Appendix A

The Generalized Modular Framework

A.1   GMF Representation of Units

Using the GMF building blocks (Section 2.1.1) and appropriate interconnection principles, structural alternatives can result as combinations of *He* and *M/H* modules. The following process units have been represented by a single, or a combination, of the framework's building blocks (Papalexandri and Pistikopoulos, 1996).

Condenser/Reboiler/Heat Exchanger

A condenser, a reboiler or a heat exchanger can be represented in this framework through a *He* module where the two heat exchanging streams do not come into mass active contact. In the case of a condenser, the hot process stream is in the vapour phase, which changes phase while exchanging heat with a cold utility or a cold process stream. For a reboiler, the cold process stream is in the liquid phase, which changes phase while exchanging heat with a hot utility or a hot process stream. In a heat exchanger a hot process stream or utility exchanges heat with a cold process stream or utility, with or without phase changes.

A partial reboiler or condenser may be similarly defined, by relaxing the Phase Defining Constraints (presented in Appendix A.2) so that two phase streams are taken into consideration (a flash operation could then be used for the phase separation and the further stream processing within the framework).

Distillation Columns

A distillation column (equilibrium or not) which separates, for example, a binary mixture AB (assuming A more volatile than B) into two products A(B) and (A)B (with higher concentration of A and B, respectively), involves mass and heat transfer between the liquid and vapour mixtures $L_{A(B)}$-$V_{A(B)}$ and $V_{(A)B}$-$L_{(A)B}$ due to volatility differences. Therefore, a binary distillation column can be represented with at least two *M/H* modules (representing a rectifier and a stripper) and two *He* modules (representing a condenser and a reboiler).

In the lower module, representing the stripper, the liquid stream is enriched in the heavier com-

ponent, B, which is transferred from the vapour stream $V_{(A)B}$ (rich in B, as its concentration in B decreases) to the liquid stream $L_{(A)B}$ (lean in B, as its concentration in B increases). At the same time A is transferred from the liquid (rich in A) to the vapour (lean in A) stream. In the Upper *M/H* module which represents the rectifier, A is transferred from the liquid stream (rich in A) to the vapour stream (lean in A), therefore enriching the vapour stream in A (the most volatile component) in the higher part of the column. Additionally, appropriate liquid and vapour interconnecting streams are necessary between the *M/H* and *He* modules.

Homogeneous Reaction

A reactor can be represented as a *M/H* module between the reagent mixture and the reaction product mixture. In the case of a reaction $(A + B \rightarrow C)$, the liquid - liquid match occurs between: $L_{AB(C)}$ - $L_{(AB)C}$. In this case only one inlet and outlet streams are allowed in the module. But the framework can include possibilities of recycle using bypass streams from the splitter of the *M/H* module outlet (product mixture stream). The possibility of a jacketed reactor can also be represented by interlinking the *M/H* module with a *He* module. In this case the product mixture stream (from the *M/H* module) exchanges heat with a cold utility. A CSTR is represented by the homogeneous liquid - liquid *M/H* module, assuming that the two streams in the match are well mixed. In the same way, a PFR can be realized as a battery of *M/H* modules.

Absorption/ Extraction

A single *M/H* module can represent an absorber or an extractor where a set of components is transferred between a process stream and a mass separating agent (not between the same process streams as in distillation). The *M/H* module could correspond to trayed or to packed absorption/extractive columns.

Two Phase Reaction

The difference between the homogeneous reactor and the two phase reactor is that in the latter, streams of different phases are involved, where all the components of the reacting system can be found. Here, the lean side is the stream in which the concentration of the component of interest increases. The mass transfer term consists of two parts, one for the chemical equilibrium (reaction) and one for the phase equilibrium. The streams, as before are immiscible and recycle (bypass) streams can only be directed from the exchanger outlet stream splitters to the same stream inlet module mixers.

Reactive Distillation

As mentioned above, liquid - vapour matches with reaction can be represented in the GMF as a cluster of trays of reactive distillation. A reactive distillation column can be represented through the GMF with the minimum requirements of three liquid - vapour *M/H* modules (*1* reactive/separating and *2* pure separating). In the reactive/separating *M/H* module, mass transfer is due to consumption/generation (reaction) and to volatility differences. In the case of the reaction of the type $(A + B \rightarrow C)$ all possible stream combinations are being considered in the superstructure: $L_{AB(CD)}, V_{AB(CD)}, L_{(ABC)D}, V_{(ABC)D}, L_{(AB)C(D)}, V_{(AB)C(D)}$, *etc.* Depending on the synthesis objectives different structures can evolve out of the superstructure, in which the reaction could take

place in the liquid phase with the simultaneous transfer of some components from the vapour phase to the liquid and vice versa due to volatility differences in order to aid the chemical reaction. In similar fashion, reactive absorption or extraction can be accordingly represented.

The above show the versatility of the proposed framework, as process units can be identified from a process flowsheet of *M/H* and *He* modules, without the need to postulate these units during the synthesis task, since the superstructure only considers as building blocks modules, which are physically modelled including only fundamental mass and heat exchange principles.

A.2   Phase Defining Constraints

The streams that participate in the superstructure have postulated phases, depending on their composition, temperature and pressure. The Phase Defining Constraints are continuous inequality constraints applied in order to define the phase of each stream (liquid or vapour). The importance of having well defined liquid and vapour streams lies in the fact that the interconnections between the various blocks are such that allow mixing of streams of the same phase. Moreover, the Phase Defining Constraints, along with the Driving Force Constraints are needed for the thermodynamic consistency of the model, upon which the whole framework is based, since in the GMF no phase equilibrium constraints are applied directly between streams of different phases leaving the same *M/H* module.

For liquid phase streams at a given composition and pressure, the Phase Defining Constraints impose that the stream should be subcooled or, at the limit, saturated:

$$\sum_j^C (K_j x_j)^L \leq 1 \tag{A.1}$$

$$K_j - \frac{\gamma_j Psat_j}{\phi_j P} = 0 \tag{A.2}$$

$$\sum_j^C x_j = 1 \tag{A.3}$$

$$Psat_j - Psat_j(T) = 0 \tag{A.4}$$

$$\gamma_j - \gamma_j(x_j, T, P) = 0 \tag{A.5}$$

$$\phi_j - \phi_j(y_j^\star, T, P) = 0 \tag{A.6}$$

where, L, x_j, T, P, K_j, $Psat_j$, γ_j, ϕ_j, $y_j^\star$ are the examined liquid stream and its liquid molar fraction, temperature, pressure, phase equilibrium constant, vapour pressure, liquid activity coefficient, fugacity coefficient and incipient vapour molar fraction, respectively.

Accordingly, for vapour streams at a given composition and pressure, the Phase Defining Constraints impose that the stream should be superheated or, at the limit, saturated:

$$\sum_j^C \left(\frac{y_j}{K_j}\right)^V \leq 1 \tag{A.7}$$

$$K_j - \frac{\gamma_j Psat_j}{\phi_j P} = 0 \tag{A.8}$$

$$\sum_j^C y_j = 1 \tag{A.9}$$

$$Psat_j - Psat_j(T) = 0 \tag{A.10}$$

$$\gamma_j - \gamma_j(x_j^\star, T, P) = 0 \tag{A.11}$$

$$\phi_j - \phi_j(y_j, T, P) = 0 \tag{A.12}$$

where, $V, y_j, T, P, K_j, Psat_j, \gamma_j, \phi_j, x_j^\star$ are the examined vapour stream and its vapour molar fraction, temperature, pressure, phase equilibrium constant, vapour pressure, liquid activity coefficient, fugacity coefficient and incipient liquid molar fraction, respectively.

In the above constraints any method for calculating the thermophysical properties can be incorporated. Therefore, the framework can be applied beyond cases where ideality is assumed. If however ideality can be assumed, then the following simplifications can be made:

- For ideality in the vapour phase (common assumption when pressures are lower than *10* atm), the fugacity coefficient can be assumed equal to unity: $\phi_j = 1$.

- For ideality in the liquid phase (when known ideal liquid mixtures are used and the pressures are low), the liquid activity coefficient is also assumed equal to unity: $\gamma_j = 1$.

Both the expressions for the liquid and the vapour phase defining constraints have an upper bound of unity. A lower bound is imposed on these constraints, with the nominal value of *0.8* (Ismail, 1998). This bound is not necessary and it is used in order to prohibit the system from high levels of superheating and supercooling.

A.3 Driving Force Constraints

The Driving Force Constraints were developed based on the analogies between mass and heat transfer. In the case of pure heat exchange, heat is transferred from a hot to a cold stream due to a temperature gradient. The pure heat transfer constraints are constructed according to the type of contact (countercurrent, concurrent, etc). For instance, in the case of the countercurrent *He* modules of the GMF, assuming a minimum temperature approach of ΔT_{min}, the Driving Force Constraints, applied at both sides of the module, are:

$$T_{hot}^{in} - T_{cold}^{out} \geq \Delta T_{min} \tag{A.13}$$

$$T_{hot}^{out} - T_{cold}^{in} \geq \Delta T_{min} \tag{A.14}$$

However, in the case of mass transfer between two streams, the phenomena are multidimensional due to the number of components that simultaneously exchange mass and on the type of mass exchange mechanisms taking place. Usually, mass exchange occurs due to a concentration gradient between different immiscible phases, or between reactive streams (between reagent and product

streams) or in combinations of the two. In these cases, the limiting condition for mass exchange is the physical equilibrium, the chemical equilibrium or a combination of the two, respectively. This limiting condition is a function of stream composition, temperature and pressure and it constitutes the basis of the Driving Force Constraints. Since temperature changes are allowed in the *M/H* modules, the latter can represent cases of either sequential or simultaneous mass and heat exchange. Therefore, the framework's *M/H* modules can be used for the representation of both energy and mass separating agent processes.

According to Papalexandri and Pistikopoulos (1996), mass and heat transfer occurs between streams of different phase and between reagent/product streams when reactions are possible. In Ismail (1998), these cases were extended to the combination of the two, covering simultaneous hybrid reactive/separating systems. The Driving Force Constraints were developed in order to ensure mass transfer feasibility between a rich and a lean stream, same as the heat Driving Force Constraints between a hot and a cold stream and to define the distribution of the components, in conjunction with the conservation laws. A rich stream, in a component of interest, j, is a stream with decreasing j concentration and a lean stream is the one with increasing j concentration (El-Halwalgi and Manousiouthakis, 1989). It is possible that the same stream could have the opposite identity for another component in a multicomponent mass transfer process. For instance, in the stripper of an ideal binary distillation column, the light component is transferred from the liquid to the vapour phase (hence, the liquid is the rich stream and the vapour is the lean stream). At the same time, the heavy component is transferred from the vapour to the liquid phase, hence, for that component the vapour is the rich stream and the liquid is the lean stream. Therefore, Driving Force Constraints have to be imposed for all transferred components, defining their distribution.

The condition for mass transfer between a rich and a lean stream is shown below. Lets assume two streams, Y and X with y_j and x_j concentrations in j, respectively. If the Y stream is the rich stream in j then, the following mass transfer condition should hold:

$$y_j \geq x_j \tag{A.15}$$

on the contrary, if the X stream is the rich stream in j, then:

$$x_j \geq y_j \tag{A.16}$$

To be more precise, mass transfer feasibility is ensured when the concentration of the transferred component in the rich stream is higher than its concentration that would have been in equilibrium with that of the lean stream. For instance, when physical equilibrium takes place between the above X and Y streams, the equilibrium relation and the mass transfer feasibility condition (assuming that Y is the rich stream in j), are:

$$(y_j)^{eq} = f_j^{eq}(x_j) \tag{A.17}$$

$$y_j \geq (y_j)^{eq} \Rightarrow y_j \geq f_j^{eq}(x_j) \tag{A.18}$$

In the above binary distillation example, these mean that for a rich stream in component j, the operating line should always be above the equilibrium line in a *x-y* diagram (the opposite should hold for the lean stream).

Similarly to the heat Driving Force Constraints, the Driving Force Constraints for mass and heat exchange are dependent on the type of contact. The Driving Force Constraints should be written for both sides of a *M/H* module, ensuring mass transfer feasibility inside the module. However, this holds when the equilibrium lines are convex for the rich and concave for the lean streams (as defined
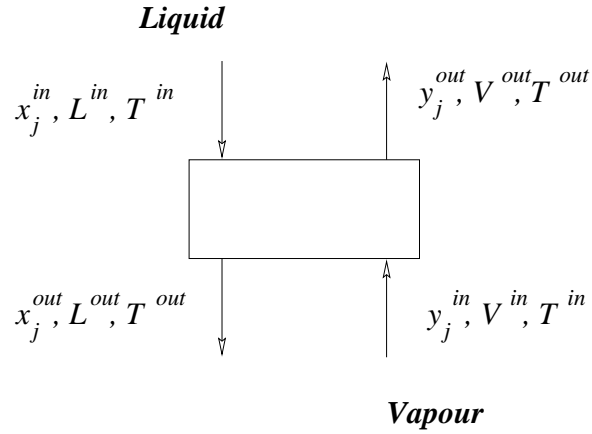
Liquid

$$x_j^{in}, L^{in}, T^{in} \qquad\qquad y_j^{out}, V^{out}, T^{out}$$

$$x_j^{out}, L^{out}, T^{out} \qquad\qquad y_j^{in}, V^{in}, T^{in}$$

Vapour

Figure A.1: Mass/Heat module

for each component). When this is not the case, driving force constraints should be taken in discrete points inside the *M/H* module.

Driving Force Constraint Property

An interesting point is that the Driving Force Constraints of the GMF do not require an *a-priori* knowledge of the mass transfer direction for each component in the various *M/H* modules. The framework determines the mass transfer direction for each component according to the phenomena taking place. The condition that always holds is that, *for each component, the product of the distance from the equilibrium and the change of the component's amount after passing through a M/H module, will always be greater or equal to zero, regardless of the mass transfer direction*. This property is demonstrated in the following example.

Lets assume the countercurrent *M/H* module of Figure A.1 between two streams (for instance a liquid and a vapour stream) with a physical equilibrium condition, as in equation (A.17).

Case 1

If component j is transferred from the vapour (rich) to the liquid (lean) stream, then the amount of this component in the effluent vapour stream should decrease, defining the quantity $g1_j$, as:

$$g1_j = V^{in}\, y_j^{in} - V^{out}\, y_j^{out} \geq 0 \tag{A.19}$$

The feasibility condition is based on the limiting countercurrent equilibrium condition, defining the distance from equilibrium ($g2_j$ and $g3_j$) at the two sides of the module, as:

$$g2_j = y_j^{in} - (y_j^{in})^{eq} \geq 0 \;\Rightarrow\; y_j^{in} - f_j^{eq}(x_j^{out}) \geq 0 \tag{A.20}$$

$$g3_j = y_j^{out} - (y_j^{out})^{eq} \geq 0 \;\Rightarrow\; y_j^{out} - f_j^{eq}(x_j^{in}) \geq 0 \tag{A.21}$$

The Driving Force Constraints are defined as:

$$(g1_j\, g2_j) \geq 0 \tag{A.22}$$

$$(g1_j\, g3_j) \geq 0 \tag{A.23}$$

Case 2

If however, j is actually transferred from the liquid to the vapour streams, then:

$$g1_j = V^{in} \, y_j^{in} - V^{out} \, y_j^{out} \leq 0 \tag{A.24}$$
$$g2_j = y_j^{in} - (y_j^{in})^{eq} \leq 0 \;\Rightarrow\; y_j^{in} - f_j^{eq}(x_j^{out}) \leq 0 \tag{A.25}$$

$$g3_j = y_j^{out} - (y_j^{out})^{eq} \leq 0 \;\Rightarrow\; y_j^{out} - f_j^{eq}(x_j^{in}) \leq 0 \tag{A.26}$$

The Driving Force Constraints in this case will also be:

$$(g1_j \, g2_j) \geq 0 \tag{A.27}$$

$$(g1_j \, g3_j) \geq 0 \tag{A.28}$$

As it can be seen, the Driving Force Constraints (equations (A.22) and (A.23)) hold for any direction of mass transfer for each component. The actual mass transfer direction for each component does not need to be postulated and it is determined by these general Driving Force Constraints in conjunction with the other constraints of the GMF physical model.

A.4   Simple Distillation Column Statistics - Trayed Model

Model Equations

Feeds Splitter	*(I)*
Feed Bubble Point	*(I)*
Total Mass Balances	*(N)*
Component Mass Balances	*(N C)*
Energy Balances	*(N)*
Phase Equilibrium	*(N C)*
Summation Corrections	*(N)*
Reflux Ratio Definition	*(1)*
Product P2 Definition	*(1)*
Zeroing of V_N	*(1)*
Liquid and Vapour Enthalpy Definitions	*2(N)*
Equilibrium Constant Definitions	*(N C)*
Uniform Column Pressure Spec	*(1)*
Distillate Purity Spec	*(1)*
Overall:	*N (3C+5)+2I+5*

Model Variables

Feed Interconnection	*(I)*
Feed Temperature	*(I)*
Liquid and Vapour Flowrates	*2(N)*
Distillate Flowrate	*(1)*
Bottoms Flowrate	*(1)*
Liquid and Vapour Molar Fractions	*2(N C)*
Reboiler Duty	*(1)*
Condenser Duty	*(1)*
Reflux Ratio	*(1)*
Column Pressure	*(1)*
Liquid and Vapour Enthalpies	*2(N)*
Equilibrium Constant	*(N C)*
Overall	*N (3C+5)+2I+6*

The above statistics are based on the tray-by-tray rigorous distillation column model of Viswanathan and Grossmann (1993). For the examined optimization problem of Section 2.4.3 (where *N=25* and *C=2*) the number of equations and variables is *282* and *283*, respectively. The remaining degree of freedom is the reflux ratio, which will be optimized in the optimization problem posed.

A.5 Simple Distillation Column Statistics - GMF Model

According to the GMF Physical Model of Section 2.3.3 and to the problem specific specifications of the binary distillation separation case study of Section 2.4.3, the system equality constraints and variables are given below, on a GMF building block basis. For simplicity C, I, E^E, E^{CE} and E^{HE} represent here the corresponding sets' cardinalities.

Model Equations

Feed Splitters	$2(I)$
Upper Auxiliary Block	$(4E^E + 2E^E C)$
M/H Main Block	$(3E^E + E^E C)$
Lower Auxiliary Block	$(4E^E + 2E^E C)$
Cooler Module	$(4E^{CE} + E^{CE} C)$
Heater Module	$(4E^{HE} + E^{HE} C)$
Product Mixers	$(3P + P\,C)$
Enthalpy Definitions	$(I + 6E^E + 2E^{HE} + 2E^{CE} + P)$
Equil. Const. Definitions	$(I + 6E^E + 2E^{HE} + 2E^{CE} + P)\,C$
Module Pressure Spec	(E^E)
Reflux Ratio Definition	(1)
Distillate Purity Spec	(1)
Total	$E^E(11C+18) + (E^{CE} + E^{HE})(3C+6) + P(2C+4) + I(C+3) + 2$

Model Variables

Flowrates (†)	$(4E^E + E^{CE} + E^{HE} + P)$
Molar Fractions (‡)	$(6E^E + E^{CE} + E^{HE} + P)C$
Temperatures (♯)	$(I + 6E^E + 2E^{CE} + 2E^{HE} + P)$
Heater Duty (Q_e^H)	(E^{HE})
Cooler Duty (Q_e^C)	(E^{CE})
Enthalpies (§)	$(I + 6E^E + 2E^{CE} + 2E^{HE} + P)$
Equilibrium Constants (♮)	$(I + 6E^E + 2E^{CE} + 2E^{HE} + P)C$
M/H module Pressure (P_e)	(E^E)
Reflux Ratio (r)	(1)
Total	$E^E(12C+17) + (E^{CE} + E^{HE})(3C+6) + P(2C+3) + I(C+2) + 1$

where:

† $(f_e^{LI}, f_e^{LO}, f_e^{VI}, f_e^{VO}, f_e^C, f_e^H, f_p^P)$

‡ $(x_{e,c}^{LI}, x_{e,c}^{LO}, x_{e,c}^{VI}, x_{e,c}^{VO}, x_{e,c}^{LA}, x_{e,c}^{VA}, x_{e,c}^C, x_{e,c}^H, x_{p,c}^P)$

♯ $(T_i^F, T_e^{LI}, T_e^{LO}, T_e^{VI}, T_e^{VO}, T_e^{LA}, T_e^{VA}, T_e^{CI}, T_e^{CO}, T_e^{HI}, T_e^{HO}, T_p^P)$

§ $(H_i^F, H_e^{LI}, H_e^{LO}, H_e^{VI}, H_e^{VO}, H_e^{LA}, H_e^{VA}, H_e^{CI}, H_e^{CO}, H_e^{HI}, H_e^{HO}, H_p^P)$

♮ $(K_{i,c}^F, K_{e,c}^{LI}, K_{e,c}^{LO}, K_{e,c}^{VI}, K_{e,c}^{VO}, K_{e,c}^{LA}, K_{e,c}^{VA}, K_{e,c}^{CI}, K_{e,c}^{CO}, K_{e,c}^{HI}, K_{e,c}^{HO}, K_{p,c}^P)$

The above sets of variables are not complete unless the system includes the *case specific* stream Interconnections. These are represented in the Structural Model through the secondary binary variables and in the Physical Model through the corresponding flowrates. The Mixed Integer constraints

included in the model of Section 2.3.3, become continuous inequality constraints in the Primal sub-problem (through the parameterization of the binary variables to the values they obtained by the solution of the Master subproblem). These inequality constraints either impose flowrate bounds for existing interconnections, or zero the flowrates of non-chosen (non-existing) interconnections. In the simple distillation column, the existing interconnections are known *a-priori* and they are given in detail in the GMF Structural Sets of Table 2.3. The remaining interconnections are treated as non-existing.

For the examined problem where *C=2, E^E=2, E^{CE}=E^{HE}=1, P=2* and *I=1*, the *non-zero* continuous interconnection flowrates are given below:

$$f^{FL}_{1,1}, f^{LL}_{2,1}, f^{VV}_{1,2}, f^{VC}_{2,2}, f^{CL}_{2,2}, f^{LH}_{1,1}, f^{HV}_{1,1}, f^{CP}_{2,P1}, f^{LP}_{1,P2}$$

The above *9* flowrates are added to the other *125* system variables (calculated above for the specified number of building blocks, feeds, products and components specified in the examined case study), thus generating *134* variables overall. The number of equality constraints is *127*.