}{m_j}\right)\right]}{\left[x_j^{in} - \left(\frac{y_i^{out} - b_j}{m_j}\right)\right]}\right\}}$$

- *Number of Transfer Units,*

$$NTU_y = \frac{x_j^{in} - x_j^{out}}{(x_j - x_j^*)_{\log\ mean}}$$

- *Absorber column height,* $H = NTU_y HTU_y$
- *Column diameter,*

$$D = \sqrt{\frac{4(volumetric\ flowrate\ of\ gas)}{\pi(gas\ superficial\ velocity)}}$$

Cost equations:

- *Annual operating cost,* $AOC = C_o L_j (8000$ yrs/annum)
- *Fixed cost of installed shell and auxiliaries,* $FC1 = 2300 H^{0.85} D^{0.95}$
- *Cost of packing,* $FC2 = 800(\pi/4)HD^2$
- *Annualized Fixed Cost,* $AFC = (FC1 + FC2)/$ *Depreciation*
- *Total Annualized Cost,* $TAC = AOC + AFC$

Constraints:

- *Mass velocity of oil,*

$$\frac{L_j M_{oil}}{\frac{\pi}{4} D^2} \geq 2.7 \frac{kg}{m^2 s}$$

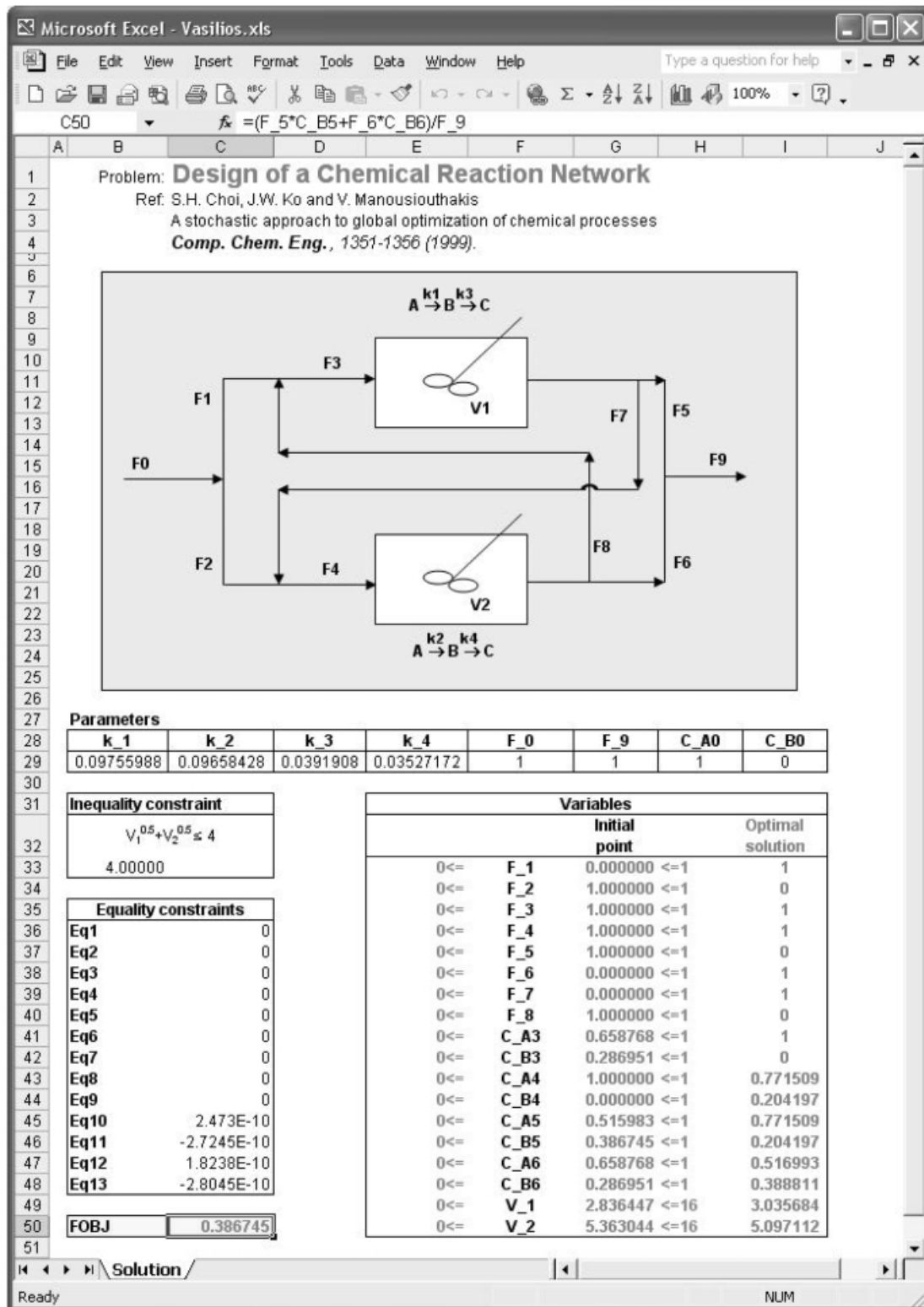- $\varepsilon_j \leq 0.005$
- $\varepsilon_j \geq 0.00072$

Fig. 7. Reactor network optimization.

These last constraints on the minimum allowable composition difference at the lean end of the mass exchanger are upper and lower bounds to the search space. The lower bound, $\varepsilon_j \geq 0.00072$, is equivalent to the constraint on mass velocity of oil being less than $2.7 \, \text{kg} \, \text{m}^{-2} \, \text{s}^{-1}$ and was calculated using the 'Goal Seek' tool available in EXCEL. This feature allows one to find a specific result for a cell by adjusting the value of any other cell by solving iteratively the sequence of nonlinear equations. The goal cell (mass velocity of oil) was set to 2.7 by changing the ε_j cell value (see Fig. 6).

Table 5. Local optima for the reactor network optimization [12]

Variables	Local 1	Local 2	Local 3	Local 4	Global
F_6	0	0	0	1	1
F_7	0	0	0	0	1
C_{A4}	0	undefined	1	1	0.771509
C_{A6}	0	undefined	0.658770	0.392874	0.516993
V_2	0	0	5.362991	16	5.097112
F_{obj}	0	0.374617	0.386745	0.388102	0.388811

The EXCEL Solver was then used to find the best value ε_j to minimize the total annualized cost. The initial value of ε_j was set to 5×10^{-4} and the optimum one was 1.25×10^{-3} which corresponds to a minimum TAC of \$41,386/yr. In [11] an optimum of \$41,560/yr was found by trying several initial values of ε_j until a minimum TAC was identified.

By limiting the search space for ε_j with upper and lower bounds, the EXCEL Solver converges to the optimum irrespectively of the initial value for this parameter. A previous attempt without these bounds, and using only the constraint on mass velocity of oil, was too sensitive to the initial value of ε_j.

Example 4: Design of a chemical reaction network

The optimal way to solve network problems is by specifying binary variables that multiply in an appropriate (logical) way the continuous variables, such that nonexistent units (corresponding to a zero binary variable associated with that unit) are treated with mathematical consistency. Thus, a network problem becomes a mixed integer nonlinear programming (MINLP) problem. However, there are many examples of such problems that are specified as pure nonlinear programming (NLP) problems, e.g. Fig. 7 [12].

The reactions are first order, the reactors are perfectly mixed (steady-state) and there is no variation in density of the reacting mixture. The problem may be formulated as follows:

$$F_{obj} = max\{C_{B9}\} = max\left\{\frac{F_5 C_{B5} + F_6 C_{B6}}{F_9}\right\}$$

subject to;

$$F_1 + F_2 - F_0 = 0$$
$$F_1 + F_8 - F_3 = 0$$
$$F_2 + F_7 - F_4 = 0$$
$$F_5 + F_7 - F_3 = 0$$
$$F_6 + F_8 - F_4 = 0$$
$$F_1 C_{A0} + F_8 C_{A6} - F_3 C_{A3} = 0$$
$$F_1 C_{B0} + F_8 C_{B6} - F_3 C_{B3} = 0$$
$$F_2 C_{A0} + F_7 C_{A5} - F_4 C_{A4} = 0$$
$$F_2 C_{B0} + F_7 C_{B5} - F_4 C_{B4} = 0$$
$$F_3 (C_{A3} - C_{A5}) - k_1 V_1 C_{A5} = 0$$
$$F_3 (C_{B3} - C_{B5}) + (k_1 C_{A5} - k_3 C_{B5}) V_1 = 0$$
$$F_4 (C_{A4} - C_{A6}) - k_2 V_2 C_{A6} = 0$$
$$F_4 (C_{B4} - C_{B6}) + (k_2 C_{A6} - k_4 C_{B6}) V_2 = 0$$
$$k_1 = 0.09755988 \text{ h}^{-1}$$
$$k_2 = 0.99 k_1 \text{ h}^{-1}$$
$$k_3 = 0.0391908 \text{ h}^{-1}$$
$$k_4 = 0.90 k_3 \text{ h}^{-1}$$
$$C_{A0} = 1 \text{ kg.m}^{-3}$$
$$C_{B0} = 0 \text{ kg.m}^{-3}$$
$$F_0 = 1 \text{ m}^3.\text{h}^{-1}$$

and to the inequality constraints:

$0 \leq F_i \leq 1$ (*volumetric flow rates, $m^3\,h^{-1}$*);
    $i = 1, \ldots, 9$
$0 \leq C_{Ai}, C_{Bi} \leq 1$ (*concentrations, $kg.m^{-3}$*);
    $i = 1, \ldots, 9$
$0 \leq V_i \leq 16$ (*reactor volumes, m^3*);
    $i = 1, 2$
$V_1^{0.5} + V_2^{0.5} \leq 4$

The k_i are 1st order rate constants.

This problem has 5 degrees of freedom, and a decomposition algorithm can be employed to optimize the simulation step [13]. A sequential

Table 6. Comparison between GAMS and the EXCEL Solver for the reactor network optimization

Algorithm	Starting point Lower bounds (10^{-5})	Upper bounds	Midpoints
GAMS Solvers:			
MINOS	Local2	Local3	**Global**
MINOS5	Local4	Local3	Local3
SNOPT	Local2	Local2	Local4
CONOPT	**Global**	Local4	**Global**
CONOPT2	**Global**	Local4	Local4
EXCEL Solver:			
Quasi-Newton	Non-feasible	**Global**	**Global**
Conjugate gradient	Non-feasible	Local3	**Global**

solution is not possible, no matter what the choice of decision variables, and several solutions with a subsystem of a minimum of 4 equations were encountered [14]. This subsystem is linear and readily solved. However, since in this example we compare the results obtained by the EXCEL Solver to the optimizers available within GAMS [15], the full nonlinear set of equations was solved as an alternative. The problem was solved starting from 3 different solution vectors, corresponding respectively to the lower bounds (assumed 10^{-5} in order to avoid numerical difficulties with the optimizers), to the upper bounds and to the midpoints of the search intervals. Table 5 demonstrates the four local optima obtained by [12] using a systematic search coupled with deterministic algorithms for some selected variables corresponding to the 5 degrees of freedom. Also shown is another local optima obtained with GAMS in a previous study [14], which simply corresponds to no reaction and to the closure of the mass balances (Table 6). Thus, in only 27% of the runs was the global optimum obtained with the algorithms available within GAMS. The EXCEL Solver found it in 50% of the runs. However, GAMS could always find some local optimum, while the EXCEL Solver failed to find feasible solutions in 33% of the runs, irrespective of the options available (derivatives and step sizes). This behavior cannot be extrapolated to other problems, and many more examples are required to compare these solvers.

This example also demonstrates how the Excel Solver may handle floating point exceptions (violations on the equality or inequality mathematical domain, viz. divisions by zero and forbidden arguments of transcendental functions). This may be simply circumvented by checking for forbidden operations or values before the expression is evaluated. If a violation occurs, a flag is enforced and the objective function is penalized directly, and avoids premature stoppage of the optimization procedure. This approach may be easily verified by downloading Example 4 and specifying as

initial vector $[10^{-2}, \ldots . . 10^{-2}]^{T}$ in both worksheets available.

CONCLUSIONS

The problems analyzed in this paper are of sufficient complexity to allow the observation of some convergence problems within the EXCEL Solver. The solution may be dependent on the initialization and is in general a local optimum. Since the optimizers within the EXCEL environment are local search algorithms [7], convergence to the global optimum is only guaranteed with convex problems. This is also applicable to the nonlinear optimizers available within GAMS [15]. However, initializations that correspond to reasonable and practical designs generally progress towards feasible and locally optimal solutions.

The EXCEL Solver is not as good as robust global optimizers [14]. However, it does provide an integrated framework for problem setting, visualization, inspection and solving of particular utility for practicing engineers. The ease with which these and similar process problems can be formulated and solved within the Excel environment constitutes a major step towards teaching practical optimization and design concepts, ultimately benefiting students with knowledge acquisition procedures and later in an effortless continuing practice throughout careers.

Despite these benefits, the use of modular simulators such as ASPEN Plus is probably warranted for complex processes that need detailed stage calculations and extensive use of physical and thermodynamic data libraries.

All these Excel workbook files and other examples are available for download on the Internet at www.deb.uminho.pt/ecferreira/download.

REFERENCES

1. E. C. Ferreira and R. L. Salcedo, A tool to optimize VOC removal during absorption and stripping, *Chemical Engineering,* **108**(1), January 2001, pp. 94–98.
2. E. C. Ferreira and R. L. Salcedo, Can spreadsheets solve demanding optimization problems? *Comp. Appl. in Eng. Education,* **9**(1), 2001, pp. 49–56.
3. W. G. Filby (ed.), *Spreadsheets in Science and Engineering,* Springer, Berlin, (1998).
4. T. F. Edgar, D. M. Himmelbau and L. S. Lasdon, *Optimization of Chemical Processes,* 2nd ed., McGraw-Hill Education, New York (2001).
5. B. V. Liengme, *Excel 2002 for Scientists and Engineers,* 3rd ed., Butterworth-Heinemann, London (2002).
6. P. Cornell, *Accessing and Analyzing Data with Microsoft® Excel,* Microsoft Press, Redmond (2003).
7. D. Fylstra, L. Lasdon, J. Watson and A. Waren, Design and use of the Microsoft Excel Solver, *Interfaces,* **28**(5), 1998, pp. 29–55.
8. R. Lima and R. L. Salcedo, An optimized strategy for equation-oriented global optimization, *European Symp. on Comp. Aided Chem. Eng, Vol. 10,* J. Grievink and J. V. Schijndel (eds), Elsevier Science BV, pp. 913–918 (2002).
9. L. S. Lasdon, A. D. Waren, A. Jain and M. Ratner, Design and testing of a generalized reduced gradient code for nonlinear programming, *ACM Trans. Math Software,* **1**(4), 1978, pp. 34–50.
10. G. B. DeLancey, Process analysis – an electronic version, *Chemical Engineering Education,* Winter, pp. 40–45, (1999).

11. M. M. El-Halwagi, *Pollution Prevention through Process Integration: Systematic Design Tools*, Academic Press, San Diego (1997).
12. S. H. Choi, J. W. Ko and V. Manousiouthakis, A stochastic approach to global optimization of chemical processes, *Comp. Chem. Eng*., 1999, pp. 1351–1356.
13. R. L. Salcedo and R. Lima, On the optimum choice of decision variables for equation-oriented global optimization, *Ind. Eng. Chem. Res.,* **38**, 1999, p. 4742.
14. R. L. Salcedo, R. Lima and M. F. Cardoso, Global optimization of chemical processes using simulated annealing, *Proc. Indian Nat. Sci. Ac.,* **69A**(3–4), 2003, pp. 359–401.
15. A. Brooke, D. Kendrick and A. Meeraus, GAMS: A user's guide, release 2.25, *The Scientific Press Series*, Boyd Fraser Pub. Co., San Francisco (1992).

Eugénio C. Ferreira is Associate Professor of biological engineering at the University of Minho in Braga, Portugal. He received a B.Che.E. degree and Ph.D. degree from the University of Porto in 1986 and 1995, respectively. His current research interests include modeling and control in bio(chemical) and wastewater treatment processes. E. C. Ferreira is currently teaching Strategy of Process Engineering, Process Control, Wastewater Treatment, and Air Pollution. More details at author's homepage: www.deb.uminho.pt/ecferreira.

Romualdo Salcedo is Professor of chemical engineering at the University of Porto, Portugal. He received a B.Che.E. degree from the University of Porto in 1975, a M.Eng. and a Ph.D. degree from McGill University, Montreal, Canada respectively in 1977 and 1981. His current research interests include simulation and optimization of nonlinear processes and air pollution control. R. Salcedo is currently teaching Process Design and Optimization and Air Pollution Control. He holds patents on numerically optimized gas cyclones and recirculation systems, which resulted in industrial applications.

Ricardo Lima is a Ph.D. graduate student in chemical engineering at the University of Porto. His work relates to the development of an integrated strategy for simulation and optimization of large-scale processes, using stochastic optimizers.