

# OPTIMAL PROGRAMMING OF BATCH DISTILLATION: VESSEL NETWORK OPERATIONS

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**Abstract--** This work presents an alternative structure for multivessel batch distillation and focuses on the determination of an optimal programming for it. The system is composed by a set of heated or cooled vessels connected by total reflux distillation cascades. This structure is able for separating multicomponent mixtures achieving simultaneously desirable specifications for all components, without loss of material and avoiding complex control strategies. An optimization problem is formulated in order to maximize a profit function assigned to a separation task. Transformed decision variables together with a smooth price function, are used to pose the problem according to an unconstrained form. The decision variables are the vapor molar flow rate and the operating time of each column. Batch separations of ideal quaternary mixtures are optimally programmed regarding purity specifications under fixed number of stages in each cascade and with an upper bound on the total rate of heat consumption.

**Keywords:** Batch Distillation, Optimal Programming and Vessel Network.

## I. Introduction

The recent expansion of specialty chemical industries has led to a renewed interest in batch distillation. This may be attributed to the inherent simplicity of batch distillation and its flexibility to process small volumes. Batch distillation may be divided into single vessel and multivessel. Single vessel batch distillation includes the Batch Rectifier (BR), the Batch Stripper (BS) and the Middle Vessel Column (MVC). Hasebe *et al.* (1995) extended the MVC concept to a Multivessel Batch Distillation (MVBD). The MVBD uses a single reboiler and a single condenser, operating at total reflux with intermediate vessels (one per product) connected to the liquid downflow circuit of the column. The MVBD separates  $N_c$  components with  $N_c$  constant hold-up vessels, calculated from the feed composition. Wittgens *et al.* (1996) pointed that MVBDs have comparative advantages to BRs because there is no need of optimal times for slop cuts. However they mentioned that the constant hold-up policy may hinder the achievement of specifications. To overcome this, Hasebe *et al.* (1995, 1997) controlled composition by manipulating vessel

hold-ups, while Skogestad *et al.* (1997) did the same by controlling column temperatures.

The object of this work is an alternative batch distillation scheme, the Vessel Network (VN). VN exhibits comparative advantages to the MVBD. The idea is to by-pass the drawbacks of the MVBD due to the fact that vessels access only *the liquid circuit*. If, for instance, a light impurity goes to a vessel rich in heavy species, it can only be removed by (slow) elution, i.e. the impurity would be protected against a (fast) expulsion by stripping. So, it is no surprise that MVBDs require maneuvers on the vessel streams to meet stringent specifications.

VNs resemble MVBD configurations, but they work differently. For ideal or non-ideal moderate systems, VN separates multicomponent mixtures achieving specifications for all components without flow rate maneuvers, loss of material or slop cuts. It operates with constant mass where heat is continuously supplied to some vessels and removed from others.

An important aspect is that VN vessels are contacted with both vapor and liquid streams, so that stripping and rectifying effects occur inside and around them. A VN is composed by a set of vessels operating with constant hold-up, arranged in a vertical planar frame (Fig. 1) interconnected by total reflux distillation cascades. Total reflux cascades establish true constant hold-up in all vessels, so each vessel must be charged with a hold-up equal to the amount of product designed to be recovered there. The network connectivity is determined by cascades, defining oriented connections according to the flow of vapor phase (arcs) between vessels (vertices). VNs can be represented as digraphs (Mah, 1990) if we choose the orientation of arcs according to the vapor flow. For global separation of a mixture there must exist at least one oriented path for vapor and liquid between any two vessels.

In general, a VN with higher degree of connectivity will accomplish a separation task in a shorter time at expenses of higher capital costs. Assuming, as a basis of reasoning, a certain level of available heating utility, an optimization problem then arises as a compromise between operational time (i.e., productivity) and capital costs. Optimal batch distillation campaigns dealing with cheap products, will probably distort the above compromise to favor the choice for simpler equipment. On the other hand, with gradual increase of the unitary separation reward (i.e. the monetary value difference

between specified products and feedstock per unit of feedstock), capital costs tend to become less important compared with productivity. One can then conclude that faster distillation schemes (i.e. using more sophisticated equipment) now become more and more the best economic alternatives in unitary basis of feedstock. It is exactly in connection with the last point that VNs can be justified as engineering devices.

Separation is generated in the VN by the interaction between vessels and cascades. The rate of separation is *naturally regulated* by the rates of enthalpy crossing the VN. This means that there exists a *natural* high degree of thermal integration among the cascades. For mixtures not too far from ideality, each species is naturally enriched in an *unique vessel* defined by its relative volatility: the heaviest component is gradually enriched in the lowest vessel, whereas the lightest one concentrates in the highest vessel. Intermediate components are enriched in intermediary vessels. Exists, thus, an association between a separable species and its destination vessel (and the height of this vessel in the VN). Vessels and species can be both numbered according to the ascending order of relative volatility. This unique species-vessel association allows a convenient sketching of VNs by means of digraph drawings (Fig. 1A), which use oriented arcs (as oriented cascades according to vapor flow) and vertices (as numbered enrichment vessels). Figures 1A and 1B depict a fully connected VN for quaternary separation.

This work also addresses a limited optimization of VN operations as Maximum Annualized Profit Problems under fixed number of stages per cascade, constant vessel hold-ups and a limitation on the available heat duty. Decision variables are the vapor flow rates and operating times of arcs, assuming all proposed arcs active at startup. These variables were transformed in order to pose the problem unconstrained. The economic objective is the unitary profit generated by the annual campaign. Products being enriched in vessels are continuously valued by a separation Price Function (Ahón and Medeiros, 2001). The Price Function is a perfectly smooth and differentiable composition function that associates market prices to specified vessels and penalizes incomplete separations by assigning depreciated prices to under-specified vessels. Nevertheless, it must be realized that our Price Function *is not just another classical arbitrary penalty function* for two main reasons: first, it is naturally compliant with the thermodynamic/market logic which assigns (does not assign) appropriate rewards for accomplished (incomplete) separation tasks; second, it is not a mere artificial negative counterweight to be added to the objective, eventually distorting its physical nature. Finally, we sought a *local optimum* of this problem in terms of: (i) purity of products; (ii) vapor flows and operating times of cascades.

## II. Dynamic Modeling of VN Operations

The number of vessels of a VN is equal to the number of components ( $N_c$ ). All vessels may be mutually connected so that the maximum number of cascades is  $N_c(N_c-1)/2$ . Heat may be added to (or removed from) each vessel causing changes to the vapor (and liquid) distribution, but without disturbing the total reflux regime of cascades. Due to the ascending numbering, it is only possible to flow vapor phase from vessel  $i$  to vessel  $j$ , if  $i < j$ . In the digraph form (Fig. 1A), vertices and arcs correspond, respectively, to vessels and distillation cascades, where arc  $i-j$  symbolizes a cascade linking vessel  $i$  to vessel  $j$ . A VN may be described by the ordered set of initially active arcs, so that the digraph in Fig. 1A sketches the VN {1-2, 1-3, 1-4, 2-3, 2-4, 3-4}. The simplest VN for a quaternary separation has a tree like form {1-2, 2-3, 3-4}. We use vertex adjacency matrices, whose rows and columns correspond to vertices. Element  $(i,j)$  of an adjacency matrix is nonzero if there is an arc from vertex  $i$  to vertex  $j$ .  $C_{ij}$  is the identification number of cascade  $i-j$ , while  $N_{ij}$  and  $T_{ij}$  are, respectively, its number of stages and operating time.  $L_{j,i}$  and  $V_{ij}$  represent liquid and vapor molar flow rates through cascade  $i-j$ .

For VN dynamic simulation process parameters and decision variables must be known. Process parameters are: (i) components and levels of purity ( $LP$ ) for specification; (ii) total batch hold-up ( $H_0$ ) and feedstock composition; (iii) hold-up and initial composition of vessels; (iv) prices of specified products; (v) number of stages ( $N_{ij}$ ) and stage efficiencies of cascades (numbered from top to bottom); and (vi) pressure of vessels. Decision variables are vapor molar flow rates and operating times of cascades. The dynamic system is modeled with simplifying assumptions: (i) VN hold-ups are concentrated in vessels; (ii) Cascade model uses the McCabe-Thiele approximation (Ahón and Medeiros, 2001). These assumptions let us with only  $N_c$  transient vessel mass balances. The following symbols are also defined ( $N_c$  by 1 vectors): (i)  $\underline{H}_i$  are species moles in vessel  $i$ ; (ii)  $\underline{X}_{N,C_{i,j}}$ ,  $\underline{Y}_{1,C_{i,j}}$  are mole fractions of bottom and top products of  $C_{i,j}$ ; (iii)  $\underline{Y}^* = \underline{g}(\underline{X})$  is the vapor-liquid isobaric equilibrium relationship. Transient mass balances for vessel  $i$  then read:

$$\frac{d\underline{H}_i}{dt} = \sum_{j=1}^{i-1} V_{j,i} \underline{Y}_{1,C_{j,i}} - \sum_{j=1}^{i-1} L_{i,j} (\underline{H}_i / \underline{1}^t \underline{H}_i) \quad (1a)$$

$$+ \sum_{j=i+1}^{N_c} L_{j,i} \underline{X}_{N,C_{i,j}} - \sum_{j=i+1}^{N_c} V_{i,j} \underline{g}(\underline{H}_i / \underline{1}^t \underline{H}_i) \quad (1b)$$

$$t = 0, \quad \underline{H}_i = \underline{H}_{i,0}$$

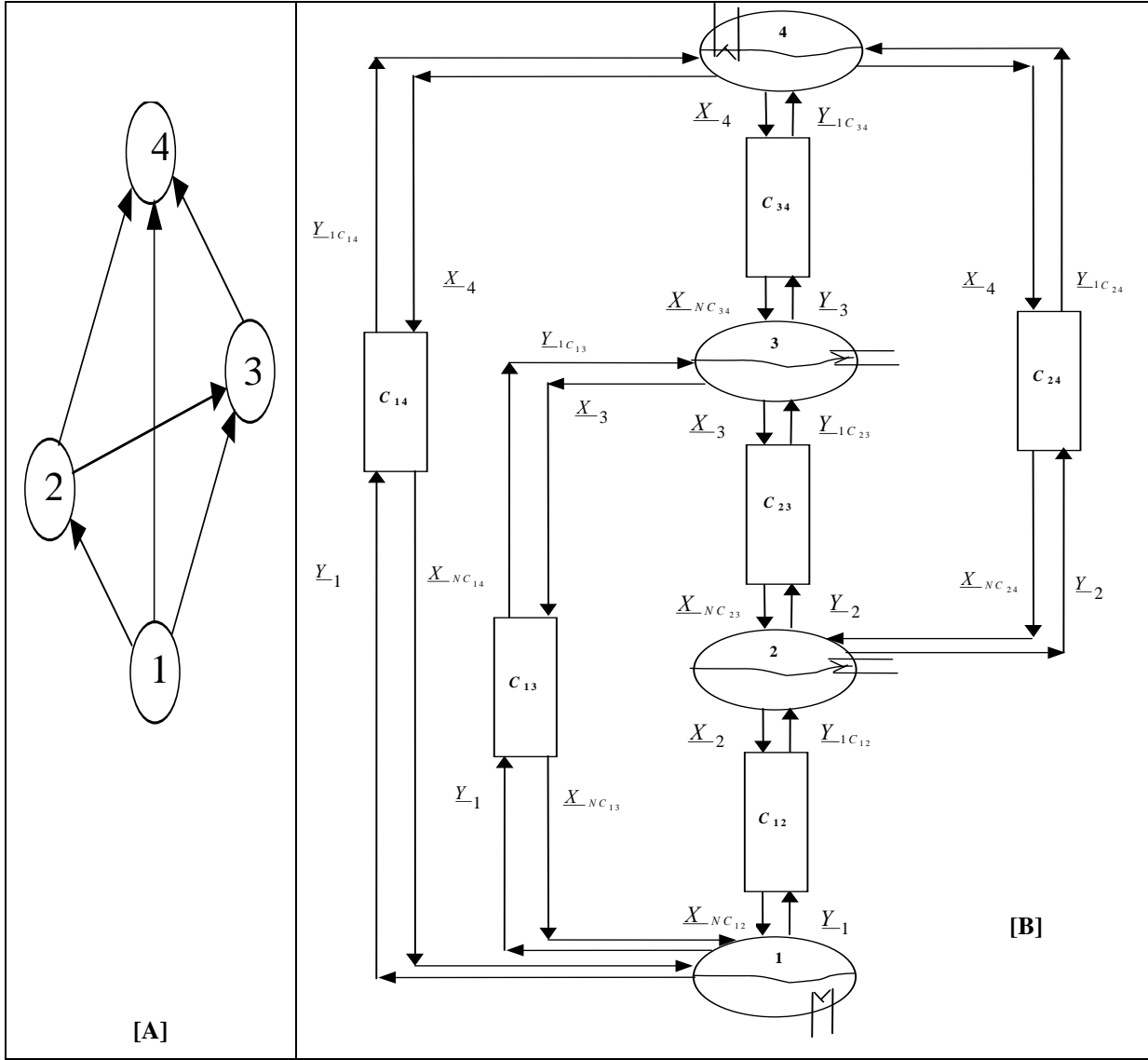


Figure 1 –Fully connected Vessel Network with 4 vessels and 6 cascades : [A] Digraph form; [B] Schematic diagram

Vessel mass balances presume a fully connected VN. If an arc  $i-j$  ( $i < j$ ) is not used or has been turned-off after a certain time, the respective  $V_{ij}$ ,  $L_{ji}$  terms have to be zeroed. The interactions between vertices and arcs are regulated by cascade specifications and parameters. A Cascade is fed with liquid and vapor streams coming from two vessels. At the same time, it feeds these two vessels with its top and bottom product streams ( $\underline{Y}_{1,C_{ji}}$  and  $\underline{X}_{N,C_{ji}}$ , Eq. (1)). Thus, operational parameters of a cascade consist of its two feed streams. A feed stream entering stage  $n$  of cascade  $k$  has molar flow rate  $F_{n,k}$ , whereas  $\underline{Z}_{n,k}$  and  $\beta_{n,k}$  represent its species mole fractions and vaporized fraction. The heat duty of stage  $n$  on cascade  $k$  is  $Q_{n,k}$ . We have:

**Cascade specifications:**

$$\begin{aligned} Q_{k,C_{ji}}^* &= 0 \quad (k=1,\dots,N_{j,i}, j=1,\dots,i-1) \\ Q_{k,C_{ij}}^* &= 0 \quad (k=1,\dots,N_{i,j}, j=i+1,\dots,Nc) \end{aligned} \quad (2)$$

**Cascade operational parameters:**

$$F_{1,C_{ji}} = L_{i,j}, \quad \underline{Z}_{1,C_{ji}} = (\underline{H}_i / \underline{1}' \underline{H}_i), \quad (3a)$$

$$\beta_{1,C_{ji}} = 0 \quad (j=1,\dots,i-1)$$

$$F_{N,C_{ji}} = V_{j,i}, \quad \underline{Z}_{N,C_{ji}} = \underline{g}(\underline{H}_j / \underline{1}' \underline{H}_j), \quad (3b)$$

$$\beta_{N,C_{ji}} = 1 \quad (j=1,\dots,i-1)$$

$$F_{1,C_{ij}} = L_{j,i}, \quad \underline{Z}_{1,C_{ij}} = (\underline{H}_j / \underline{1}' \underline{H}_j), \quad (3c)$$

$$\beta_{1,C_{ij}} = 0 \quad (j=i+1,\dots,Nc)$$

$$F_{N,C_{ij}} = V_{i,j}, \quad \underline{Z}_{N,C_{ij}} = \underline{g}(\underline{H}_i / \underline{1}' \underline{H}_i), \quad (3d)$$

$$\beta_{N,C_{ij}} = 1 \quad (j=i+1,\dots,Nc)$$

Since all active arcs operate at total reflux ( $L_{j,i}=V_{j,i}$ ,  $i < j$ ), vessel hold-ups are constant. Thus vessel  $i$  must be charged at  $t=0$  with an initial hold-up ( $\underline{1}' \underline{H}_{i,0}$ ) given by

the number of moles of product  $i$ . If product  $i$  is mainly component  $i$ , and there is only one feedstock with  $H_0$  moles and molar fraction vector  $\underline{Z}_F$ , vessel  $i$  must be initially loaded with  $H_0 Z_{Fi}$  moles having composition  $\underline{Z}_F$ :

$$\underline{H}_{i,0} = \underline{Z}_F \cdot (H_0 Z_{Fi}) \quad (4)$$

The decision variables for VN optimization comprehends all non-zero elements of the matrix of arc operating times ( $\underline{T}$ ) and their counterparts in the matrix of arc vapor molar flow rates ( $\underline{V}$ ). These two sets correspond to vectors  $\underline{\Theta}$ ,  $\underline{\Phi}$  obeying  $\Theta_k = T_{ij}$ ,  $\Phi_k = V_{ij}$ , where  $i-j$  (with  $i < j$ ) is the  $k$ -th element in the ordered list of active arcs. The number of decision variables is then twice the number of initially active arcs in the VN, represented by  $N_{CSC}(0)$ . The number of active cascades at time  $t$  ( $N_{CSC}(t)$ ) is given by the number of nonzero elements in  $\underline{T}$  greater than or equal to  $t$ . An auxiliary vertex-arc incidence matrix,  $\underline{S}_V(t)$  (size  $Nc$  by  $N_{CSC}(t)$ ), describes VN connectivity with reference to the oriented flow of vapor phase as a function of time. Elements of  $\underline{S}_V(t)$  obey:  $S_{V(i,k)}(t) = +1$ , if  $\Theta_k \geq t$  and arc  $k$  points to vertex  $i$ ;  $S_{V(i,k)}(t) = -1$ , if  $\Theta_k \geq t$  and arc  $k$  leaves vertex  $i$ ; otherwise  $S_{V(i,k)}(t) = 0$ . Assuming McCabe-Thiele heat integration,  $\underline{S}_V(t)$  leads to the vector of vertex generation of vapor phase ( $\underline{v}(t)$ ) at time  $t$ , as shown in Eq. (5). VN performance is then obtained integrating Eq. (1) for all  $i$  and  $t \in (0, \Omega)$ . The batch time ( $\Omega$ ) is given by the cascade with the largest operating time:  $\Omega = \max(\Theta_k)$ .

$$\underline{v}(t) = -\underline{S}_V(t) \underline{\Phi} \quad (5)$$

### III. Formulation for VN Optimization

Even with McCabe-Thiele cascades and ideal mixtures, VN response is strongly non linear. Its optimization is a highly non-convex problem prone to exhibit multiple optima. This scene can be aggravated if, for the sake of completeness, one realize that VN optimization unavoidably belongs to the class of mixed-integer problems.

On the other hand, this work is by no means intended to approach mixed-integer global optimization of VNs. Our objectives are indeed modest. First, we described and modeled VN systems; and, second, we approached a limited VN optimization based on three simple points: (i) search for a local optimum; (ii) unconstrained non linear continuous optimization; (iii) Maximum annualized profit problem (MaxAPP) formulation.

In this context, VN optimization is constrained by: (A) zero lower bound for  $\underline{\Theta}$  and  $\underline{\Phi}$ ; (B) upper bound  $\Theta^{MAX}$  to elements of  $\underline{\Theta}$ ; (C) available heating power,

$\Psi$ . All available heat is supposed to be used by the VN at  $t=0$ , so that the heat duty constraint is posed as an equality constraint satisfied at the initial condition. Coherently with the McCabe-Thiele approximation, this constraint can be replaced by a constraint on the total generation of vapor phase via an average heat of vaporization,  $\lambda$ . Applying Eq. (5) at  $t=0$ , constraint (C) can be written as

$$(1/2) \underline{1}^t \left| \underline{S}_V(0) \underline{\Phi} \right| = \Psi / \lambda \quad (6)$$

Constraints (A), (B) and (C) can be removed if the decision vectors  $\underline{\Theta}$  and  $\underline{\Phi}$  are expressed via elementary smooth transformations of continuous unrestricted variables,  $(\theta_i, \phi_i)$ , as in Eqs (7) and (8). As one can easily see, Eqs. (7) and (8) are not invertible (nor convex) functions, but they are simple and usable for *direct* searches of a *local* optimum, as we planned above. They also guarantee that  $(\Theta_i, \Phi_i)$  satisfy the bounds and the heating constraint, such that variables  $(\theta_i, \phi_i)$  can be manipulated by an algorithm for unconstrained *direct* optimization.

$$\Phi_i = (\Psi / \lambda) \left\{ \phi_i^2 / [(1/2) \underline{1}^t \left| \underline{S}_V(0) \underline{Diag}(\underline{\phi}) \underline{\phi} \right|] \right\} \quad (7)$$

$$\Theta_i = \Theta^{MAX} (\theta_i^2 / (1 + \theta_i^2)) \quad (8)$$

The annualized unitary profit ( $AP$ ) is given by revenues with products minus annualized capital and costs with raw materials and utilities. The reference year has 7200 hours of operation. All products at time  $t$  ( $\underline{H}_i(t), i = 1, \dots, Nc$ ) have their unitary prices ( $P_i$ , US\$/gmol) valued by the *Price Function* proposed by Ahón and Medeiros (2001). The Price Function relationship (Eq. (9)), works with product composition, specification parameters and the unitary price of a mixture in the worst state of separation ( $P_0$ ). Parameter  $P_{RAW}$  is the unitary price of feedstock also determined by the Price Function from feedstock composition. If  $i$ -th product does not achieve specification, the Price Function assures that  $P_i \cong P_{RAW} \cong P_0$ . The  $AP$  function is given by Eq. (10).

$$P_i(\underline{H}_i(t)) = P_i(\underline{H}_i(t) / \underline{1}^t \underline{H}_i(t), \underline{P}^{Spc}, \underline{X}^{Spc}, P_0) \quad (9)$$

$$AP = \frac{\sum_{i=1}^{Nc} (\underline{1}^t \underline{H}_i) P_i(\underline{H}_i(t)) N_{BAT} - Util - ISBL}{N_{BAT} \cdot H_0} - P_{RAW} \quad (10)$$

In Eq. (10)  $N_{BAT}$  is the number of batches per year obtained from the total batch time and the operational year;  $ISBL$  is the installed cost of distillation cascades, which can be traduced (Douglas, 1988) as the annualized fixed cost of the process (US\$/year); and  $Util$  is the annual cost of cold/hot utilities (US\$/year). The denominator  $N_{BAT} \cdot H_0$  is the total amount of material processed (gmol/year). Formulae for  $N_{BAT}$ ,  $ISBL$ ,  $Util$  are presented by Ahón and Medeiros (2001). It must be pointed that  $ISBL$  is a function of vectors  $\underline{\Theta}$ ,  $\underline{\Phi}$ , since the  $k$ -th element of the ordered list of arcs

only generates capital cost if it was active at start-up ( $\Phi_k, \Theta_k > 0$ ).  $Util$  is proportional to the integral of generated vapor phase ( $\Lambda$ ) during the batch, given by Eq. (11). Matrix  $\underline{S}_V(t)$  is continuously updated, from  $\underline{S}_V(0)$  and  $\underline{\Theta}$ , via Eq. (12). The MaxAPP is stated by Eq. (13).

$$\Lambda = \int_0^{\Omega} (1/2)1^t \left| \underline{S}_V(t) \underline{\Phi} \right| dt \quad (11)$$

$$\begin{aligned} [S_V(t)]_{ij} &= [S_V(0)]_{ij} \quad \text{if } \Theta_j \geq t \quad \forall i \\ [S_V(0)]_{ij} &= 0 \quad \text{if } \Theta_j < t \quad \forall i \end{aligned} \quad (12)$$

$$\begin{aligned} \max \quad & AP \\ \{ & \underline{\phi}, \underline{\theta} \} \end{aligned} \quad (13)$$

Problem Eq. (13) is solved using the well known Simplex Method (Reklaitis et al., 1983) for non-linear unconstrained optimization. Differential equations were integrated via adaptive Runge-Kutta schemes in order to keep mole fraction truncation error below  $10^{-5}$ . The algorithm for computation of the objective  $AP$ , from the decision variables and process parameters, is summarized below.

1. From  $\theta_i$  and  $\phi_i$  supplied by optimization algorithm, calculate  $\Phi_i, \Theta_i$  with Eqs. (7),(8).
2. Calculate the batch time ( $\Omega$ ) and profiles of flow rates of liquid and vapor in all cascades.
3. Set initial conditions for all vessels.
4. Perform integration of Eqs. (1) determining products at the end of the batch. Price them all.
5. Calculate  $N_{BAT}, ISBL, Util$  and  $AP$ , with Eqs. (9), (10), (11) and (12).

#### IV. Results

For demonstration of VN systems, VN optimizations for 9 case-studies were considered. These cases were mounted from: (i) three ideal quaternary feedstocks F1, F2 and F3 (Table 1) with constant relative volatilities; and (ii) three levels of purity ( $LP=90\%$ ,  $LP=95\%$ ,  $LP=99\%$ ) for product specification. In all cases, the following choices apply: (i) total batch hold-up of 2700 gmol; (ii) cascades {1-2, 2-3, 3-4} with 15 stages, {1-3, 2-4} with 8 stages, and {1-4} with 6 stages; (iii) tray efficiency = 1; (iv) prices of specified products (US\$/gmol):  $P_1^{Spc}=0.1, P_2^{Spc}=0.1, P_3^{Spc}=0.1, P_4^{Spc}=0.1$ ; (v)  $P_0=0$  US\$/gmol; (vi)  $\Theta^{MAX}=5h$ ; (vii) available heating  $\Psi = 200kW$ ; (viii) average heat of vaporization  $\lambda=40000$  J/gmol.

**Table 1: Feedstock Mixtures and Component Relative Volatilities**

Component	$\alpha$	Feedstock Compositions ( $\underline{Z}_F$ )		
		F1	F2	F3
1	1	0.05	0.25	0.60
2	3	0.10	0.25	0.25
3	9	0.25	0.25	0.10
4	27	0.60	0.25	0.05

**Table 2: Optimal Annualized Profit ( $AP$ ) and Batch Time ( $\Omega$ ) for VN processes ( $a$ : \$/100mol)**

Configuration	LP	F1		F2		F3	
		$\Omega(h)$	$AP^a$	$\Omega(h)$	$AP^a$	$\Omega(h)$	$AP^a$
<i>f</i> -VN	90%	0.3159	7.2363	0.2348	9.8174	0.2209	7.3210
<i>m</i> -VN	90%	0.3300	7.2548	0.2131	9.8566	0.1922	7.3515
<i>t</i> -VN	90%	0.3131	7.2698	0.2082	9.8649	0.1811	7.3637
<i>f</i> -VN	95%	0.4463	7.1731	0.3251	9.7718	0.2500	7.2965
<i>m</i> -VN	95%	0.4035	7.2118	0.2510	9.8265	0.2198	7.3038
<i>t</i> -VN	95%	0.4064	7.2243	0.2774	9.8299	0.1923	7.3363
<i>f</i> -VN	99%	0.7100	6.9635	0.4101	9.6802	0.3209	7.2697
<i>m</i> -VN	99%	0.6231	7.0270	0.3623	9.7552	0.3022	7.2895
<i>t</i> -VN	99%	0.6965	7.0602	0.3675	9.7660	0.3033	7.3000

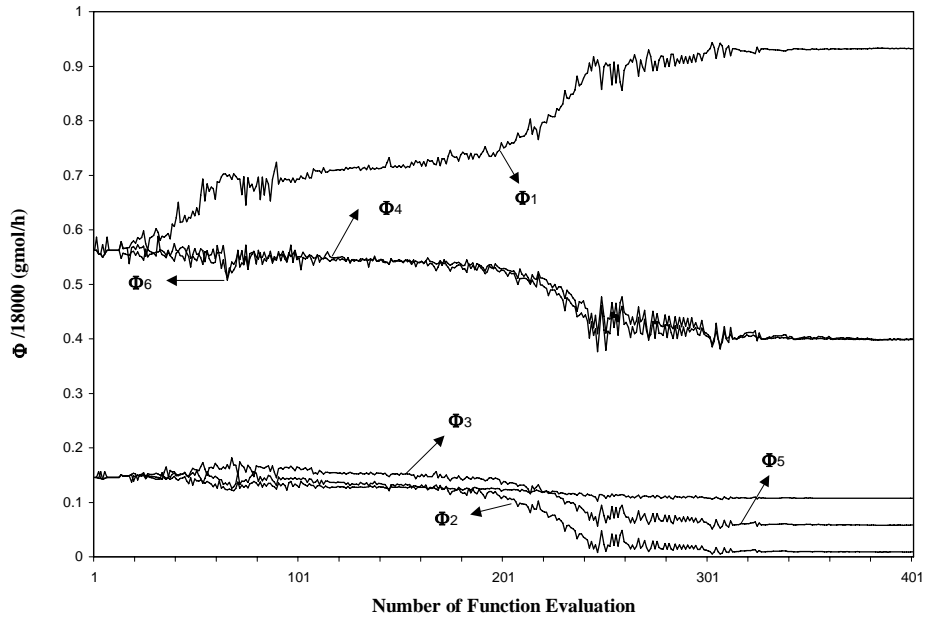


Figure 2 - Evolution of  $\Phi/18000$  (gmol/h) along simplex search [F3, LP-99%, f-VN]

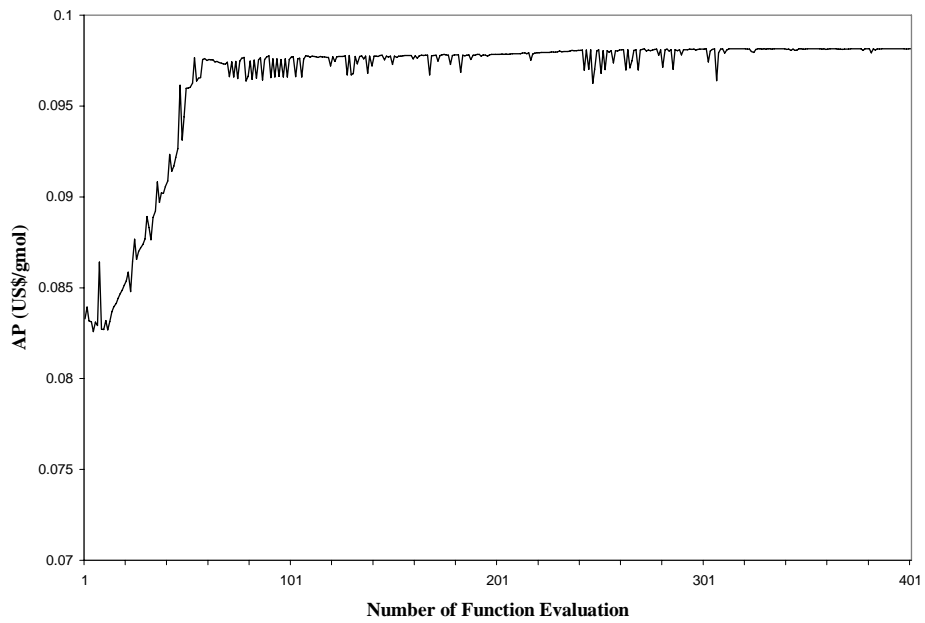


Figure 3 - Evolution of AP along simplex search [F3, LP-99%, f-VN]

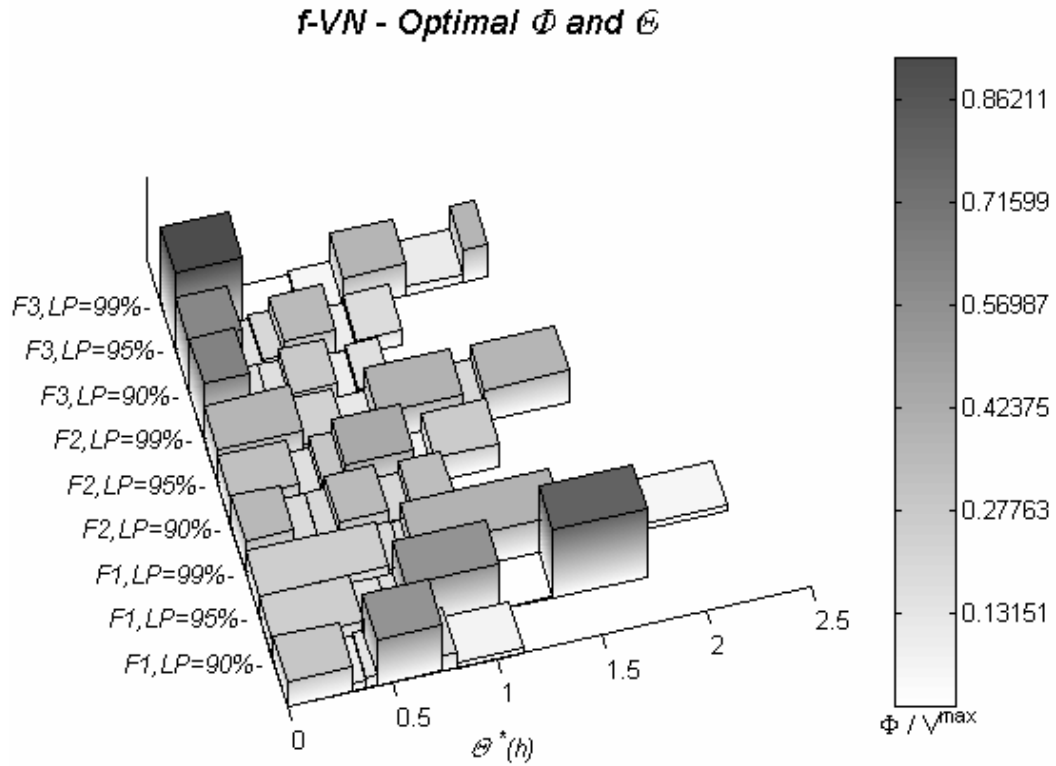


Figure 4 - Optimal  $\Phi$  and  $\Theta^*$  (cumulative operational time) for 9 case-studies (*f*-VN)

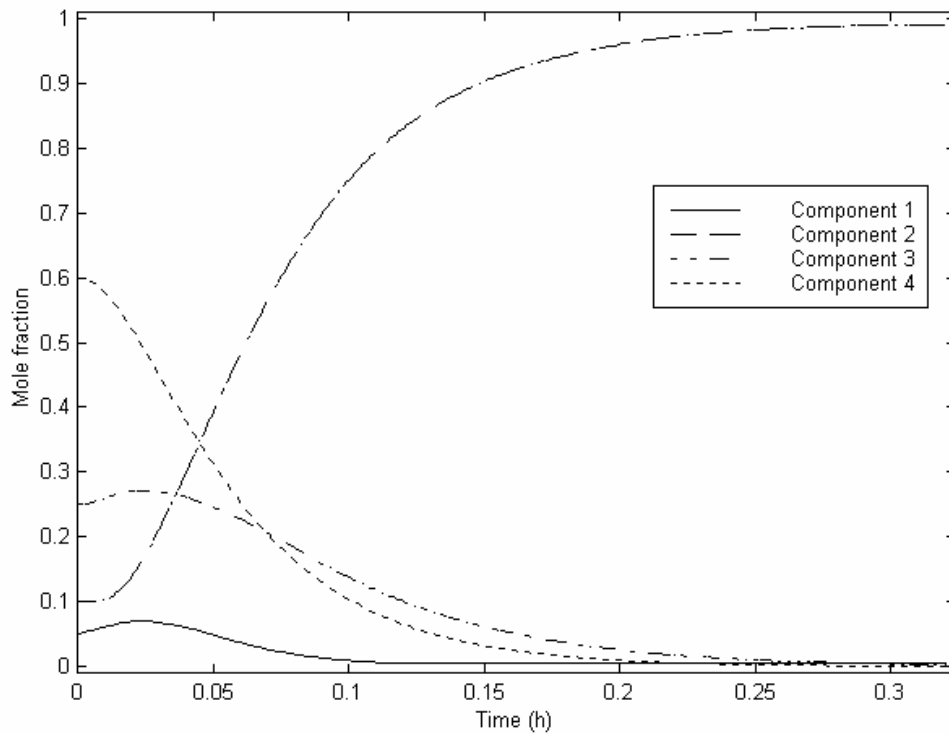


Figure 5 - Time trajectories of product composition in Vessel 3 [F3, LP-99%, *f*-VN]

Optimization involves structural and operational moves. Operational moves are defined by vectors  $\underline{\theta}$ ,  $\underline{\phi}$ , which determine the programmed operating time and vapor flow rate of all arcs. These variables also apply limited structural moves by turning-off an initially active arc or rejecting an "initially active" condition by selecting "near zero" cascade times. For comparing different optimal VN structures, the nine cases of study were submitted to three systems: (i) the fully connected VN {1-2, 1-3, 1-4, 2-3, 2-4, 3-4} (*f*-VN); (ii) a medium connected VN {1-2, 1-4, 2-3, 3-4} (*m*-VN); (iii) the minimally connected (tree) VN {1-2, 2-3, 3-4} (*t*-VN). Optimizations showed that *t*-VN achieved the best objective values in all cases of study, as seen in Table 2. Figures 2 and 3 show the evolution of simplex search for the optimization of *f*-VN with feedstock F3 and level of purity of 99% [F3, *LP*=99%, *f*-VN]. Figure 4 depicts, with 9 rows of bars, the optimal policies ( $\underline{\theta}$ ,  $\underline{\phi}$ ) for all 9 cases with *f*-VN. Each row has 6 bars: bar *j* sketches the optimal allocation of cascade *j* – height and color correspond to  $\phi_j$  and width to  $\theta_j$ . Figure 5 shows time trajectories of mole fractions in vessel 3 for optimal [F3, *LP*=99%, *f*-VN]. Although the best economic option in all cases, the *t*-VN was not always the faster processing. The underlying fact is that more connected (and expensive) VNs can be the best economical choice only if the problem offers a more difficult mission or a more substantial reward (VW-Beetle versus TR-Ferrari dilemma).

## V. Conclusions

A new batch distillation was presented, the Vessel Network (VN). VNs do not require policies for product withdrawal and separate ideal or moderate non-ideal multicomponent mixtures, achieving desired purity for all products, without losses, slop cuts or control strategies. Local continuous VN optimization was carried out with maximization of the annualized profit of a quaternary (constant relative volatilities) separation under fixed vessel hold ups, fixed number of stages per cascade and fixed heating power. This problem was put unconstrained via transformed variables together with a Price Function for product valuation. We investigated optimization of three VN operations (*t*-VN, *m*-VN, *f*-VN) for nine cases of study built with three brands of feed and three levels of purity (*LP*) for specification. The tree VN (*t*-VN) attained the best objective values. The *m*-VN gives little inferior, but similar, results,

being even faster in some instances. Unfortunately, due to strict lack of space, we can not present other examples capable to reveal that optimal densely connected VNs (e.g. *f*-VN) can be eventually the best operational choice. We indeed encountered such examples when, as mentioned in Sec. 1, the separation task is a harder one (*LP*>99%), specified products have higher prices (e.g. 0.5 US\$/gmol), and cascades 1-4, 2-4 and 1-3 have 25 or more stages. This suggests that the extra degrees of freedom of *f*-VN could be better exploited when seeking harder goals and/or when the monetary separation reward is more attractive.

## Acknowledgements

V. R. Ahón and J.L. Medeiros acknowledge financial support from CAPES-Brazil and CNPq-Brazil.

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**Received: December 19, 2005.**

**Accepted for publication: July 27, 2006.**

**Recommended by Editor A. Bandoni.**